Studies in Big Data 43

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Editors

Big Data Processing Using Spark in Cloud

Springer

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ISSN 2197-6503 ISSN 2197-6511 (electronic)
Studies in Big Data
ISBN 978-981-13-0549-8 ISBN 978-981-13-0550-4 (eBook)
https://doi.org/10.1007/978-981-13-0550-4

Library of Congress Control Number: 2018940888

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Printed on acid-free paper

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Processing Using Spark—A Potent of BD Technology

M. Venkatesh Saravanakumar and Sabibullah Mohamed Hanifa

Abstract Processing, accessing, analyzing, securing, and stockpiling of big data are the most core modalities in big data technology, where **Spark**, is a core processing layer, an open-source cluster (in-memory) computing platform, unified data processing engine, faster and reliable in a cutting-edge analysis for all types of data. It has a potent to join different datasets across multiple disparate data sources. It supports in-memory computing and enables faster query access compared to disk-based engines like Hadoop. Query ID="Q1" Text="Please check and confirm if the author names and initials are correct." This chapter sustains the major potent of processing behind Spark connected contents like Resilient Distributed Datasets (RDDs), scalable Machine Learning libraries (MLlib), Spark incremental Streaming pipeline process, parallel graph computation interface through GraphX, SQL Data frames, SparkSQL (Data processing paradigm supports columnar storage), and Recommendation systems with MlLib. All libraries operate on RDDs as the data abstraction is very easy to compose with any applications. RDDs are a fault-tolerant computing engine (RDDs are the major abstraction and provide explicit support for data-sharing (user's computations), can capture a wide range of processing workloads and parallel manipulated can be done in the cluster as a fault-tolerant manner). These are exposed through functional programming APIs (or BD-supported languages) like Scala, Python. Chapter also throws the viewpoint on core scalability of Spark to build high-level data processing libraries for the future generation application is involved. To understand and simplify the entire BD tasks, focusing of processing hindsight, insights, foresights by using Spark's core engine, its members of ecosystem components are explained with a neat interpretable way, is mandatory for data science compilers at this moment. Big contents dive (current big data tools in Spark, cloud storage) of cognizance are explored in this initiative to replace the bottlenecks towards the development of an efficient and comprehend analytics applications.

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M. Mittal et al. (eds.), *Big Data Processing Using Spark in Cloud*,
Studies in Big Data 43, https://doi.org/10.1007/978-981-13-0550-4_9

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Published by :
Vandana Publications
UG-4, Avadh Tower, Opp. Kaysons Lane, Hazratganj,
Lucknow-226001, India.
Contact Numbers
+91-522-4108552, +94-9838-604-504, +91-96960-45327
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Price : ₹ 325/-

ISBN : 978-81-932843-3-9

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சிறப்பிதழ்
Special Issue

29 புரட்டாசி 2049
15 October 2018

ISSN : 2321-0737

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UGC APPROVED INTERNATIONAL THAMIZH JOURNAL

செம்மொழித் தமிழ்

பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்

Journal of Classical Thamizh

(A Quarterly International Multilateral Thamizh Journal)

சிறப்பிதழ் : தேசியக் கருத்தரங்கம்-2018
தமிழாய்வுத்துறை
ஜமால் முகம்மது கல்லூரி (தன்னாட்சி)
திருச்சிராப்பள்ளி-620 020, தமிழ்நாடு, இந்தியா

தமிழ் இலக்கியங்களில் பெண் எழுத்தாளர்களின் படைப்பாளுமை

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Published by
RAJA PUBLICATIONS
No. 10 (Upstair), Ibrahim Nagar, Khajamalai,
Tiruchirappalli - 620 023, Tamil Nadu, India.
Mobile : 9600535241
Website : www.rajapublications.com

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Part -2

தமிழ் இலக்கியத்தில் பொன்முடியார்

பொலிகையூர ரேகா

உதவிப்பேராசிரியை, வணிகவியல் துறை, ஜமால் முகமது கல்லூரி, திருச்சி -20

முன்னுரை

தமிழ் இலக்கியத்தின் பொற்காலம் என்று கூறப்படுகின்ற சங்க காலத்தில் நிறைந்திருந்த தமிழ்ப் புலவர்களில் ஆண் புலவர்களிற்குச் சளைக்காத வண்ணம் பெண் புலவர்களும் ஆளுமை மிகுந்தவர்களாகக் காணப்பட்டனர். சங்க காலப் புலவர்களில் முதற் சங்கம் இரண்டாம் சங்கம் மூன்றாம் சங்கம் எனத் தமிழ் வளர்த்த 1446 புலவர்களில் 32 பெண்பாற் புலவர்கள் இருந்ததாகக் கூறப்படுகின்றது.

இப்பெண்பாற் புலவர்களின் இயற்பெயர் அத்தொகுப்புகளில் இல்லாததால் அவர்களின் பாடல்களிலுள்ள சிறப்பான சொற்களை அடிப்படையாகக்கொண்டு அவர்களுக்குப் பெயர் கூட்டப்பட்டது. அவ்வாறு அவரது பாடலின் மூலமாகப் பெயர்பெற்ற ஒரு புலவரே பொன்முடியார் ஆவார்.

பொன்முடியார்

இவர் சங்க காலத்தில் வாழ்ந்த தமிழ்ப் பெண் புலவர் ஆவார். இவரது பாடல்கள் புறநானூற்றில் 299,310,312 எனும் பாடல்களாக உள்ளது. சங்க இலக்கியத்தில் உள்ள இந்த மூன்று பாடல்கள் தவிர புறத் திரட்டில் தகடூர் யாத்திரையிலும் இவரது மூன்று பாடல்கள் உள்ளது.

கி.பி இரண்டாம் நூற்றாண்டில் தகடூர் போர் இடம்பெற்றது (இந்த இடம் இப்போது தர்மபுரி என்றழைக்கப்படுகின்றது). இப்போரிலே தகடூரை ஆண்ட அதியமான் நெடுமான் அஞ்சியை சேர நாட்டை ஆண்ட அவனது தம்பியாகிய பெருஞ்சேரல் இரும்பொறை வெற்றி கொண்டான். இதைப் பாராட்டிப் பாடியுள்ளார் பொன்முடியார். இதன்மூலமாக இவர் சேரநாட்டைச் சார்ந்தவராக இருக்கலாம் என்று கருதுகின்றனர் மேலும் பண்டைய சேர நாட்டில் பொன்முடி நல்லூர் என்று ஒரு ஊர் இருந்ததாகவும் அறியப்படுகின்றது. இவ்வூரின் பெயரே இவருக்கு வழங்கப்பட்டிருக்கலாம் என்று எண்ணவும் வாய்ப்புகளுண்டு. பொன்முடியாரின் பாடல்களும் செய்திகளும் பின்வருமாறு:

குதிரைகளின் வீரம்

"பருத்தி வேலிச் சீறூர் மன்னன்"(299) என்று தொடங்கும் பாடலில் குதிரைகளின் வீரத்தைப் பற்றிப் பாடுகின்றார் பொன்முடியார் சீறூர் மன்னனின் குதிரைகள் உளுந்துச் சக்கையை உணவாக உண்டு வளர்வதாயும் எதிரி நாடாகிய நண்ணாடை மன்னனின் குதிரைகள் நெய் ஊறிய மிதித்த சோறுருண்டைகளை உண்டு வளர்வதாயும் கூறுகின்றார். ஆனாலும் அங்கு போரிடுவோரையும் மீறிக்கொண்டு சீறூர் மன்னனின குதிரைகளே பாய்ந்து செல்வதாயும் நெய்சோறுண்ட குதிரைகள் ஒதுங்கி நிற்பதாயும் கூறுகின்றார். அந்தக குதிரைகளானது மாதவிடாய்க் காலத்தில் சமையல் பாத்திரங்களைத் தொடாது ஒதுங்கியிருக்கும் பெண்களைப் போல சோர்வுற்றிருப்பதாகக் கூறுகின்றார். இங்கு மன்னனின குதிரைப் படையின் வீரம் கூறப்படுகின்றது.

இன்ப வருத்தம்

புறநானூற்றில் இடம்பெறும் 312 வதாக இடம்பெறும் "பால்கொண்டு மடுப்பவும் உண்ணாள் ஆகலின்" எனும் பாடலின் மூலமாக ஒரு தாயானவள் அடைகின்ற வியப்பையும் கவலையையும் துன்பத்திலும் பேருவகை அடையும் பண்பையும் தும்பைத் திணையினூடாகக் கூறுகின்றார்.

செம்மொழித் தமிழ் (பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்) அக்டோபர் 15, 2018 - சிறப்பிதழ் (ISSN : 2321-0737)
Classical Thamizh (A Quarterly International Multilateral Thamizh Journal) October 15, 2018- Special Issue (ISSN : 2321-0737)
தமிழ் இலக்கியங்களில் பெண் எழுத்தாளர்களின் படைப்பாளுமை - தேசியக் கருத்தரங்கம்-2018
முதுகலை & தமிழாய்வுத்துறை, ஜமால் முகமது கல்லூரி (தன்னாட்சி), திருச்சிராப்பள்ளி-620 020, தமிழ்நாடு, இந்தியா

சங்க இலக்கியங்களில் காந்தள் - பொலிகையூர் ரேகா

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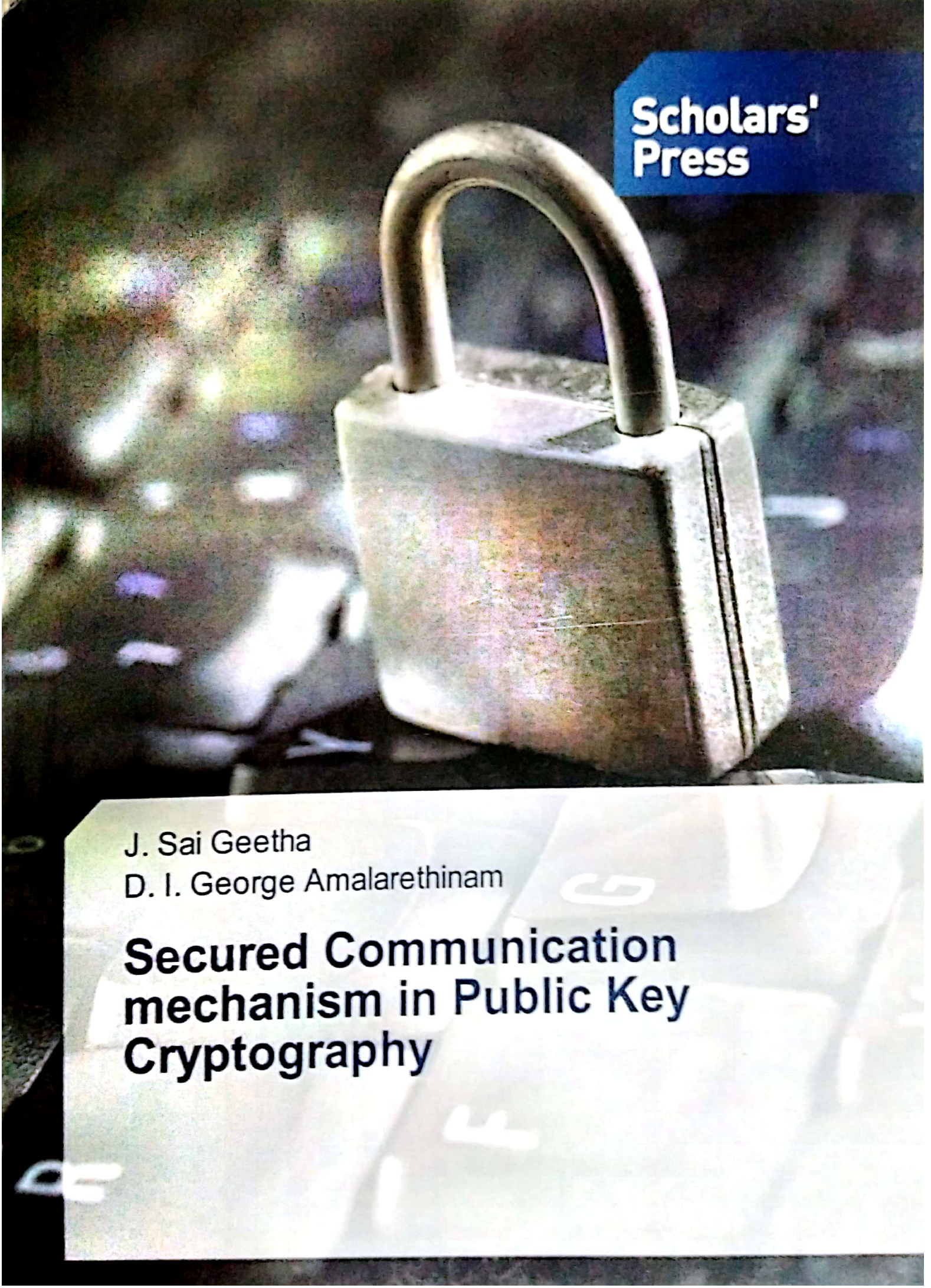

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17 Meldrum Street, Beau Bassin 71504, Mauritius

Printed at: see last page
ISBN: 978-620-2-30632-4

Zugl. / Approved by: Bharathidasan University Tiruchirappalli, 2016

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Advances in Intelligent Systems and Computing 645

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ISSN 2194-5357 ISSN 2194-5365 (electronic)
Advances in Intelligent Systems and Computing
ISBN 978-981-10-7199-7 ISBN 978-981-10-7200-0 (eBook)
https://doi.org/10.1007/978-981-10-7200-0

Library of Congress Control Number: 2017957703

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Asymmetric Addition Chaining Cryptographic Algorithm (ACCA) for Data Security in Cloud

D. I. George Amalarethinam and H. M. Leena

Abstract Cloud computing is a centralized network which enables the movement of data and application software and access the resources on demand. Although this type of computing meets the need of the users, various issues present in the cloud decreases the usage of resources. Among them, security is one of the major issues. The users move to the cloud for storing their sensitive data. Thus, data protection is a key concern. Cryptography is the conventional method applied for securing data in an efficient way. Encryption and decryption processes of cryptography proposed by various predefined algorithms take much time. Thus, the concentration must be given to reduce the time of these processes. Many methodologies exist for reducing the time which is more mathematical in nature. One among them is the concept of addition chaining method. The proposed asymmetric cryptographic algorithm uses the concept of addition chaining to reduce the time spent both in encryption and decryption processes.

Keywords Cloud computing · Data security · Cryptography
RSA · Addition chaining

1 Introduction

Cloud computing is a distributed collection of interconnected and related systems with more resources provisioned on the basis of pay-per-use. It is more related to other computing technologies like grid, utility, and autonomic computing. The Cloud is different from others especially the grid, by its virtualization technology. This technology leverage better resource utilization and dynamic resource provisioning.

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E. B. Rajsingh et al. (eds.), *Advances in Big Data and Cloud Computing*,
Advances in Intelligent Systems and Computing 645,
https://doi.org/10.1007/978-981-10-7200-0_30

Easy to Bake

Ms. D. Bhuvaneswari M.Sc., M.Phil., B.Ed., SET

Ms. V.Kavitha M.Sc., M.Phil., NET, (Ph.D)

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Affiliated to National Council For Hotel Management and Catering Technology, Noida - U.P.

L.V. KUMAR
PRINCIPAL

18th April 2016

MESSAGE

The 'Easy to Bake' book authored by Ms.D.Bhuvaneswari, Assistant Professor and Ms.V.Kavitha, Assistant Professor, Post Graduate Department of Nutrition and Dietetics, Jamal Mohamed College, Thiruchirappalli is very easy for the learners and beginners.

The book contains introduction about baking, basics of making bread, cake, biscuits, cookies and puffs. I have gone through the recipes and they are result-oriented.

I wish all the best to the authors and to come up with many editions of this book incorporating latest knowledge and skills. I also wish the student community to read, practice and get benefitted.

18/04/16

(L.V. KUMAR)

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Easy to Bake

By

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Assistant professors

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About The Book

This book is so designed that one can learn to prepare the bakery products easity on their own. This manual will familiarize the student with the recipes and concepts used by the professional bakers. Topic include chapter I introduction about baking, chapter II the bread making from basics to variation , chapter III variation of cake ,chapter IV process for biscuits and cookies , special emphasis on millet based biscuit and chapter V puffs and pastries.

The main objective of this book is to provide a thorough understanding to students for all baking category.

We hope that this book will give adequate information to a student to become a baking and pastry professionals through hands-on experience and the development of competency based skills while emphasizing management and creativity. We extend our gratitude to our Member-in-charge, Dr. M.I. Fazal Mohamed and our Colleagues Ms. Mary Jeya Praba, Ms. B.Rajalakshmi, J.Priya, J.Harine Sargunam, Dr.A.Sangeetha and K.Shahida Rizwana from the PG Department of Nutrition and Dietetics, Jamal Mohamed College, Trichy for their kind encouragement and support.

We express our heartfelt thanks to Dr.P.Nazini, Associate Professor, Periyar University, Selam and Mr.G.Annadurai, Logi Bakery. Trichy.

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Dhivakar Publications
7/145,Ayyathur,Veeramanipatty (post)
Musiri (Tk), Trichy (Dt) - 621202.

ISBN 978-81-909541-8-1

Printed @ The Printing House, Try-23. Ph : 0431-2420121

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சுந்தரரின் சோழநாட்டுத் தலப்பாடல்களில் இயற்கை வளம்

முனைவர் த. செல்வராசு,
இணைப்பேராசிரியர், தமிழாய்வுத்துறை,
ஜமால் முகம்மது கல்லூரி, திருச்சி-20.

சமய குரவர் நால்வரில் சுந்தரர் வாழ்ந்த காலம் பொற்காலமாகும். தொண்டை நாட்டிலும், பாண்டிய நாட்டிலும் அயல்நெறிவீழவும், சைவநெறி தழைக்கவும் அடிக்கோளிட்டவர்கள் நாவுக்கரசரும், ஞானசம்பந்தரும் ஆவர். சைவ நன்னெறி தழைத்தோங்கி செழித்திருந்த காலம் சுந்தரர் காலம். சோழமன்னரும் சேர மன்னரும் சைவ நன்னெறி தழைக்க வாழ்ந்தவர்கள் ஆதலின் சுந்தரர் காலத்தில் தமிழகம் முழுவதும் சைவ மணம் கமழ நின்றது. 'சுந்தரர் காலம் சமய நெறியிலும், நாட்டு வளத்திலும், அரசியல் அமைப்பிலும் நல்ல சூழல் நிலவ காரணமாயிற்று. ஆதலின் இவர் தம் காலம் பொற்காலம் என்பதில் ஐயமில்லை" என்பார் கு.சுந்தரமூர்த்தி (சுந்தரர் வரலாற்றாராய்ச்சியும் தேவாரத்திறனாய்வும், ப.2).

அடியவர்கள் வாழ்வில் சுந்தரர் வாழவு பல்வேறு வகையில் தனித்தன்மை வாய்ந்ததாக உள்ளது. அடியவர்கள் வரலாறு பலவும் மண்ணுலகில் தோன்றி விண்ணுலகில் நிறைவு பெறுமாறு அமைய, இவரோ வரலாரோ விண்ணுலகில் தோன்றி விண்ணுலகையே அடையுமாறு உள்ளது. ஏனைய அடியவர்கள் தோன்றிய மரபிலேயே வாழ்ந்து வளம் பெற்றவர்கள். இவரே வைதிக மரபில் தோன்றி அரசியல் திருவில் வளர்ந்தவர். இறைவனோடு தொடர்பு கொள்வதிலும் தோழமை நெறியைப் பின்பற்றியவர். 'அடியவர்கள் அனைவரும் இல்லற நெறியில் அல்லது துறவற நெறியில் வாழ்ந்தவர்கள் ஆவர். அவ்வில்லறத்திலும் ஒருவன் ஒருத்தி என்ற அளவிலேயே பெரிதும் வாழ்ந்தவர்கள். ஆனால், இவரோ ஒருவருக்கு இரு மனைவியர் என்ற அமைப்பில் வாழ்ந்தவர். அங்ஙனம் வாழ்ந்த பொழுது அவ்விருவருடனும் கண்டு கேட்டு உண்டு உயிர்த்து உற்றறியும் ஐம்புல இன்பத்தை ஆரத்துய்த்தமையும், அதற்கு தடை நேர்ந்த பொழுது இறைவனையே தூது விடுத்தமையும் மேலும் எண்ணுதற்குரிய இவர்தம் வாழ்வின் தனித்தன்மையாகும்." என்பார் கு.சுந்தரமூர்த்தி (சுந்தரர் வரலாற்றாராய்ச்சியும் தேவாரத்திறனாய்வும்,ப.03).

தனித்தன்மைகளில் சிறந்து விளங்கியவரும், சிவபெருமானுக்கு நெருங்கியத் தொண்டராக விளங்கியவரும் ஆலால சுந்தரரே ஆவார்.

சுந்தரர் தோன்றி வளர்ந்தது தொண்டை நாடாக இருந்தாலும் இவர் சென்று வழிபட்ட தலங்கள் சோழ, பாண்டிய, சேரநாடுகளாகப் பரந்துபட்டிருந்தன. தலங்கள் தோறும் சென்று சுந்தரர் பாடிய பதிகங்கள் 38,000 என்பர். ஆனால் கிடைத்திருப்பன 100 பதிகங்களே ஆகும். 100 பதிகங்களில் 61 பதிகங்கள் சோழநாட்டுத் தலங்களையும், 13 பதிகங்கள் தொண்டை நாட்டுத் தலங்களையும், 12 பதிகங்கள் நடுநாட்டுத்தலங்களையும், 5 பதிகங்கள் பாண்டிய நாட்டுத்தலங்களையும், 4 பதிகங்கள் கொங்கு நாட்டுத்தலங்களையும், 3 பதிகங்கள் மலைநாட்டுத் தலங்களையும், 2 பதிகங்கள் வடநாட்டுத்தலங்களாகவும், 1 பதிகம் ஈழநாட்டுத் தலமாகவும் அமைந்துள்ளன.

சுந்தரர் தான் தோன்றி வளர்ந்த தொண்டை நாட்டுத் தலங்களைவிட அதிகம் சோழநாட்டு தலங்களையே பாடியுள்ளார். அதிகநாட்கள் வாழ்ந்ததும் அதிக தலங்களுக்குச் சென்று பாடியதும் சோழநாட்டிலேயே ஆகும். தம்பிரான் தோழன் என சுந்தரரை சிவபெருமான் அழைக்குமாறு அடியார்கள் கனவில் கூறியதும், பரவையாரை சுந்தரர் மணந்து வாழ்ந்ததும், பொன்னை ஆற்றிலிட்டு குளத்தில் எடுத்ததும், சிவபெருமான் பொதிசோறு அளித்து அருளியதும், திருத்தொண்டர் தொகை அருளியதும், சிவபெருமான் சுந்தரருக்காக பரவையாரிடம் தூது சென்றதும், சேரமான் பெருமாள் நாயனாரோடு நட்பு தொடங்கியதும் சோழநாட்டிலேயே ஆகும்.

சுந்தரர் சோழநாட்டில் சென்று வழிபட்ட தலங்கள் மிகுதியும் ஆற்றங்கரை ஓரமும், மருதநில, நெய்தல் நில வயல் வெளிகளுமே ஆகும். ஆதலால் இவருடைய தலப்பாடல்களில் ஆற்றுவளச்சிறப்பும், மருதநில, நெய்தல் நிலத்தின் இயற்கை வளக்காட்சிகளுமே மிகுந்து காணப்படுகின்றன. 'ஆரூரின் வழிச்செலவு பெரிதும் ஆற்றங்கரை ஓரத்திலேயே இருந்தது. ஆதலின் அவர்தம் திருப்பதிகங்களில் காவிரி, மணிமுத்தாறு, கெடிலநதி, அரிசிலாறு, பெண்ணையாறு, நிவாநதி, கொள்ளிடம், சிற்றாறு, பாலாவி முதலிய ஆற்றின் வளம் பெரிதும் பேசப்படுகின்றது" என்பார் கு.சுந்தரமூர்த்தி (சுந்தரர் வரலாற்றாராய்ச்சியும் தேவாரத்திறனாய்வும், ப.173) இதனால் சோழநாடு சுந்தரர் காலத்தில் இயற்கை வளத்தில் சிறந்து விளங்கியது என்பது தெளிவாகின்றது.

(i) காவிரி ஆற்றின் வளம் :

காவிரியாற்றின் வெள்ளப் பெருக்கினையும் அதன் வளத்தினையும் பாடிடும் ஆரூரர்,

'அரைக்கும் சந்தனத் தோடுஅகில் உந்தி
ஐவ னம்சுமந் தார்ந்துஇரு பாலும்
இரைக்கும் காவிரித் தென்கரை தன்மேல்
இடைம ருதுறை எந்தைபி ரானை" (பதிகம்-60, பாடல்-10)

எனத்திருவிடைமருதூரில் உறையும் இறைவனைப் பாடிமகிழ்கின்றார். அதாவது சந்தனக்கட்டையையும், அகிற்கட்டையையும் இருமருங்கும் தள்ளிக்கொண்டு மலைநெல்லைத் தாளோடு சுமந்து கொண்டு நிறைந்து ஒலிக்கின்ற காவிரியாற்றின் தென்கரை மேல் உள்ள திருவிடைமருதூரில் கோயில் கொண்டிருக்கும் எம்பெருமான் எனச் சுந்தரர் பாடுகின்றார். சிவதலங்கள் அமைந்திருந்த இடங்களில் இயற்கை வளங்களும், ஆற்றுவளங்களும் பேணப்பட்ட சூழலை உடையதாக சோழநாடு விளங்கியது என்பது தெளிவாகின்றது.

(ii) கொள்ளிட ஆற்றின் வளம் :

சுந்தரர் திருவாழ்கொளிப்புத்தூரைத் தொழுதுவிட்டு திருக்கானாட்டு முள்ளூரை அடையும்போது பெருமான் காட்சி கொடுக்கக் கண்டு மகிழ்கின்றார். மகிழ்ந்த சுந்தரர் திருக்கானாட்டு முள்ளூரில் வீற்றிருக்கும் பதஞ்சலி ஈசுவரரைப் புகழ்ந்து பாடும்போது கொள்ளிட ஆற்றின் நீர்ப்பெருக்கையும், அதில் பெண்கள் குடைந்தாடி மகிழ்ந்ததையும் அப்போது அவர்கள் உடம்பில் இருந்த குங்குமம் ஆற்றில் கலந்து செல்வதையும், கொள்ளிடக் கரையில் இருக்கும் குவளையைக் களைந்தவர்களாக மருதநில மக்கள் கழனியைப் பாதுகாத்த சூழலையும்,

‘உடைஅவிழக் குழல்அவிழக் கோதைகுடைந் தாடக்
குங்குமங்கள் உந்திவரு கொள்ளிடத்தின் கரைமேல்
கடைகள்விடு வார்குவளை களைவாருங் கழனிக்
கானாட்டு முள்ளூரில் கண்டுதொழு தேனே”
(பதிகம்-40,பாடல் 6)

எனப்பாடுவதன் மூலம் சோழநாட்டு மக்கள் இயற்கைச் சூழலேடும், சுற்றுப்புறச் சூழலோடும், வயல்வளச்சிறப்போடும், ஆற்றுவளத்தோடும் வாழ்ந்தனர் என்பது தெரியவருகின்றது.

(iii) மருதநில வளமும் சூழலும் :

ஆறுகள் சூழப்பட்ட நிலையில் மருதநிலங்கள் விளங்கினமையால் உணவுப்பயன் கொள்ளும் வயல்களும் இன்பப் பயன்கொள்ளும் சோலைகளும் மிகுந்து காணப்பட்டன. எங்கும் செறிந்த வயல்கள், அவற்றருகே எண்ணிறந்த பொழில்கள், அப்பொழிலில் ஆண்வண்டு இசைகூட்டப் பெண்வண்டு அதற்கேற்பப் பண்களைப் பாடுகின்றது. இவற்றிற்கேற்ப மயில்கள் நடனமாடுகின்றன. இக்கலைக் காட்சியைக் கண்டுகளித்த குவளைமலர்கள் கரும்பின் அருகே கண் வளருகின்றன. தாமரைகள் முகமலருகின்றன. இத்தகைய அரியகாட்சியைத் திருக்கலயநல்லூரில் கோயில் கொண்டிருக்கும் அமிர்தகலாநாதர் திருத்தலத்தில் கண்ட ஆரூர்,

'அரும்பருகே கரும்பருவ அறுபதம்பண் பாட
அணிமயில்கள் நடமாடும் அணிபொழில் சூழ்அயலின்
கரும்பருகே கருங்குவளை கண்வளரும் கழனிக்
கமலங்கள் முகமலரும் கலயநல்லூர் காணே" (பதிகம்-16, பாடல்1)

எனப்பாடி மகிழ்கின்றனர். மேலும்,

'சோலைமலி குயில்கூவக் கோலமயில் ஆலச்
சுரும்பொடுவண் டிசைமுரலப் பசுங்கிளிசொல் துதிக்கக்
காலையிலும் மாலையிலும் கடவுள்அடி பணிந்து
கசிந்தமனத் தவர்பயிலும் கலயநல்லூர் காணே"
(பதிகம்-16, பாடல்-8)

எனப்பாடும் போது சோலைகள் வெறும் கலையுணர்வுக்கு மட்டும் இருப்பிடமாக இல்லை. பக்தி உணர்வுக்கும் இருப்பிடமாக உள்ளன. சோலையின் ஒரு பக்கம் குயில் கூவுகின்றது. பிறிதொருபக்கம் மயில் ஆடுகின்றது. சுரும்பும் வண்டும் அவற்றின் அருகே முரலுகின்றன. பசுங்கிளிகள் அடியவர் கூறிய பொருள் சேர் புகழை அடியவர்கள் புகன்றவாரே புகழ்கின்றன. இவ்வாறு சோலையிலும் இறையுணர்வு தழைக்கக் காலையிலும் மாலையிலும் கசிந்த மனத்தவர்கள் கடவுளடி பணிந்து இன்புறுகின்றனர் எனச் சுந்தரர் எடுத்துரைப்பதன் வழி இன்பமயமான இயற்கைச்சூழல் இருந்தமையை அறிய முடிகின்றது.

மருதநிலத்தில் மிகுதியாகக் காணப்படுவன கரும்பும் நெல்லும். கரும்பு உயர்ந்து வளர்வதும், நெற்கதிர்களில் நெல்மணிகள் செறிவாக இருப்பதும் மருதநிலத்தின் வளத்தைக் காட்டுவனவாகும். கரும்பும் நெல்லும் உயர்ந்தும் செறிந்தம் விளைவதற்கு நீர்வளம் மிகுந்து இருத்தல் வேண்டும். இந்நீர்வளத்தால் வயல்களில் தாமரை பூத்துக்குலுங்குகின்றன. இம்மலர்களில் அன்னம் விளையாடி மகிழ்கின்றன. இத்தகைய வளமும் இன்பமும் நிறைந்த காட்சியை,

"அரும்புயர்ந்த அரவிந்தத்து அணிமலர்கள் ஏறி
அன்னங்கள் விளையாடும் அகன்துறையின் அருகே
கரும்புயர்ந்து பெருஞ்செந்நெல் நெருங்கிவிளை கழனிக்
கானாட்டு முள்ளூரில் கண்டுதொழு தேனே" (பதிகம்-40,பாடல்-3)

எனத் திருக்கானாட்டு முள்ளூரில் கண்டதாக சுந்தரர் காட்சிப்படுத்துகின்றார்.

(iv) பொய்கை வளம் :

திருவாஞ்சியம் தலத்திற்குச் சென்ற சுந்தரர் அங்கு தாம் கண்ட கவினுறு காட்சியை,

"சள்ளை வெள்ளையங் குருகு
தானது வாம்எனக் கருதி

வள்ளை வெண்மலர் அஞ்சி
மறுகியோர் வாளையின் வாயில்
துள்ளு தெள்ளுநீர்ப் பொய்கைத்
துறைமல்கு வாஞ்சியத்து அடிகள்" (பதிகம்-76, பாடல்-4)

எனப்பாடி மகிழ்கின்றார். மீனினங்களுள் ஒன்று சள்ளை எனும் மீனினம். இது வள்ளைக் கொடியிலுள்ள வெண்மையான மலரைக் குருகு எனக்கருதி வெகுண்டு துள்ளியதாம். அத்துள்ளலால் பிறிதொரு வாளைமீனின் வாயில் அகப்பட்டதாம். இவ்வாறு மீன்கள் வெருவியும், துள்ளியும் விளையாடும் பொய்கைகளை உடையதாக திருவாஞ்சித் தலம் பொலிவுற்று விளங்கியது என்பது வெளிப்படுகின்றது. ஒன்றை மற்றொன்றாகக் கருதிடும் அளவிற்கு சோழநாடு இயற்கை வளத்தில் சிறந்திருந்தது என்பதைச் சுந்தரரின் பாடல் தெளிவுபடுத்துகின்றது.

வயல்களில் நீர் நிரம்பி நிற்கின்றது. ஆதலின் வரிக்கெண்டைகள் துள்ளி விளையாடுகின்றன. இச்சூழலைக் கண்ட நண்டுகள் அவற்றுடன் எதிர்த்துப் போராட விரும்பவில்லை. அருகிலே தாமரைப்பூக்கள் மலர்ந்திருப்பதைப் பார்க்கின்றன. அங்கே சென்று அவை பள்ளி கொள்ளுகின்றனவாம். சிறியவர்களைக் கண்டு பெரியவர்கள் ஒதுங்கிக் கொள்ளுதல் இயற்கை தானே! இவ்வியற்கைச் சூழல் திருப்புறம்பயத்தில் உறையும் சாட்சிவரதேசுவரர் தலத்தைச் சுற்றி விளங்கியது என்பதை,

'துள்ளிவெள்ளிள வாளைபாய்வயல்
தோன்றதாமரைப் பூக்கள்மேல்
புள்ளிநள்ளிகள் பள்ளிகொள்ளும்
புறம்பயம் தொழப் போதுமே" (பதிகம் -35, பாடல் -5)

எனப்பாடி மகிழ்கின்றார் ஆலாலசுந்தரர். ஆற்றுவளமும். மருதநிலவளமும் சோழநாட்டில் சிறப்புற்று இருந்தன போலவே நெய்தல் நிலங்களும் சிறப்புற்று இருந்ததனை சுந்தரரின் அந்நிலம் சார்ந்த தலப்பாடல்களை உற்று நோக்குவார்க்குப் புலப்படும்.

இறைவனின் அருளையும், கருணையையும், சிறப்புகளையும் எண்ணி எண்ணி மனம்மகிழ்ந்து பாடிய நாயன்மார்கள் தங்களின் தலப்பாடல்களில் சோழநாட்டின் நிலவளத்தையும், நீர்வளத்தையும் இயற்கை வளத்தையும், சுற்றுப்புறச் சூழலையும் பதிவு செய்துள்ளனர் என்பது இக்கட்டுரையின்வழி தெளிவாகின்றது. நாயன்மார்கள் தலச்சிறப்பினையும், அத்தல நாயகனின் கருணையையும் பாடியதோடு அத்தலத்தைச் சுற்றியிருந்த நிலவளத்தையும், ஆற்றுவளத்தையும, இயற்கை வளத்தையும், சுற்றுப்புறத்தின் அழகிய சூழலையும் இணைத்துப் பாடியதன் நோக்கம் தலஇறைவனை வாழ்த்தி வணங்குவதோடு இயற்கை வளத்தையும், சுற்றுப்புறச் சூழலையும் மக்கள் பாதுகாத்திட வேண்டும் என்ற உயர்ந்த எண்ணமே ஆகும்.

நாயன்மார்கள் வழியில் தலங்களை வழிபடுவதோடு தலங்களைச் சுற்றியிருக்கும் இயற்கை வளங்களையும் சுற்றுப்புறச்சூழலையும் மக்கள் பாதுகாத்திட வேண்டும் என்பதே இக்கட்டுரையின் பயனாகும்.

குறிப்பு :

சுந்தரர் பாடிய பதிகங்களும் தலங்களும்

(1) சோழநாட்டுத் தலங்களைக் கொண்ட பதிகங்கள்-61, பதிக எண்கள்: 6, 7, 8, 9, 12, 14, 15, 16, 18, 19, 20, 22, 23, 24, 27, 28, 29, 30, 32, 33, 34,35,36, 37, 39, 40, 46, 47, 51, 53, 55, 56, 57, 58, 59, 60, 62, 63, 65, 66, 67, 68, 70, 71, 72, 73, 74, 75, 76, 77, 83, 87, 88, 90, 93, 94, 95, 96, 97, 98, 99.

(2) தொண்டைநாட்டுத் தலங்களைக் கொண்ட பதிகங்கள்-13, பதிக எண்கள் : 5, 10, 21, 26, 41, 52, 54, 61, 69, 81, 86, 89, 91.

(3) நடுநாட்டுத் தலங்களைக் கொண்ட பதிகங்கள்-11, பதிக எண்கள் : 1, 3, 13, 17, 25, 31, 38, 43, 45, 64, 85.

(4) பாண்டி நாட்டுத்தலங்களைக் கொண்ட பதிகங்கள்-5, பதிக எண்கள் :2,11,50, 82, 84.

(5) கொங்குநாட்டுத்தலங்களைக் கொண்ட பதிகங்கள்-4, பதிக எண்கள் : 42, 48, 49, 91.

(6) மலைநாட்டுத்தலங்களைக் கொண்ட பதிகங்கள் -3, பதிக எண்கள் : 4 44, 100.

(7) வடநாட்டுத் தலங்களைப் பற்றிய பதிகங்கள்-2, பதிக எண்கள் : 78, 79.

(8) ஈழநாட்டுத் தலம் பற்றிய பதிகம்-1, பதிக எண் : 80

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Proceedings of the

National Seminar on

CHALLENGES AND CHANGES IN THE EVALUATION SYSTEM

Sponsored by

National Assessment and Accreditation Council, Bengaluru

26th February 2019

Organized by

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(d) Bloom's Taxonomy – Some Alternative Perspectives

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Jamal Mohamed College (Autonomous), Tiruchirappalli – 620020

Bloom's Taxonomy is an effective concept in the field of education that has since 1956 rendered a major contribution and influence upon curriculum development and examination system at international level in general and, American and European nations in particular. Bloom's Taxonomy is the outcome model of the critical analysis and synthesis of the discussions on educational issues carried out in various conferences in the five years period from 1948 to 1953, by the team headed by Benjamin Samuel Bloom, an eminent American educational psychologist. He himself records with a sense of gratitude that this model is the result of the meticulous work done by his team: "Thus, this handbook is truly a group product. It is the direct outgrowth of the thinking of over thirty persons who attended the taxonomy conferences." ("Taxonomy of Educational Objectives", p.9)

The Structure of Bloom's Taxonomy

Bloom's Taxonomy consists of three domains namely Cognitive Domain, Affective Domain and Psychomotor Domain. These three domains each have their own sub levels of educational objectives.

The first domain of the taxonomy called as the cognitive domain (published in 1956 as "Handbook I: Cognitive) is knowledge-based and consists of six objectives numbered as K1 to K6, listed by Samuel Bloom as "the six major classes". They are Knowledge, Comprehension, Application, Analysis, Synthesis and Evaluation. In Bloom's book these six objectives are listed serially from top to bottom, contrary to the pyramidal illustration where they are shown hierarchically bottom to top levels. The keywords are given as nouns.

The second domain called the Affective domain is emotional-based and consists of five objectives. They are Receiving, Responding, Valuing, Organizing and Characterizing.

The third domain named as the Psychomotor Domain is action-based and consists of seven objectives. They are Perception, Set, Guided Response, Mechanism, Complex Overt Response, Adaptation and Origination.

In view point of curriculum development Bloom considered the cognitive domain to be the central and important one and emphasized that the six objectives of this domain "deal with the recall of recognition of knowledge and the development of intellectual abilities and skills" ("Taxonomy of Educational Objectives", p.7)

Revised Bloom's Taxonomy

The synchronization of the three domains and their objectives is necessary for the wholesome educational process. With this aim, the Bloom's taxonomy has been tried or practiced all over the world for nearly forty-five years.

In 2001, Lorin W. Anderson, who is one of the students of Bloom, and David R. Krathwohl, who was one of the member of the team headed by Bloom earlier, came up with a revised version of Bloom's taxonomy with corrections made to the cognitive domain. They have changed the noun terminology of the objectives to verbs. Anderson explained the change his team made as follows, "*Educational objectives indicate that the student should be able to do something (verb) to or with something (noun) – a verb-noun relationship. ... ... We decided to re-label these categories in their verb forms (e.g. Apply, Analyze, etc.) to reflect the verb-noun relationship.*" ("A Taxonomy for Learning, Teaching and Assessing", p.265)

The revision work was initiated in November 1995 and was completed 'during the summer of 1999' and was published in 2001. The team comprised of eight members who were cognitive psychologists, curriculum theorists and instructional researchers, and testing and assessment specialists. Like Bloom's taxonomy which was framed in the context of American society, this revised version was also done on the American context which is worth pondering. Justifying the revision, Anderson says, "*New changes in American society since 1956 have influenced the way we think about and practice education. Now we know more about how children develop and learn and how teachers plan for, teach, and assess their students. These increases in knowledge support the need for a revision" ("A Taxonomy for Learning, Teaching and Assessing*", Preface, p. xxii)

Bloom's Taxonomy from the View Point of Biology

Biology (i.e. the traditional sciences like Botany and Zoology, and newer sciences like Micro-Biology and Bio-Technology) is a knowledge science that has keen observation as its basis. Biological researches mostly start from the act of keen observing. But in Bloom's taxonomy this rather crucial exercise of Biology has been put in somewhat lower level of the psychomotor domain. Maura C Flannery in her research paper "Observations on Biology" observes that in the world of science, Biology is usually looked upon as an inferior science that does only observations and is unlike Mathematics or Physics which has strong theoretical foundations, and says, "*Benjamin Bloom's taxonomy of learning tasks puts observation at the lowest level, with recall of information. This denigration of observation has long bothered me because I see it as*

often difficult and complex, a skill that needs to be learned and a talent that is much more developed in some." ("bioone.org/journals/the-american-biology-teacher/volume-69/issue-9")

In Biology, particularly in Ecology, keen observation, identification and classification are basically required field skills. In Bloom's taxonomy these skills are put in the lower levels. For these reason some biologists have criticized Bloom's taxonomy. Susan Lawler in her article "Identification of animals and plants is an essential skill set" writes, "Ironically, the dogma that has been so detrimental to field taxonomy is known as Bloom's taxonomy" (www.theconversation.com).

What's interesting is that in framing the taxonomy of educational objectives Bloom and his team got the clue only from the science of Biology. Bloom says, "Most readers will have heard of the biological taxonomies which permits classification into such categories as phylum, class, order, family, genus, species, variety. Biologists have found their taxonomy markedly helpful as a means of insuring accuracy of communication about their science and as a means of understanding the organization and interrelation of the various parts of the animal and the plant world. You are reading about an attempt to build a taxonomy of educational objectives" ("Taxonomy of Educational Objectives", p.1)

Is the Process Hierarchical or Parallel?

Another criticism on Bloom's taxonomy as well as its revised version by Anderson and Krathwohl comes from Ron Berger in his article "Here's What's Wrong with Bloom's Taxonomy: A Deeper Learning Perspective" who questions the models approach to the objectives. He says, "The problem is that both versions present a false vision of learning. Learning is not a hierarchy or a linear process. This graphic gives a mistaken impression that these cognitive processes are discrete, that it's possible to perform one of these skills separately from others. It also gives the mistaken impression that some of these skills are more difficult and more important than others." (blogs.edweek.org).

Ron Berger continues to elucidate questions raised by the critique of educator Doug Lemov. He also points to the misinterpretations and misunderstandings that arise from the usual multi layered pyramidal representation of the taxonomy. Since teachers wrongly understand that the objectives given in the lower levels are not important and of lesser value and those in the higher levels are more important and of higher value they tend to develop in their students only those higher level objectives and neglect the lower level ones. Even though Bloom's concept is that those objectives framed in the lower levels of the model are fundamental ones and are pre-requisites for the development of the higher level objectives it is not usually understood that way.

The important observation given by the criticism of Ron Berger is that the objectives of the Bloom's taxonomy are parallel and simultaneous. Also, they could be rearranged. For example, through synthesis and creating at the same time, one could be developing understanding of the subject as well. Hence all those three objectives are attained simultaneously. Also, in an alternate case, creating may occur at first and then analysis and then understanding. There is no fixed one-way hierarchy as many understand the model.

Need for Newer Structures

Usually all the three domains of Bloom's taxonomy are represented as pyramids / triangle structures. The misunderstandings criticized by educators like Ron Berger, Doug Lemov have sprung from those representations only. The triangle diagram representation of the model can lead to another misunderstanding also. To understand it easily we shall compare this model to the "Hierarchy of Needs" model of Abraham Maslow. The model is represented in a triangle / pyramid that consist of five levels of hierarchy from lower to upper. Each level corresponds to a need of human being. The needs are physical / body needs, security needs, belongingness (relationship) needs, esteem needs (social recognition) and self-realization needs (spiritual). To say that only on the fulfilment of a lower need humans move further seeking the immediate higher need. This holds good for majority of the humans. The physical / body needs viz. food air water etc. are necessities for all those who have a corporeal body. No one can rule out that need level completely. But not all humans move to the top levels. Hence, as we go up the number of people coming to those levels get decreased. Only a few individuals get it to the topmost level of self-realization. Majority of the people settle down in lower levels. For this reason, it is correct that the model proposed by Abraham Maslow was represented as a triangle.

But when we talk of visions like "education for all" it is only appropriate to give the model in a rectangle rather than in a triangle. Or, if we see the objectives as simultaneously occurring phenomena then we have to represent the model in star topology or mesh topology or some other more appropriate structure.

Furthermore, rather than treating the objectives as discrete and well defined ones, we shall look them as overlapping ones and try to find out intersecting sub-objectives. To propose a single model common for all subjects of knowledge is not correct. We can have separate modified models for science and arts, and if possible we shall have uniquely modified models for every department of knowledge. On the footsteps of Anderson and Krathwohl who in 2001 came up with a revised model of Bloom's taxonomy by interchanging the Synthesis and Evaluation objectives and changing the nomenclature as Evaluating and Creating, we can rearrange and/or rename the objectives accordingly for each subject. When we move the

education onto the levels of specialization, development of such unique models will be the need of the hour.

Can we develop an Eastern / Indian Model?

As we saw earlier in this paper, the Bloom's Taxonomy and its revised models were developed on the context of American culture. Its approach is strongly from the western mindset. Following it strictly in the eastern countries like India and China, which have considerably longer traditions of knowledge than the western world, would prove only to be cumbersome and detrimental. We have to incorporate objectives that have been upheld for millennia by the scholars and seers of the eastern world.

The short comings of Bloom's taxonomy are already being addressed in the western part of the sphere. For nearly half a century it has led the teachers into downplaying the importance of 'lower level objectives', as we saw it in the example of Biology. Now, emphasis is put on the lower level objectives such as remembering and comprehension. When these objectives are neglected and not given proper emphasis that leads to the liquefaction of the vocabulary and terminology in any field of knowledge, which will make many of its literature unreadable within a short span. Such a condition will surely not be healthy. E.D.Hirsch, Jr., while emphasizing on the need of creating knowledge-based schools says, "*The whole linguistic scene in the United States and the other modern nations begins to look like an amoeba that is changing its shape. Some words enter usage and memory, others depart.*" ("Why Knowledge Matters – Rescuing Our Children from Failed Educational Theories", p.161). Be it primary or secondary or higher level, the neglect of native elements in education will effect in a rootless society. "You who learn not the tongue of your home, go away, go away, go away" sang Poet Bharathi on despising the deviated Indians.

Incorporating as objectives, traditional and time tested values like intuition and imagination into education, we can build a taxonomy that suits our nation in all aspects. Then only we can achieve an organic development of educational objectives.

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ISSN 2454-3993

JOURNAL WITH 3.085 IMPACT FACTOR SIJ TAMIL STUDIES

மலர் 3 சிறப்பிதழ் 1 மார்ச், 2019

சான்லாக்ஸ் பன்னாட்டுத் தமிழியல் ஆய்விதழ்

SHANLAX #SINCE1990

பொருநை இலக்கியக் களமும்

காஞ்சிபுரம் ஸ்ரீ கிருஷ்ணா கலை மற்றும் அறிவியல் கல்லூரியும்

சான்லாக்ஸ் பன்னாட்டுத் தமிழியல் ஆய்விதழும்

(UGC Approved Journal: 40729. ISSN: 2454-3993)

இணைந்து நடத்திய

பன்னாட்டுக் கருத்தரங்கக் கட்டுரைகளின் தொகுப்பு

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தொகுதி 1

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முனைவர் வே.நிர்மலர் செல்வி

UGC Approved Journal Number: 40729
VOLUME 3| SPECIAL ISSUE 1 | MARCH 2019
Shanlax International Journal of Tamil Studies
A Peer-reviewed- Refereed Scholarly Quarterly Journal Globally Indexed with Impact Factor

ISSN INTERNATIONAL STANDARD SERIAL NUMBER INTERNATIONAL CENTRE
PKP PUBLIC KNOWLEDGE PROJECT
OJS OPEN JOURNAL SYSTEMS
SHANLAX INTERNATIONAL JOURNALS
editorsij@shanlaxjournals.in | www.shanlaxjournals.in

மரமும் மனிதமும் - நற்றிணை வாயிலாக ஓர் ஆய்வு

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மலர்: 3

சிறப்பிதழ்: 1

மாதம்: மார்ச்

வருடம்: 2019

ISSN: 2454-3993

முன்னுரை

அனைத்து உயிர்களுக்கும் அன்பு பிரதானமானது. மனிதர்கள், சக மனிதர்கள் மீது அன்பு, அக்கறை கொள்வது இயல்பு. இவ்வியல்பையும் தாண்டி சங்ககால மக்கள் இயற்கையை விரும்பினர். குறிப்பாக மரங்களை நேசித்தனர். தம் உறவாக எண்ணினர். தம் செய்யுள்களில் பாடு பொருளாக்கினர். தம் கருத்துக்கு மரங்களை உவமையாக்கி மகிழ்ந்தனர். இவ்வாறாக மனிதர்களுக்கு மரங்கள் மீதான அன்பை நற்றிணை வாயிலாக ஆய்வதே இக்கட்டுரையின் நோக்கமாகும்.

விழுமியங்கள்

மனித வாழ்வியலின் விழுமியங்களில் அன்பும் ஒன்றாகும். இதனை "அன்பு, அகிம்சை, உண்மை, சாந்தி, மானுடம், நல்லொழுக்கப் பண்புகள் என்பன மனித விழுமியங்கள்"[1] என குமாரசாமி சோமசுந்தரம் குறிப்பிடுகிறார்.

நற்றிணை

நற்றிணை சங்க இலக்கியங்களில் உள்ள எட்டுத்தொகை நூல்களுள் முதலாவதாகும். இதனை,

"நற்றிணை நல்ல குறுந்தொகை ஐங்குறுநூறு
ஒத்த பதிற்றுப்பத்து ஓங்கு பரிபாடல்
கற்றறிந்தோர் ஏத்தும் கலியே, அகம், புறம் என்று
இத்திறத்த எட்டுத்தொகை"[2]

என்ற பாடல் உணர்த்துகிறது.

நல்+திணை = நற்றிணை என்றாகும். வாழ்வில் கடைபிடிக்க வேண்டிய ஒழுக்க லாறுகளை, விழுமியங்களை முறையாக கடைபிடிக்க வேண்டும் என்று கூறுவதே நற்றிணை ஆகும். நற்றிணை அகம் பற்றிய செய்திகளை கூறுகின்றது.

நற்றிணைப் பாடல்களைத் தொகுக்கச் செய்தவர் பன்னாடு தந்த பாண்டியன் மாறன்வழுதி. இவர் புலவராகவும் அரசராகவும் இருந்தார். "192 புலவர்களால் பாடப்பெற்றது நற்றிணை"[3] என ச.வே. சுப்பிரமணியம் கூறுகிறார். 7அடி முதல் 13 அடி வரை உள்ள 399 பாடல்களால் ஆனது நற்றிணையாகும்.

உறவாகும் மரங்கள்

ஏழு வயது சிறுமி ஒருத்தி கடற்கரை மணலில் புன்னைக் காயை மறைத்து வைத்து விளையாடுகின்றாள். மழை பெய்ததால் வீட்டிற்கு திரும்பி விடுகிறாள். சில நாட்கள் கழித்து சென்று பார்த்த போது அப்புன்னை விதை முளைத்து விட்டதைக் கண்டு மகிழ்ந்து, அதை எடுத்து தன் வீட்டின் பின் தோட்டத்தில் வைக்க அது வளர்கின்றது. அச்சிறுமியும் வளர்ந்து, திருமணமாகி ஒரு குழந்தையும் பெறுகிறாள்.

அப்பெண், தன் குழந்தையிடம் தான் வளர்த்த புன்னை மரமே தனது முதல் குழந்தை எனவும், அம்மரமே உன்னுடைய அக்கா எனவும் கூறுகின்றாள். பிறகு அக்குழந்தை பெரியவளாகி, தன் காதலனுடன் அப்புன்னை மரத்தடியில் பேச நாணுகின்றாள். இவ்விடத்தில் அவள் புன்னை மரத்தை தன் சகோதரியாக கருதுகின்றாள். இங்கு மரத்தை தன் குழந்தையாக பார்த்த தாயையும், சகோதரியாக எண்ணிய மகளையும் காண முடிகிறது. இவ்விழுமியம் சங்ககால மக்களிடம் மட்டுமே காணக்கிடைக்கும் ஒன்றாகும். இந்நிகழ்ச்சியை,

"விளையாடு ஆயமொடு வெண்மணல் அழுத்தி
மறந்தனம் துறந்த காழ்முளை அகைய
நெய்பெய் தீம்பால் பெய்துஇனி வளர்ப்ப
நும்மினும் சிறந்தது நுவ்வை ஆகும்என்று
அன்னை கூறினாள், புன்னையது சிறப்பே
அம்ம நாணுதும், நும்மோடு நகையே"[4]

என்ற நற்றிணை பாடல் உரைக்கின்றது.

தோழனாகும் மரங்கள்

தலைவன் ஒருவன் தன்னைக் காப்பாற்றும் தோழனாக வேங்கை மரத்தை கருதியதை நற்றிணையில்

"மழகளிறு உரிஞ்சிய பராரை வேங்கை"[5]

என்ற வரியுடைய பாடல் வழி உணர முடிகின்றது. தலைவி தன் வீட்டை விட்டு வெளியேறி தலைவனுடன் காட்டிற்கு வந்து விடுகின்றாள். அங்கு தலைவியைத் தேடி அவளின் சுற்றத்தார்கள் வருவார்கள் என்றெண்ணிய தலைவன் ஒரு வேங்கை மரத்தின் பின்னால் ஒளிந்து கொள்கிறான். காரணம் புரியாது நின்ற தலைவியிடம், தலைவன் 'வழிப்பறிக் கள்வர் யாரேனும், அவர்களிடம் போர் செய்து உன்னைக் காப்பேன். உன் சுற்றத்தார் வந்தால், இவ்வேங்கை மரத்தின் பின் மறைந்து நிற்பேன்' என்கின்றான்.

இவ்வாறாக தலைவன் மறைந்து கொள்ள ஏதுவாக விளங்கும் வேங்கை மரம் ஒரு தோழனாக பாதுகாப்பு தருவதை காண முடிகின்றது.

தலைவியும் பலா மரமும்

பலா மரத்தை உன்னிப்பாக கவனித்த சங்ககால மக்கள் பலாவின் தன்மையுடன், தலைவியை ஒப்பிட்டனர். இதனை,

"மலை சார்ந்த பகுதியில் நிறைந்துள்ள பலா மரங்களின் பலாச் சுளைகள் இனியச் சுவையை உடையன பலாமரத்தின் மேற்புறம் கடினமானத் தோற்றமுடையது. இத்தன்மை கொண்ட பலா மரங்கள் சூழ்ந்த தலைவியின் பண்பும் ஒழுக்கமும் பலா மரத்தின் இயல்போடு ஒத்துள்ளதை காணமுடிகின்றது"[6] என நாராயணசாமி ஐயர் குறிப்பிடுகின்றார்.

தலைவியானவள் தலைவன் மீது கோபம் கொண்டாலும், அவனிடம் கடுமையாக நடந்து கொண்டாலும் அவள் உள்ளத்தில் தலைவன் பால் இனிமையான அன்பு இருப்பதை பலாப்பழத்தின் வாயிலாக உணர முடிகின்றது.

தலைவி யாராலும் எளிதில் அனுக முடியாதவள். அவளின் அன்பும் அழகும் பலாக் கனியின் இனிய சுவை போன்றதாகும். அவளின் அன்பை பெறுதல் கடினமான ஒன்றாகும். இதற்கு அதிக முயற்சி எடுக்க வேண்டும். இதன் வழி தலைவியின் பண்புகள் உணர்த்தப்படுகின்றன.
பலா மரத்தின் வேறு பெயர்கள் பலவு, ஆசினி என்பதை

"பேதை ஆசினி ஒசித்த"[7]

"பல்கோள் பலவின் சாரல் அவர் நாட்டு"[8]

என்ற நற்றிணை வரிகள் மெய்ப்பிக்கின்றன.

மழலைகளுக்கு மகிழ்ச்சியூட்டுதல்

சங்ககால மக்கள் மழலைகளுக்கு மகிழ்ச்சியூட்ட பனை ஓலையால் செய்யப்பட்ட குதிரை பொம்மைகளை பயன்படுத்தினர். இதனை,

"உண்ணா நல்மாப் பண்ணி, எம்முடன்"[9]

என்ற வரி எடுத்துரைக்கின்றது. பனை மடலால் உணவு உண்ணாத குதிரை பொம்மைகளைச் செய்து அதற்கு சிறுசிறு மணிகளைப் பூட்டி அதனை மழலைகள் வீதியில் இழுத்துச் சென்று விளையாடியதை மேற்கண்ட பாடல்வழி காண முடிகின்றது.

தம் குழந்தைகள் நடைபயிலும் போது, தமக்கு விருப்பான மரத்தினால் செய்யப்பட்ட நடை வண்டியில் நடை பழக்கியதை,

"தேர்நடை பயிற்றம் தேமொழிப் புதல்வன்"[10]

என்ற நற்றிணை வரி விரித்துரைக்கின்றது.

காவல் மரங்கள்

பண்டைய தமிழரசர்கள், மரங்களின் மீது கொண்ட அன்பினால் தம் வீரத்தின் வெற்றியின் அடையாளமாக மரங்களை ஏற்படுத்தினர். இவை காவல் மரங்கள் எனப்படும். தம் வேற்றியின் அடையாளச் சின்னமாக ஒரு மரத்தை தமது கோட்டைகளின் சோலைகளில் வைத்து வளர்த்து அதனை பாதுகாப்பார்கள். படையெடுத்து வரும் எதிரி மன்னர்கள், அக்காவல் மரத்தையே வெட்ட முற்படுவார்கள். காவல் மரம் வெட்டப்பட்டால் அம்மரத்துக்குரிய அரசருக்கு பெருந்தோல்வியும், பேரவமானமும் ஏற்பட்டதாக கருதப்படும்.

"தமிழ் வேந்தர்கள் வெற்றியைக் குறிக்கும் மரமாகக் கடம்பமரம், புன்னைமரம், கணையமரம், கடிமரம், வேப்பமரம், மாமரம், வாகை மரம் முதலிய மரங்களை காப்பாற்றி வந்தனர்□11 திதியன் என்ற மன்னனுக்கு புன்னைமரம் காவல் மரமாக இருந்தது என்று நற்றிணை கூறுகின்றது. இதனை,

"இருபெரு வேந்தர், பொருளகத்து ஒழித்த
புன்னை விழுமம் போல"[12]

மன்னனது மாபெரும் வீரத்தின் அடையாளமாக மரங்கள் அமைந்திருந்ததை இதன் மூலம் உணரமுடிகின்றது.

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முடிவுரை

மனித வாழ்வின் ஒவ்வொரு தருணத்திலும் ஏதேனும் ஒரு வகையில் மரங்கள், மனிதனுக்கு நேராகவோ, மறைமுகமாகவோ பயன் தருவதை, புரிந்து கொண்டனர் சங்ககால மக்கள். எனவே, அம்மரங்களை நேசித்து பாதுகாத்ததுடன், தம் வாழ்க்கையின் ஓர் அங்கமாகவே கருதியதை நற்றிணை பாடல்கள் வழிநின்று உணர முடிகின்றது.

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4. நற்றிணை பாடல் 172 வரிகள் 1-6
5. நற்றிணை பாடல் 362 வரி 7
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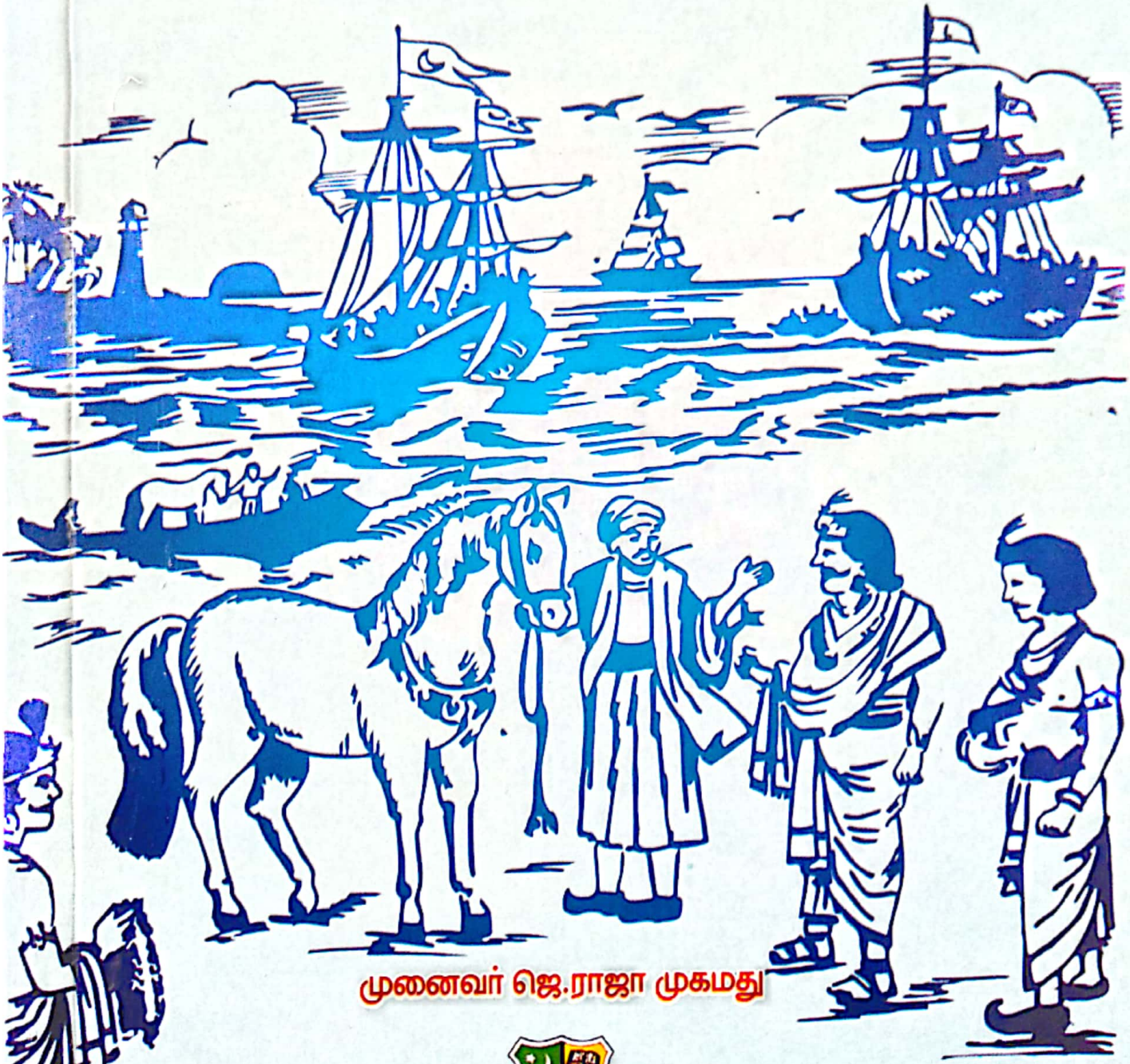
தமிழகத்தில் இஸ்லாம்

வந்ததும், வளர்ந்ததும், வாழ்வதும்

வரலாறு

தொகுதி– 1



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வந்ததும் வளர்ந்ததும் வாழ்வதும்

வரலாறு

(தொகுதி-I)

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தமிழகத்தில் இஸ்லாம் - வந்ததும் வளர்ந்ததும் வாழ்வதும் - வரலாறு

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முதல் பதிப்பு - 2018

இரண்டாம் பதிப்பு - 2020

வெளியீடு : ஜமால் முகமது கல்லூரி
இஸ்லாமிய தமிழ்ப் பண்பாட்டு
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அச்சிட்டோர் : டீக்யூ பிரஸ்., திருச்சி - 20.

ISBN : 978-81-944322-4-1

விலை : ரூ. 75/-

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வாழ்த்துரை

தென்னகத்தின் அலிகார் என்று மக்களிடம் அறிமுகமாகியுள்ள திருச்சிராப்பள்ளி ஜமால் முகமது கல்லூரி, உயர்கல்வி பயிற்றுவிப்பதை மட்டும் கடமையாகக்கொள்ளாமல் மக்களின் வாழ்வியல் குறித்த பல்வேறு அம்சங்கள் குறித்தும் ஆய்வுகள் மேற்கொண்டு வெளியிட்டு வருகிறது. இவ்வகையில் தமிழக முஸ்லிம் மக்களின் வரலாறு பண்பாடு குறித்த செய்திகளை உள்ளடக்கிய நூல்கள் இல்லாத குறையை, நிவர்த்தி செய்யும் பொருட்டு, "இஸ்லாமியப் பண்பாட்டு ஆய்வு மையம்" என்ற ஆய்வு இருக்கைத் தொடங்கப்பட்டது. மைய இயக்குநராக வரலாற்று ஆய்வாளர் முனைவர். ஜெ.ராஜாமுகமது பொறுப்பேற்றிருப்பது இதன் செயல்பாடுகள் துரிதமாக நடைபெறுவதற்கு வகையானது. முனைவர் ராஜாமுகமது "தமிழக முஸ்லிம்களின் கடல் வாணிப வரலாறு" குறித்து எழுதியுள்ள ஆய்வு நூல், இந்த சமுதாயத்தின் தொன்மையான வரலாற்றினையும், முஸ்லிம் கடலோடிகள், தங்களது சொந்தக்கப்பல்களில் இந்தியக்கடல் வெளிகளில் பயணித்து உலகக்கடல் வாணிபத்தில் பங்கு கொண்ட பாங்கினை ஆவணங்களின் துணை கொண்டு விளக்கி, உலகப் பல்கலைக்கழகங்களின் கவனத்தைக் கவர்ந்துள்ளார். இது தமிழ் முஸ்லிம் சமுதாயத்திற்குப் பெருமை சேர்க்கிறது.

நமது மக்கள் தங்களது முன்னோர்களின் வரலாற்றினைப் பதிவுசெய்து வைப்பதில் கவனம் செலுத்தவில்லை. இதன் காரணமாக 1400 ஆண்டுகளுக்கு முன் இஸ்லாம் இந்த நாட்டிற்கு வந்து பரவிய வரலாறு குறித்து கர்ணப்பரம்பரைக் கதைகளே சொல்லப்பட்டு வருகின்றன. இந்திய இனங்களுக்கிடையே வேற்றுமையை உருப்பெருக்கும் சக்திகள், இதனைப் பயன்படுத்திக் கொண்டு தமிழகத்தில் "கட்டாயமாக இஸ்லாம் மதம் திணிக்கப்பட்டது" எனத் தொன்றுதொட்டு சொல்லுவதையும் எழுதப்படுவதையும் நாம் காண்கிறோம். இதை எதிர்கொள்ள இஸ்லாமிய எழுத்தாளர்கள், ஆய்வாளர்கள் ஆங்காங்கே முயற்சிகள் மேற்கொண்டிருப்பினும், அவை பல திக்குகளுக்குச் சென்றடையாத நிலையே உள்ளது. இதனால் இந்த நாட்டின் சமரச வாழ்வு வெகுவாகப் பாதிக்கப்பட்டிருக்கிறது.

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"தமிழகத்தில் கத்தியின்றி ரத்தமின்றி இஸ்லாம் பரவியது" எப்படி என்பதை இந்த நூல் ஆய்வுத்தரவுகளுடன் விளக்குகிறது. வட இந்தியாவில் முஸ்லிம்கள், ஆளும் சக்தியாக உருவெடுப்பதற்கு ஒரு நூற்றாண்டிற்கு முன்பே வணிகநிமித்தம் வந்த அரேபிய முஸ்லிம்களின் மூலமாகத் தமிழகத்துக் கடற்கரைக்கு வந்து சேர்ந்த இஸ்லாம் மக்களின் மனங்களில் இடம் பெற்று வாழ்ந்து வருவதை நூலாசிரியர் சான்றுகளுடன் விளக்கியுள்ளார். படித்தவர், பாமரர், மாணவர்கள் என அனைவர் மத்தியிலும் இது ஒரு சரியான விளக்கத்தை அளிக்கும் நூலாகும்.

இன்றைக்கு 1300 ஆண்டுகளுக்கு முன்பு இஸ்லாம் மதம் திருச்சிராப்பள்ளி பகுதியில் அமைதியாகத் தடம்பதித்து ஹிஜ்ரி 116-ம் ஆண்டில் ஒரு பள்ளிவாசலும் கட்டப்பட்ட செய்தியினை ஆசிரியர் தக்க சான்றுகளுடன் விளக்கியுள்ளார். இவ்வகையில் தமிழக முஸ்லிம்களின் தொன்மைக்குச் சான்று திருச்சியிலிருந்து தொடங்குகிறது என்பது வரலாறு எழுதுபவர்களுக்கு நல்ல செய்தியாகும். இஸ்லாம் சமயத்தை மக்களிடம் கொண்டு சேர்ப்பதில் இஸ்லாமிய மெய்ஞானியரின் பங்களிப்பு மகத்தானது. கடல் கடந்த நாடுகள் பலவற்றிலிருந்து இந்த நாட்டிற்கு வந்து, இஸ்லாமிய நல்லற போதனைகள் செய்து, ஆயிரக்கணக்கான மக்களை இஸ்லாம் மதத்தைத் தழுவச்செய்து , தங்கள் வாழ்நாளை இந்த மண்ணில் நிறைவுசெய்து இங்கேயே அடக்கமாகி இருக்கும் இவர்களது துயிலிடங்கள் தர்காக்கள் என அழைக்கப்படுகின்றன. இவ்வகையில் தமிழ்நாட்டிற்கு வந்து காலத்தால் முற்பட்ட ஞானியர் பெருமகனார் திருச்சியில் அடக்கமாகி இருக்கும் நத்ஹர் வலி என்னும் இறைநேசச் செல்வராவார். இவரது அழைப்புப் பணியாலும், அன்பான அணுகுமுறையாலும், இஸ்லாம் மதம் இப்பகுதியில் எப்படிப் பரவியது என்பது இந்த நூலில் விரிவாகச் சொல்லப்பட்டுள்ளது. தவறானப்பிரச்சாரங்களுக்கு இவையே தக்கபதில் சொல்லும்.

"தமிழ்நாட்டில் இஸ்லாம் வளர்வதற்கு இந்த நாட்டை ஆண்டுவந்த இந்து சமய மன்னர்கள் அளித்து வந்த ஆதரவை, கல்வெட்டுகள், செப்பேடுகள், இலக்கியங்கள் துணைகொண்டு இந்த நூலில் நீண்டதொரு பட்டியல் கொடுக்கப்பட்டுள்ளது. அப்போது நிலவிய சமுதாய சூழலில் இஸ்லாம் இங்கு வளர்ச்சிக் காண்பதற்குக் கிடைத்த நல்வாய்ப்புகளை ஆசிரியர் நன்கு விளக்கியுள்ளார். இளைய தலைமுறையினருக்கு இது எழுச்சியூட்டுவதாகும்.

ஆய்வு மையத்திலிருந்து க ஆக வெளிவரும் இந்த நூல் தவறாக ஊதிப்பெருக்கப்பட்டு பரந்து கொண்டிருக்கும் கட்டுக்கதை பலூன்களை உடைத்தெறியும் "Bullet", என்று சொல்லலாம்.

இந்த நல்ல பணியைச் செய்துள்ள முனைவர் ஜெ.ராஜாமுகமது அவர்களைப் பாராட்டுவதோடு, மேலும் பல ஆய்வு நூல்களை அவர் உருவாக்கித் தரவேண்டுமென்பது நமது விருப்பமாகும்.

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வாழ்த்துரை

எல்லாப்புகழும் இறைவனுக்கே

வரலாறு தெரியாத சமுதாயம் எழுச்சி பெறமுடியாது. எனவேதான் 1300 ஆண்டுகளுக்கு முன் தமிழ்நாட்டிற்கு இஸ்லாம் எப்படி வந்தது என்பதும், எவ்வாறு பரவியது என்பதும் வரலாற்று ரீதியாக அறியப்படாத காரணத்தால் இஸ்லாம் சமயம் இங்கு வன்முறையில் பரப்பப்பட்டது என்றதொரு பொய்ப் பிரச்சாரத்தை மீண்டும் மீண்டும் பிரிவினை சக்திகள் சொல்லி வருகின்றன. இதற்கு ஒரு நிரந்தர தீர்வு காணவே திருச்சிராப்பள்ளி ஜமால் முகமது கல்லூரி "இஸ்லாமியத் தமிழ்ப் பண்பாட்டு ஆய்வு மையம்" என்ற ஆய்வுத்துறையைத் தொடங்கியுள்ளது.

வரலாற்று ஆய்வுமையம் தொடங்கி 6 மாதமே ஆன நிலையிலும், இதன் பணிகள் துரிதப்படுத்தப்பட்டு இந்த நூல் வெளிவருகிறது. "தமிழகத்தில் இஸ்லாம் - வந்ததும், வளர்ந்ததும், வாழ்வதும் - வரலாறு" என்ற இந்த நூல் இந்தியாவில், குறிப்பாகத் தமிழ்நாட்டில் எப்படிப் பரவியது என்பதை அனைவரும் எளிதில் புரிந்து கொள்ளும் வண்ணம் எழுதப்பட்டுள்ளது. இஸ்லாம் தோன்றிய கி.பி. 7-ம் நூற்றாண்டிலேயே, தென்னிந்தியாவில் தமிழ்நாட்டில் (இஸ்லாமிய அரசியல் சக்திகள் ஏதும் இல்லாத நிலையில்) அமைதியாக மக்கள் மனதில் இடம்பிடித்து வாழ்ந்து கொண்டிருக்கிறது. இத்தகைய அரிய பணியைச் செய்தவர்கள் மக்களிடம் எளிதில் பழகும் வாய்ப்புப் பெற்றிருந்த அரேபிய முஸ்லிம் வணிகர்கள் மற்றும் அவர்களுக்குத் துணைநின்ற தன்னார்வ மதப்பிரச்சாரத் தொண்டர்கள் மற்றும் இஸ்லாமிய மெய்ஞானியர் ஆவார்கள் என்பதை நூலாசிரியர் சான்றுகளுடன் விளக்கியுள்ளார்.

இஸ்லாம் அன்றும் இன்றும் தவறாகப்புரிந்து கொள்ளப்பட்டிருப்பதற்கு, இதுபோன்ற சான்றுகளுடன் கூடிய நூல்கள் இல்லாததும் முக்கிய இடைவெளியாகும். இதன் காரணமாகத் தாக்கங்களும் விளைவுகளும் இந்த நாட்டு இனங்களுக்கு இடையே பிணக்கத்தை உண்டு பண்ணியுள்ளதும் நமது அமைதியான வாழவிற்குப் பங்கம் விளைவித்தும் வந்துள்ளது.

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தவறான கருத்துக்களுக்கு வரலாற்றுச் சான்றுகளுடன் இந்த நூல் சரியான விளக்கத்தினை அளிக்கிறது. இது கற்றவர்கள் மத்தியில், குறிப்பாக மாணவர்கள் மத்தியில் ஒரு தெளிவை ஏற்படுத்தும் என்பதில் ஐயமில்லை. எதிர்காலத்தில் அவர்கள் ஒருவரை ஒருவர் புரிந்து கொண்டு வாழ்வதற்கு இது வழிவகுக்கும்.

ஆய்வு மைய இயக்குநர் முனைவர் ஜெ.ராஜாமுகமது தமிழக முஸ்லிம்களின் வரலாறு குறித்து ஆய்வுகள் செய்து வருபவர். அவரது ஆழ்ந்த வரலாற்று அணுகுமுறை இந்த நூலில் பளிச்சிடுகிறது. ஆய்வு மையம் தமிழ் முஸ்லிம்களின் வாழ்வியல் குறித்து மேலும் பல நூல்களை வெளியிடவுள்ளது. ஜமால் முகமது கல்லூரி, முஸ்லிம்களின் பண்பாட்டினை உலகறியச் செய்யும் இப்பணியினை மேற்கொண்டிருப்பதில் மிகுந்த மகிழ்ச்சியடைகிறது. முனைவர் ஜெ.ராஜாமுகமது அவர்களுக்கு நமது வாழ்த்துக்களைத் தெரிவிப்பதோடு, அவரது ஆய்வுப்பணி தொடர எல்லாம் வல்ல இறைவன் நல்லருள் புரிவானாக.

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முனைவர் **K. அப்துஸ் சமது**
துணைச் செயலாளர்

வாழ்த்துரை

அளவற்ற அருளாளன் நிகரற்ற அன்புடையோன்
அல்லாஹ்வின் திருப்பெயரால்.....

திருச்சிராப்பள்ளி ஜமால் முகமது கல்லூரி தனது சீரிய கல்விப்பணிகளோடு, பல்வேறு துறைகளிலும், ஆய்வுகளையும் மேற்கொண்டு வருகிறது. தமிழக முஸ்லிம்களின் வரலாறு பண்பாடு குறித்து ஆய்வு செய்து ஆவணப்படுத்தும் பொருட்டு, "இஸ்லாமிய தமிழ்ப் பண்பாட்டு ஆய்வு மையம்" என்றதொரு ஆய்வு இருக்கை டிசம்பர் 2018ல் துவங்கப்பட்டது. வரலாற்று ஆய்வாளர் முனைவர் ஜெ.ராஜாமுகமது இந்த ஆய்வு மைய இயக்குநராகப் பொறுப்பேற்றுள்ளார். தமிழ்நாடு அரசு அருங்காட்சியகத்துறையில் பணிபுரிந்து ஓய்வுபெற்ற இவர், தமிழ்நாட்டு முஸ்லிம்கள் குறித்து ஆய்வு மேற்கொண்டு வருபவர்.

இஸ்லாமிய தமிழ்ப் பண்பாட்டு ஆய்வு மைய முதல் வெளியீடாக, "தமிழகத்தில் இஸ்லாம் - வந்ததும், வளர்ந்ததும், வாழ்வதும் - வரலாறு" என்னும் இந்த ஆய்வுரை நூலாக வெளிவருகிறது. இந்த ஆய்வுரையில் தமிழ்நாட்டில் இஸ்லாம் சமயம் அமைதிவழியில் பரவியது என்பது தக்க சான்றுகளுடன் விளக்கப்பட்டுள்ளன. இதன்மூலம் தவறாகப் பரப்பப்பட்டுவரும் பல செய்திகள் மறுபரிசீலனைக்குட்படும். இளைய தலைமுறையினரின் சிந்தனையைத் தூண்டும், ஆயிரக்கணக்கான ஆண்டுகளாக நிலவி வரும் மத நல்லிணக்கம் உறுதிபெறும். எதிர்வரும் சமுதாயம் இணக்கத்துடன் வாழ வாய்ப்பாகும்.

இஸ்லாமிய பண்பாட்டு ஆய்வு மையப்பணிகள் தொடருகின்றன. தொடர்ந்து ஆய்வு முடிவுகள் வெளியிடப்படும். இந்த நல்லதொரு பணியினை மேற்கொண்டு வரும் முனைவர். ஜெ.ராஜாமுகமது பாராட்டுக்குரியவர்.

K. Abdus Samad

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முனைவர் **S. இஸ்மாயில் முகைதீன்**
முதல்வர்

வாழ்த்துரை

புகழனைத்தும் ஏக இறைவனுக்கே.....

திருச்சி மாநகரில் 1951-ம் ஆண்டு, பின் தங்கிய சமுதாய இளைஞர்களின் வாழ்வில், குறிப்பாக முஸ்லிம்கள், ஏற்றம் காண ஜமால் முகமது கல்லூரி தொடங்கப்பட்டு இன்றைக்கு சுமார் 12,000 மாணவ-மாணவியரின் கல்வித் தேவையைப்பூர்த்தி செய்துகொண்டிருக்கிறது. எதிர்காலத்தை ஆளப்போகும் இந்த இளைஞர் பட்டாளத்தை கல்வியறிவில் முன்னனியில் இருக்கச் செய்வதோடு இந்த நாட்டின் சரியான வரலாற்றினையும், பண்பாட்டு விழுமியங்களையும், மத நல்லிணக்கத்தையும் எடுத்துக்காட்ட வேண்டியதும் அவசியமாகிறது. இது இந்த இளைஞர்கள் மத்தியில் நேச உணர்வை வளர்க்கும். இதன்வழி இந்த நாடு அமைதியான முன்னேற்றம் காண வாய்ப்பாகும்.

"சரித்திரத்தேர்ச்சி கொள்", என்றான் பாரதி, ஆனால் சரித்திரத்தைப் பற்றி அதிகம் கவலைப்படாமல் தமிழக இஸ்லாமிய சமுதாயம் காலக்கிரமமான வரலாற்றுத்தரவுகளை ஆவணப்படுத்தி வைப்பதில் பின் தங்கி விட்டது. இதன் காரணமாக 1400 ஆண்டுகளுக்கு முற்பட்ட இஸ்லாம் சமுதாயத்தின் வரலாறு, முஸ்லிம்களின் வாழ்வியல் ஆகியனவற்றை இந்த நாட்டிற்கு வணிகர்களாக வந்து நாடாளுபவராக உருவான ஆங்கிலேயர் (The British) எழுதினர். நல்ல செயல்தான்! ஆனால் தங்களது ஆட்சியைத் தக்கவைத்துக் கொள்ள இந்த நாட்டு இனங்களுக்கிடையே ஒற்றுமை ஏற்பட்டு விடக்கூடாது என்பதற்காக திட்டமிட்டு இந்நாட்டு வரலாறு திரித்து எழுதப்பட்டது. அவற்றில், இந்த நாட்டை 700 ஆண்டுகள் நடைபெற்ற முஸ்லிம்களின் ஆட்சி ஒரு கோர கனவாக சித்தரிக்கப்பட்டு, இந்த நாட்டுப் பெரும்பான்மை இந்துமக்களின் வரலாறு பண்பாட்டை அழித்தவர்களாகப் படம்பிடித்துக் காட்டப்பட்டன. பின்னர் வந்த எழுத்தாளர்களும், மக்களும் இந்த நாட்டின் வரலாற்றினை, "ஆங்கிலேயரின் கண் கொண்டு பார்க்கத் தொடங்கினர்" பகைமை தீ மூட்டப்பட்டது.

இவ்வாறு எழுதப்பட்ட வரலாற்று நூல்களில், இந்த நாட்டில் இஸ்லாம் மதம், வாள்கொண்டு பரப்பப்பட்டது எனவும், கட்டாயப்படுத்தி மதம் மக்களிடம் திணிக்கப்பட்டது எனவும், இந்துக்களின் கோவில்கள் அழிக்கப்பட்டு கொள்ளையிடப்பட்டது எனவும் பலவாறாகப் பொய் மூட்டைகளை அவிழ்த்து

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விட்டனர். இவையெல்லாம் சரியா? தவறா? என்ற எண்ணப்போக்கு அப்போதைய சூழ்நிலையில் உருவாகாமல் போனது. இதனால் இந்த நாட்டில் இந்து முஸ்லிம் ஒற்றுமைக்கு பெரும் சவால்கள் தோன்றின.

இதற்கு இயன்றதொரு தீர்வுகாணும் தொடக்கமாக திருச்சி ஜமால் முகமது கல்லூரி இஸ்லாமிய தமிழ்ப் பண்பாட்டு ஆய்வு மையம் என்ற ஆய்வு இருக்கையைத் தொடங்கியுள்ளது. தமிழக முஸ்லிம்களின் வரலாற்றை, வரலாற்று வரைவியல் ரீதியாக எழுதி ஆவணப்படுத்துவது இதன் நோக்கம். நமது கவனத்திலிருந்து தப்பிப்போன இந்த நற்பணியை இப்போது ஜமால் முகமது கல்லூரி மேற்கொண்டதில் பெருமை அடைகிறோம். ஆய்வு மையம் தொடங்கி 6 மாதங்களே ஆனாலும் அதன் பணி மிகவும் வேகமாகச் சென்று கொண்டிருப்பதற்கு அடையாளமாக தமிழகத்தில் இஸ்லாம் எப்படிப் பரவியது? இதற்கான காரணிகள், சூழல்கள் குறித்து முதல் ஆய்வு நூல் வெளிவருகிறது. இது ஒரு தொடக்கமே. இன்னும் இது குறித்தும் நிறைய செய்திகள் சொல்லப்பட வேண்டியுள்ளது.

இஸ்லாமிய தமிழ்ப் பண்பாட்டு ஆய்வு மையம் தொடங்கப்பட்ட போது இதற்கு பொறுப்பேற்க பொருத்தமான ஒருவர் எங்களுக்குக் கிடைத்தது இறையருள். முனைவர் ஜெ.ராஜா முகமது, தமிழ்நாடு அரசு அருங்காட்சியகத் துறையில் பணிபுரிந்தவர். சிறந்த ஆய்வுப்புலமை மிக்கவர். முஸ்லிம்களின் வரலாறு குறித்த இவரது ஆய்வுகள் உலக வரலாற்றாளர்களின் கவனத்தை ஈர்த்துள்ளன. இவரது தலைமையின் கீழ் எங்களது எண்ணக்கிடக்கை இனிதே நிறைவேறும் என்பதற்கு, "தமிழகத்தில் இஸ்லாம் - வந்ததும், வளர்ந்ததும், வாழ்வதும் - வரலாறு" என்னும் இந்த நூல் அமைகிறது.

தமிழகத்தில் இஸ்லாம் எப்படிப் பரவியது என்பதை மிக விரிவான வரலாற்றுச் சான்றுகளுடன் விளக்குகிறது இந்த நூல். சில முக்கிய செய்திகளை இங்கு முன்னிலைப்படுத்தி குறிப்பிடலாம். தமிழக முஸ்லிம்களின் தொன்மையான வரலாற்றிற்கு அறுதியான சான்று திருச்சியில் கிடைக்கிறது என்பதை நூலில் காணும்போது இந்த மண்ணின் சிறப்பு புலப்படுகிறது. இங்கு 1300 ஆண்டுகளுக்கு முன் நிலவிய சமய நல்லிணக்கம் நமக்கு வியப்பூட்டுகிறது.

"இஸ்லாம் இந்த நாட்டில் வாள்கொண்டு பரப்பப்பட்டது, கட்டாயமாக விடாப்பிடியாகப் பிடித்து வந்து சுன்னத் செய்தார்கள். ஏற்காதவர்கள் துன்புறுத்தப்பட்டார்கள்" என்ற புனையுரைகளுக்குத் தக்க பதில் இங்கு கிடைக்கிறது. ஏனெனில் ஹிஜ்ரி 116 - கி.பி. 734-ல் முஸ்லிம் மன்னர்கள் யாரும் ஆட்சி செய்யவில்லை. இஸ்லாம் என்னும் இனிய மார்க்கம், மக்கள் மனங்களுக்குள் புகுந்து ஆன்மீக ரீதியாக, அமைதியாக வாழ்ந்து கொண்டிருக்கிறது. மக்கள் வரலாறு இங்கு பேசப்படுகிறது. அப்போது ஆண்ட இந்து மன்னர்களின் ஆதரவு கடல் கடந்து வந்த இந்த மார்க்கத்திற்குக் கிடைத்ததை இது புலப்படுத்துகிறது என்பதை ஆசிரியர் ஆணித்தரமாக நிலைநிறுத்துகிறார்.

இஸ்லாம் மார்க்கத்தை - மதத்தை - இந்த நாட்டில் அறிமுகப்படுத்தியவர்கள் யார்? இந்த நாட்டிற்கு வணிகநிமித்தம் வந்த அரேபிய முஸ்லிம் வணிகர்கள். இவர்களுடன் பின்னர் தன்னார்வப் பிரச்சாரகர்களும், இஸ்லாமிய

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மெய்ஞானியர்களும் இணைந்து கொண்டனர். இவர்களது கூட்டு முயற்சியால் இஸ்லாம் இந்த நாட்டில் வளர்ந்தது. மக்களின் ஆதரவுடன் வாழ்ந்து கொண்டிருக்கிறது.

வடஇந்தியாவிற்கும், தென்னிந்தியாவிற்கும் இஸ்லாம் வந்தவிதம் வெவ்வேறானது. முன்னது அரசியல் நோக்கம் கொண்டது. பின்னது அமைதியானது. இருப்பினும், இந்த நாட்டை 700 ஆண்டுகளுக்கு மேலாக ஆட்சி செய்த முஸ்லிம் மன்னர்கள் இந்த நாட்டை ஓர் " இஸ்லாமிய நாடாக மாற்றும் முயற்சியில் ஈடுபடவில்லை". அப்படி அவர்கள் நினைத்திருந்தால் இந்தியா இன்று இஸ்லாமிய குடியரசாக இருந்திருக்கும் என்பதை வரலாற்று ரீதியான சான்றுகளுடன் ஆசிரியர் எடுத்துரைக்கிறார்.

இந்நாட்டில் இஸ்லாம் பரவுவதற்கு அன்றைய சமுதாய சூழல் சாதகமாக இருந்தது. சாதி ஏற்றத்தாழ்வுகளில் சிக்கித் தவித்த சமுதாய அடித்தள மக்கள் தங்கள் மனித உரிமைகளை உறுதி செய்து கொள்ள தாங்களாகவே முன்வந்து இஸ்லாம் மதத்தைத் தழுவிக் கொண்டார்கள். அப்போது நடந்து கொண்டிருந்த சமயங்களுக்கிடையேயான மோதல்களில் இஸ்லாம் தனித்திருந்தது. இஸ்லாமியக் கோட்பாடுகள் அப்போதிருந்த மதங்களின் கோட்பாடுகளுக்கு ஏற்புடையதாக இருந்ததால், பிற மதங்கள் இஸ்லாம் மதம் பரவுவதற்குத் தடையாக இருக்கவில்லை. இஸ்லாத்திற்கு மத மாற்றங்கள் ஒரு சர்ச்சையாகவும் இருக்கவில்லை. இணக்கமாக மக்கள் மனதில் இடம்பெற்ற இஸ்லாம் எல்லா தரப்பு மக்களின் ஆதரவுடன் வளர்ந்து, வாழ்ந்து வருகிறது என்பதை கல்வெட்டுகள், இலக்கியம், தொன்மங்கள் ஆகியவற்றின் துணைகொண்டு ஆசிரியர் விளக்குவது, தமிழ்நாட்டில் இஸ்லாம் மதத்தின் தொன்மை வரலாற்றை வெளிச்சம் போட்டுக் காட்டுகிறது.

இஸ்லாம் மதத்தைத் தழுவிய மக்களின் தொன்மங்கள் குறித்து இதுவரை சொல்லப்படாத செய்திகளை ஆசிரியர் திறம்பட விளக்கியுள்ளார். இவ்வகையில் மேலும் இதுகுறித்து செய்திகளையும் தேடிச்சேர்க்க வேண்டும். நல்லதொரு நூலை நமக்கு அளித்துள்ள முனைவர் ஜெ.ராஜாமுகமது அவர்களுக்கு பாராட்டுக்கள். தமிழக முஸ்லிம் சமுதாயம் இந்த நூலை வரவேற்கும் என்பதில் ஐயமில்லை. ஆய்வு மையத்தின் மூலம் தமிழக முஸ்லிம்களின் வாழ்வியல் குறித்து மேலும் பல அரிய செய்திகள் தொடர்ந்து வெளிவர வேண்டுமென்பது நமது அவா.

இத்தகையதொரு நல்ல பணியினை மேற்கொள்ள ஊக்கமளித்து, கல்லூரியில் "இஸ்லாமிய தமிழ்ப் பண்பாட்டு ஆய்வு மையம்" தொடங்கி செயல்பட அனுமதியளித்த கல்லூரியின் நிர்வாகக்குழுவினருக்கு எனது நன்றி.

தமிழக முஸ்லிம்களின் பன்முக வளர்ச்சியில் ஜமால் முகமது கல்லூரி என்றும் முன்னனியில் இருக்கும். இன்ஷா அல்லாஹ்

முனைவர் **S. இஸ்மாயில் முகைதீன்**
முதல்வர்

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Prof. K.M.KADER MOHIDEEN, Ex.M.P.
National President

வாழ்த்துரை

திருச்சி ஜமால் முகமது கல்லூரியில் இயங்கி வரும் இஸ்லாமிய தமிழ்ப் பண்பாட்டு ஆய்வு மையம் இயக்குநர் முனைவர் ஜெ. ராஜா முகமது அவர்களின் ஆய்வு மையத்தின் முதல் நூலாக "தமிழகத்தில் இஸ்லாம் வந்ததும் வளர்ந்ததும் வாழ்வதும் வரலாறு (தொகுதி-I)" உருவாக்கப்பட்டிருக்கிறது.

முனைவர் ஜெ. ராஜா முகமது, எத்துணை நுண்மான் நுழைபுலம் மிக்கத் தேர்ந்த ஆய்வறிஞர் என்பதை இந்த வரலாற்று நூலின் ஒவ்வொரு வரியும் சாட்சியம் பகரிகிறது.

இஸ்லாமிய தமிழ்ப் பண்பாட்டு ஆய்வு மையத்திற்கு இத்தகு மெத்தகு மெய்யறிஞரைத் தேர்வு செய்து நியமித்திருக்கும் கல்லூரி நிர்வாகத்திற்கு வாழ்த்துக் கூற வேண்டும்.

இஸ்லாமிய நெறி, நபிகள் நாயகம் முகம்மது (சல் - அம்) அவர்களின் காலத்திலேயே தமிழகத்திற்குள் நுழைந்து, மக்களின் இதயங்களை ஈர்த்துள்ளது என்று தொடங்கி, அரபி வணிகர்கள், ஆன்மீகச் செல்வர்கள் மூலம் தமிழகத்தில் இஸ்லாம் எவ்வாறு விரிவடைந்தது என்பதை விளக்கி, பின்னர் வட இந்தியாவில் முஸ்லீம்களின் ஆட்சியின்போது, தமிழகத்தில் எழுந்த முஸ்லீம் ஆட்சியாளர்களின் வரலாற்றை விவரித்து, ஆங்கிலேயர் ஆட்சி காலத்தில் இஸ்லாம் எதிர்கொண்ட அறை கூவல்களும் அவற்றை இஸ்லாமிய நெறி எவ்வாறு தனது கட்டுக்குள் அடக்கி மிகைத்தது என்பதை வருணித்து, தமிழகத்தில் பல்வேறு பிரிவினர் இஸ்லாமை ஏற்றுப்போற்றிய சரித்திரத்தையும் எடுத்து விளக்கி சமீபத்தில் மீனாட்சிபுரம் 'தீனாட்சிபுரமானது' வரையிலும் தொகுத்துத் தந்திருக்கும் தமிழக முஸ்லீம்களின் வரலாற்றுப் பெட்டகம் இந்தப் பனுவல்.

தமிழகத்தில் இஸ்லாமின் தோற்றமும், வளர்ச்சியும் பற்றிய ஒரு முழுமையான நூலாகத் திகழ்கிறது இந்த ஆய்வு. இனி வருங்காலங்களில் பலப்பல ஆய்வுகள் தோன்றுவதற்கும், தொடர்வதற்கும் இந்த ஆய்வு நூல் தூண்டு சக்தியாக விளங்கும்.

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தமிழகத்தில் வலிமார்கள் எனப் போற்றப் பெறும் ஆனமீகச் செல்வர்கள் மூலம் இஸ்லாமிய நெறி பரவிய வரலாற்றுக்கு மிக உன்னத இடமளித்துள்ளது, நூலாசிரியரின் ஆழ்ந்த ஞானத்தை வெளிப்படுத்துகிறது. "உள்ளத்தைப் புடமிட்டு, தூய்மைபடுத்தி, மாசற்ற உயர் பண்புகளை வளர்த்து அகத்தையும், புறத்தையும் பரிபக்குவப்படுத்தி இறைவனிடம் நெருக்கம் கொண்டவர்கள் சூஃபி மெய்ஞானியர்". "இந்த ஞானியரது தன்னலமற்ற போக்கு, ஆன்மீகப் பயணம், பாமர மக்களைப் பெரிதும் கவர்ந்தது. இவர்களது முயற்சியால் மக்கள் கூட்டம் கூட்டமாக இஸ்லாத்தில் இணையலாயினர்". (பக் - 51) இத்தகைய ஞானியரின் பட்டியலில் 180 பேர்களைக் கணக்கிட்டிருக்கிறார். இவர்களில் ஒவ்வொருவர் பற்றியும் விரிந்த ஆய்வுரை மேற்கொள்ளும் காலம் நிச்சியம் கனிந்து வரும்.

தமிழகத்தை ஆட்சி செய்த இந்து சமுதாயத்தை ச் சார்ந்த அரசர்கள் இஸ்லாம் பற்றியும், முஸ்லீம்கள் பற்றியும், எவ்வளவு உயர்வாக மதித்துப் போற்றியுள்ளனர் என்பதற்கு நூலாசிரியர் கல்வெட்டுக்களையும், இலக்கியச் சான்றுகளையும் தந்திருப்பது, தமிழகம் என்றைக்கும் அமைதிப் பூங்கா - சமூக நல்லிணக்கத் தோட்டம் - சமயப்பொறைக்கோர் முன்மாதிரி என்பதை உறுதிப்படுத்தியிருக்கிறது.

சுருங்கச் சொல்லுமிடத்து, இந்த ஆய்வு நூல், வரலாற்று நூலாகவும், வரலாற்றாசிரியர்களுக்கு வரலாறு போதிக்கும் பாட நூலாகவும், ஆராய்ச்சி நூலாகவும், ஆராய்ச்சியில் ஈடுபட்டோருக்கு வழிகாட்டும் நூலாகவும், ஆராய்ச்சியில் ஈடுபட எண்ணுவோருக்கு ஒளியூட்டி உற்சாகமூட்டும் உந்து சக்தியாகவும் திகழ்கிறது.

தமிழகத்தில் இஸ்லாம் பற்றிய வரலாறு, இனி ஜமால் முகமது கல்லூரி இஸ்லாமியப் பண்பாட்டு ஆய்வு மையத்திலிருந்து தொடங்கும்; தொடரும்; பாருலகமெங்கும் இந்த வரலாற்று ஆய்வு ஒளிவெள்ளம் பாயும்.

முனைவர் ராஜா முகமது, உண்மையில் வரலாற்று ஆய்விடம் 'ராஜா' என்று நிரூபித்திருக்கிறார். இதயம் நிறைந்த நல்வாழ்த்துக்கள்.

(Prof. K.M. Kadhar Mohideen)

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தலைவர், இந்திய யூனியன் முஸ்லிம் லீக்,
இந்தியா.

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ISSN 0973-0303

Part A : Arts & Humanities
vol - 1 (Spl) :2018
Issue - 1 : Section (A) - Arabic

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Special Issue

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Chapter	Title of Dissertation	Research Supervisor	Research Scholar
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2	الشيخ النّواب صدّيق حسن خان القنوجي و مكانته العلمية والادبية و ثقافته	الدكتور. خواجة محيّ الدين بن محمد إسماعيل	ريحانة الأدوية بنت محمد حبيب
3	بلاغة الحوار في سورة يوسف دراسة تحليلية	الدكتور. ح. محبوب علي خان	محمد فياز جولاكل
4	قصص أون انعزو بظلال انقرآن	الدكتور. ح. محبوب علي خان	ريشاد رحيم
5	الرواية العربية المصرية : نشأتها وتطورها	الدكتور. ح. محبوب علي خان	محمّد سهل – ك

ISSN 0973-0303

Part A : Life Sciences
Vol - 1 (Spl) :2018
Issue - 1 : Section(A) - Botany

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

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1	Effect of 6-Benzylaminopurine on in vitro flower induction in Withania somnifera (L.) Dunal	Dr. A. SHAJAHAN	D. DHANALAKSHMI
2	Antibacterial Activity of Nickel Oxide Nanoparticle doped with leaf extract of Pedalium murex L.	Dr. K. MOHAMED RAFI	V. VISHNUPRIYA
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ISSN 0973-0303

Part A : Arts & Humanities
Vol - 1 (Spl) :2018
Issue - 1 : Section (C) - Commerce

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

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S. No.	Title of the Dissertation	Research Supervisor	Research Scholar
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2	A Study On Financial Performance Of Wipro Limited	Dr. E. MUBARAK ALI	A. ASMA BANU
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4	A Comparative Study On Financial Performance Of Ultra-Tech Cements Limited And India Cements Limited	Dr. A. M. MOHAMED SINDHASHA	M. ARAVINDH

ISSN 0973-0303

Part A : Physical, Mathematical & Computer Science
Vol - 1 (Spl) :2018
Issue - 1 : Section(D) - Computer Science

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

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Compendium of Pre-Doctoral Dissertations : Computer Science -2018

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2	COMPARATIVE ANALYSIS ON NOISE ADAPTIVE FUZZY SWITCHING MEDIAN FILTER AND FUZZY-BASED DECISION ALGORITHM FOR GRAY-SCALE IMAGES	Dr. S. ABDUL SALEEM	M. THAHA
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4	PRIORITY BASED IMPROVED RASA ALGORITHM IN TASK SCHEDULING	Dr. O.S. ABDUL QADIR	S.KALAIARASI
5	EFFICIENT ATTRIBUTE SELECTION ALGORITHM BASED ON DISCERNIBILITY MATRIX	Lt. J. HAJIRAM BEEVI	B.SUMAIYA PARVEEN

ISSN 0973-0303

Part A : Arts & Humanities
Vol - 1 (Spl) :2018
Issue - 1 : Section (D) - English

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Special Issue

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S. No.	Title of the Dissertation	Research Supervisor	Research Scholar	Month & Year
1	Quest For Identity In And Slavery In Andrea Levy's Small Island And The Long Song	Dr. S. Kathar Usean	J. Jeni Jovitha	June 2018

ISSN 0973-0303

Part A : Arts & Humanities
Vol - 1 (Spl) :2018
Issue - 1 : Section (E) - History

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

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S.No	Title of the Dissertation	Research Supervisor	Research Scholar
1.	SOCIO- ECONOMIC AND EDUCATIONAL CONDITION OF SRIRANGAM TALUK – A STUDY	Dr.M.MOHAMED TAJDEEN	M.BALAMURALI
2.	WOMEN SELF HELP GROUPS IN TAMIL NADU WITH SPECIAL REFERENCE TO LALGUDI TALUK -A STUDY	Dr.T.UMAR SADIQ	C.LATHA
3.	LOCAL SELF GOVERNANCE IN TAMIL NADU WITH SPECIAL REFERENCE TO MALAYADIPATTI VILLAGE – A STUDY	Dr.T.UMAR SADIQ	I.MARGARET MALA
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ISSN 0973-0303

Part A : Physical, Mathematical & Computer Science
Vol - 1 (Spl) :2018
Issue - 1 : Section(C) - Mathematics

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF PREDOCTORAL DISSERTATIONS : *Mathematics*

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Compendium of Pre-Doctoral Dissertations : Mathematics -2018

Sl. No.	Title of the Dissertation	Research Supervisor	Research Scholar
1	CHANGES ON DOMINATION PARAMETERS IN GRAPHS	Dr. N. MOHAMED THOIYAB	C. SELVA SIVALINGAM
2	A STUDY ON SOME TYPES OF DOMINATION IN ADVANCE GRAPH THEORY	Dr. A. MOHAMED ISMAYIL	M. KUMAR
3	A STUDY ON GLOBAL DOMINATION IN INTUITIONISTIC FUZZY GRAPH	Dr. A.PRASANNA	J.JAYASRI
4	ASTUDYONHARMONICANDHERONIANMEANLABELING OFSOMESPECIAL GRAPHS	Dr. S. MOHAMED YUSUFF ANSARI	P.ARCHANA
5	A STUDY ON COLORING OF HYPERGRAPHS	Dr. A. SOLAI RAJU	P. JAYASRI
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ISSN 0973-0303

Part B : Management Studies
Vol - 1 (Spl) :2018
Issue - 1 : Section(A) - Management Studies

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF PREDOCTORAL DISSERTATIONS : MBA

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Compendium of Pre-Doctoral Dissertations : MBA -2018

Sl. No.	Title of the Dissertation	Research Supervisor	Research Scholar
1	A STUDY ON INVESTMENT DECISIONS WITH SPECIAL REFERENCE TO INVESTORS IN TIRUCHIRAPPALLI DISTRICT	Dr. U. SYED AKTHARSHA	S. GHOUSEBE

ISSN 0973-0303

Part A : Life Sciences
Vol - 1 (Spl) :2018
Issue - 1 : Section(C) - Microbiology

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

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S.No	Title of the Dissertation	Research Supervisor	Research Scholar
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2.	CHARACTERIZATION OF PREBIOTIC COMPOUND (INULIN) DERIVED FROM GARLIC: A SYNBIOTIC APPROACH	Dr. N. REEHANA	A. FASILABEGUM
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ISSN 0973-0303

Part A : Physical, Mathematical & Computer Science
Vol - 1 (Spl) :2018
Issue - 1 : Section(A) - Physics

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF PREDOCTORAL DISSERTATIONS : *Physics*

Jamal Mohamed College
(Autonomous)
Tiruchirappalli – 620 020
Tamil Nadu, India

Compendium of Pre-Doctoral Dissertations : Physics -2018

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ISSN 0973-0303

Part A : Arts & Humanities
vol - 1 (Spl) :2018
Issue - 1 : Section (F) - Tamil

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF PREDOCTORAL DISSERTATIONS : *Tamil*

Jamal Mohamed College
(Autonomous)
Tiruchirappalli – 620 020
Tamil Nadu, India

Compendium of Pre-Doctoral Dissertations: Tamil -2018

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ISSN 0973-0303

Part A : Life Sciences
Vol - 1 (Spl) :2018
Issue - 1 : Section(E) - Zoology

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF PREDOCTORAL DISSERTATIONS : *Zoology*

Jamal Mohamed College
(Autonomous)
Tiruchirappalli – 620 020
Tamil Nadu, India

Compendium of Pre-Doctoral Dissertations: Zoology 2018

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ISSN 0973-0303

Part A : Arts & Humanities
Vol - 1 (Spl) :2019
Issue - 1 : Section (A) - Arabic

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF POST GRADUATE DISSERTATIONS : *ARABIC*

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(Autonomous)
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ISSN 0973-0303

Part D : Life Sciences
Vol - 1 (Spl) :2019
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Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

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Effect Of Secondary Metabolites Of Actinobacteria Strain On Leucinodes Orbonalis (Guen.)

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ISSN 0973-0303

Part D : Life Sciences
Vol - 1 (Spl) :2019
Issue - 1 : Section(B) – Bio-Technology

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF POST GRADUATE DISSERTATIONS : *BIO-TECHNOLOGY*

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ISSN 0973-0303

Part C : Physical, Mathematical & Computer Science Vol - 1 (Spl) :2019
Issue - 1 : Section(B) - Chemistry

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF POST GRADUATE DISSERTATIONS : *Chemistry*

Jamal Mohamed College
(Autonomous)
Tiruchirappalli – 620 020
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ISSN 0973-0303

Part C : Physical, Mathematical & Computer Science Vol - 1 (Spl) :2019
Issue - 2 : Section(B) - Chemistry

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF POST GRADUATE DISSERTATIONS : *Chemistry*

Jamal Mohamed College
(Autonomous)
Tiruchirappalli – 620 020
Tamil Nadu, India

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SUBMITTED MARCH 2019

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ISSN 0973-0303

Part C : Physical, Mathematical & Computer Science Vol - 1 (Spl) :2019
Issue - 3 : Section(B) - Chemistry

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF POST GRADUATE DISSERTATIONS : *Chemistry*

Jamal Mohamed College
(Autonomous)
Tiruchirappalli – 620 020
Tamil Nadu, India

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2019

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Post Graduate Project 1

Inhibitory Action of Aqueous Extract of *Cosmos Sulphureus* Leaves on Mild Steel in 1.0 M H_2SO_4 solution

Name of the Guide: Dr. A. SamsathBegum
Name of the Candidate: P. Kiruba Priya

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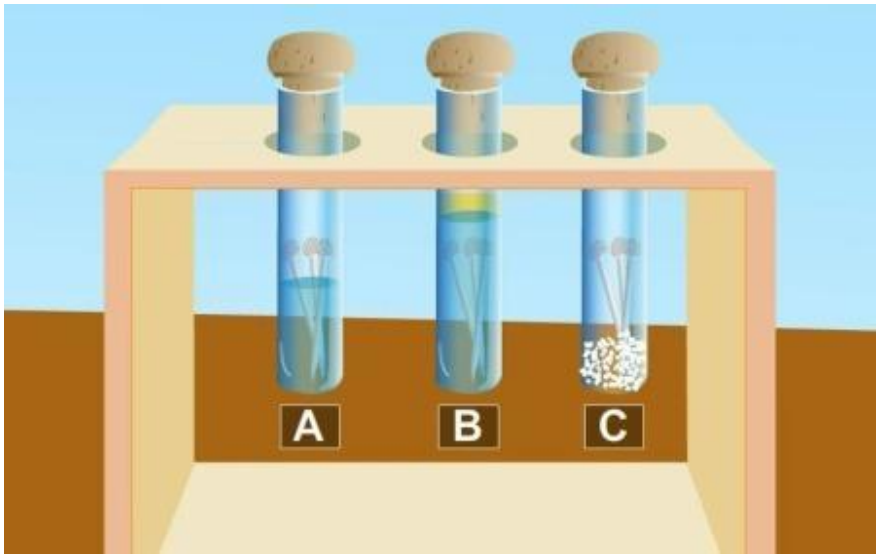

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CHAPTER-1

INTRODUCTION

CORROSION

Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Both the type of metal and the environmental conditions, particularly gasses that are in contact with the metal, determine the form and rate of deterioration.

Corrosion is a natural process, which converts a refined metal to a more chemically table form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and electrochemical reaction with their environment.

Figure- 1: deterioration on metal surface

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media.

Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its location. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media.

DEFINITION OF CORROSION

- Corrosion is the irreversible damage or destruction of living tissue or material due to a chemical or electrochemical reaction. A prime example of corrosion is rusting of iron or steel.

- Corrosion is a natural process, which converts refined metal to a more chemically stable form, such as its oxide, hydroxide or sulfide. It is the gradual destruction of materials (usually metals) by chemical or electro chemical reaction with their environment.

- Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species.

- Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment.

- Corrosion is the destructive attack on a metal through interaction.

THEORIES OF CORROSION

➢ Homogeneous theory

Accorroding metal irrespective of the presence or absence on its surface of any micro heterogeneity can be regarded as single electrode on which reactions take place. Metal becomes unstable due to the charge transfer reaction taking place at the interface. Hence, it is necessary that the potential difference across the interface be more negative than the equilibrium potential for the metal dissolution (anodic) reaction or more positive than the equilibrium potential for the electronation (cathodic) reaction.

➢ Heterogeneous theory

According to this theory, corrosion is caused by local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity. Corroding metal consists of an electron sink area, where de-electronation reaction occurs. b. an electron source area, where electronation reaction occurs in an ionic conductor to keep the current flowing.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I cor. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

The most common and important electrochemical reactions in the corrosion of iron are thus,

Anodic reaction (corrosion)

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Cathodic reactions (simplified)

$$2H^+ + 2e^- \longrightarrow H_2$$

$$H_2O + 1/2\ O_2 + 2e^- \longrightarrow OH^-$$

This reaction is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

MECHANISM OF CORROSION

Although several mechanisms have been proposed for the corrosion process, corrosion is mainly electrochemical in nature and hence in this chapter, the electrochemical mechanistic aspects have been discussed. According to this approach, the corrosion reaction can be considered as taking place by two simultaneous reactions; the oxidation of a metal at an anode (a corroded end releasing electrons) and the reduction of a substance at a cathode (a protected end receiving electrons). In order for the reaction to occur, the following conditions must exist:

- A chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition).
- An electrolyte must be present to provide solution conductivity and act as a source of material to be reduced at the cathode.

- An electrical path through the metal or between metals must be available to permit electron flow.

The below diagram illustrates the typical electrochemical corrosion of iron in contact with water.

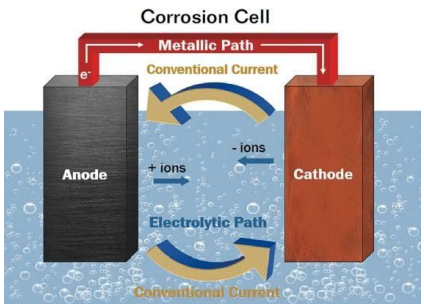

Figure- 2: Electrolyte corrosion cell

In a nearly neutral or slightly acid environment, the water is dissociated into hydrogen ions (H^+) and hydroxyl ions (OH^-) as

$$H_2O \rightleftharpoons H^+ + OH^-$$

When metal is placed in contact with a liquid, surface ionization occurs, because of the electric charge difference at the solid-liquid interface. For example, iron dissolves in water in the form of positively charged ferrous ions (Fe^{++})

$$Fe \rightleftharpoons Fe^{++} + 2e^-$$

Electrochemically, a chemical substance is “oxidized”, when it loses electrons to a second substance. The electrode at which the oxidation takes place is called as the “anode”. A chemical substance is “reduced”, when it acquires electrons. The electrode at which reduction takes place is called the “cathode”. Hence, oxidation reaction results in the formation of positive charge ferrous ions at the anode. Ferrous ions moving away from the metal surface are further oxidized to ferric ions (Fe^{++}) as follows

$$Fe^{++} \rightleftarrows Fe^{++++} + e^-$$

The positively charged ferric ions are attracted to the negatively charged hydroxyl ions and form the corrosion product $Fe(OH)_3$

$$Fe^{+++} + 3(OH)^- \rightleftarrows Fe(OH)_3$$

The rust consists of iron hydroxide or iron oxide hydrates in various states, depending on the degree of oxidation and dehydration.

The reduction reaction at the cathode must take place concurrently in order to continue the corrosion process. Several reactions are possible and the one that occurs is determined by the environment. Without the presence of air or oxygen, hydrogen ions can be reduced by the excess of electrons at the cathode surface and evolve as molecular hydrogen by

$$2H^+ + 2e^- \rightleftarrows H_2$$

If hydrogen is not removed from the surface, the cathodic reaction decreases and the corrosion rate is reduced. With the presence of air, the more likely reaction is the reduction of oxygen. Two possible reactions occur:

$$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$$

$$O_2 + 2H_2O + 4e^- \rightleftarrows 4(OH)^-$$

Hydrogen evolution or oxygen reduction with the formation of water is likely to occur in acid media.

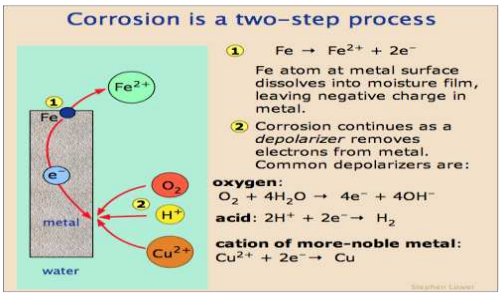

Figure -3: Two step process of corrosion

Corrosion occurs when metal atoms detach themselves from the metal surface at the anode and enter the solution as ions, leaving behind electrons in the metal. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen ions that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In solutions, where hydrogen tends to evolve too slowly, oxygen is reduced and combines with hydrogen ions or water to form hydroxyl ions.

TYPES OF CORROSION

They are many different types of corrosion, each of which can be classified by the cause of the metals chemical deterioration. Classification by appearance is manifested by the morphology of the corrosion attack and this can be visualized either by naked eye or magnification. The schematic in the given below diagram illustrates some of the most common forms of corrosion.

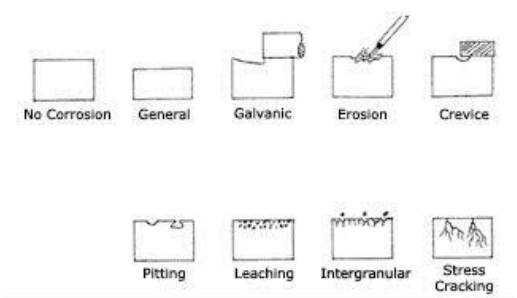

Figure 4.Schematics of the common forms of corrosion

General attack corrosion

It is also known as uniform attack corrosion. General attack corrosion is the most common type of corrosion and is caused by a chemical or electrochemical reaction that results

in the deterioration of the entire exposed surface of a metal. Ultimately, the metal deteriorates to the point of failure.

Figure-5: Uniform corrosion

General attack corrosion accounts for the greatest amount of metal destruction by corrosion but is considered as a safe form of corrosion, due to the fact that it is predictable, manageable and often preventable.

Localized corrosion

Unlike general attack corrosion, localized corrosion specifically targets one area of the metal structure. Localized corrosion is classified as one of three types:

Pitting

Pitting results when a small hole, or cavity, forms in the metal, usually as a result of depassivation of a small area. This area becomes anodic, while part of the remaining metal becomes cathodic, producing a localized galvanic reaction. The deterioration of this small area penetrates . This type of corrosion is often associated with a stagnant micro-environment, like those found under gaskets and washers and clamps. Acidic conditions or a depletion of oxygen in a crevice can lead to crevice corrosion

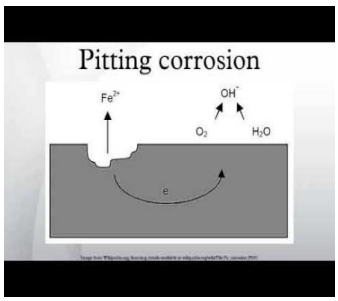

Figure-6: Pitting corrosion

Filiform corrosion

Occurring under painted or plated surfaces when water breaches the coating, filiform corrosion begins at small defects in the coating and spreads to cause structure.This form of corrosion is often difficult to detect due to the fact that it is usually relatively small and may be covered and hidden by corrosion-produced compounds.

Galvanic corrosion

Galvanic corrosion or dissimilar metal corrosion, occurs when two different metals are located together in a corrosive electrolyte. A galvanic couple forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly.

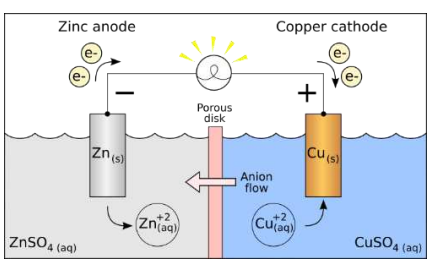

Figure-7: Galvonic corrosion

Three conditions must exist for galvanic corrosion to occur

- Electrochemically dissimilar metals must be present
- The metals must be in electrical contact
- The metals must be exposed to an electrolyte

Environmental cracking

Environmental cracking is a corrosion process that can result from a combination of environmental conditions affecting the metal. Chemical, temperature and stress-related conditions can result in the following types of environmental corrosion:

Figure-8:Environmental cracking

- Corrosion cracking
- Corrosion fatigue
- Hydrogen-induced racking
- Liquid metal embrittlement

Flow-assisted corrosion (FAC)

Figure-9:Flow-assisted corrosion

FAC entails a process where a metal's protective oxide film dissolves when exposed to fast-moving water, steam or a combination of the two. For instance, in carbon steels, this phenomenon takes place under well-organized and specific parameters. Some of the major parameters include the following:

- pH
- Oxygen content
- Temperature
- Water velocity

Intergranular corrosion

Figure-10:Intergranular corrosion

Intergranular corrosion is a chemical or electrochemical attack on the grain boundaries of a metal. It often occurs due to impurities in the metal, which tend to be present in higher contents near grain boundaries. These boundaries can be more vulnerable to corrosion than the bulk of the metal.

De-alloying corrosion

De-alloying, or selective leaching, is the selective corrosion of a specific element in an alloy. The most common type of de-alloying is de-zincification of unstabilized brass. The result of corrosion in such cases is a deteriorated and porous copper.

Figure-11:De-alloying corrosion

It is the removal of one solid element from alloy by corrosion processes. De alloying corrosion is also called de-zincification.

The most common example is de-zincification which is select removal of zinc in brass alloy. Similar processes occur in other alloy systems in which aluminium, Iron, Cobalt, Chromium and other elements are removed**.**

Fretting corrosion

Fretting corrosion occurs as a result of repeated wearing, weight and/or vibration on an uneven, rough surface. Corrosion, resulting in pits and grooves, occurs on the surface.

Figure-12:Fretting corrosion

Fretting corrosion is often found in rotation and impact machinery, bolted assemblies and bearings, as well as to surfaces exposed to vibration during transportation.

High temperature corrosion

Figure-13: High temperature corrosion

High temperature corrosion is a mechanism of corrosion that takes place ingas, turbines, diesel, engines furnacesor other machinery coming in contact with hot gas containing certain contaminants. Fuel sometimes contains vanadium compounds or sulfates which can form compounds during combustion having a low melting point. These liquid melted salts are strongly corrosive for stainless steel and other alloys normally inert against the corrosion and high temperatures. Other high-temperature corrosions include high-temperature oxidation , sulfidation and carbonization**.**

Crevice corrosion

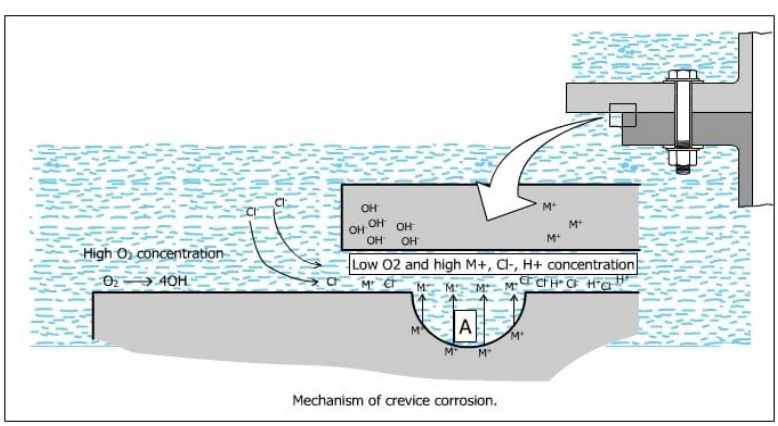

Figure-14: Crevice corrosion

Crevice corrosion is also a localized form of corrosion and usually results from a stagnant microenvironment in which there is a difference in the concentration of ions between two areas of a metal. Crevice corrosion occurs in shielded areas such as those under washers, bolt heads, gaskets, etc. where oxygen is restricted. These smaller areas allow for a corrosive agent to enter but do not allow enough circulation within, depleting the oxygen content, which prevents repassivation. As a stagnant solution builds, pH shifts away from neutral. This growing imbalance between the crevice (micro environment) and the external surface (bulk environment) contributes to higher rates of corrosion. Crevice corrosion can often occur at lower temperatures than pitting. Proper joint design helps to minimize crevice corrosion.

Stress corrosion cracking

Stress corrosion cracking is a result of the combination of tensile stress and a corrosive environment, often at elevated temperatures. Stress corrosion may result from external stress such as actual tensile loads on the metal or expansion/contraction due to rapid temperature changes.

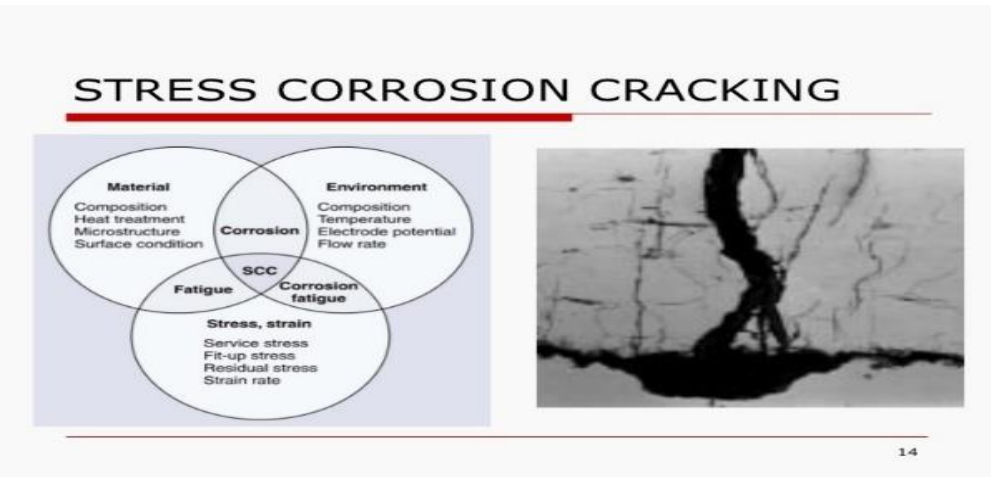

Figure-15:Stress corrosion cracking

It may also result from residual stress imparted during the manufacturing process such as from cold forming, welding, machining, grinding, etc. In stress corrosion, the majority of the surface usually remains intact; however, fine cracks appear in the microstructure, making the corrosion hard to detect. The cracks typically have a brittle appearance and form and spread in a direction perpendicular to the location of the stress. Selecting proper materials for

a given environment (including temperature and management of external loads) can mitigate the potential for catastrophic failure due to SCC.

Caustic agent corrosion

Figure-16: Caustic agent corrosion

Caustic agent corrosion occurs when impure gas, liquids, or solids wear a material down. Although most impure gases do not damage metal in dry form, when exposed to moisture they dissolve to form harmful corrosive droplets. Hydrogen sulfide is an example of one such caustic agent.

Microbial corrosion

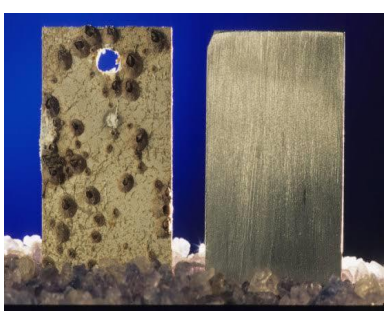

Figure-17: Microbial corrosion

Microbial corrosion, commonly referred to as microbiologically influenced corrosion (MIC) is caused by microorganisms. It applies to both metallic and non-metallic materials with or without oxygen. When oxygen is absent, sulfate-reducing bacteria are active and produce hydrogen sulfide causing sulfide stress cracking. When oxygen is present, some

bacteria may directly oxidize iron to iron oxides and hydroxides. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

Filiform corrosion

It is basically a special type of crevice corrosion, sometimes termed as “under film” corrosion. This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating.

Figure-18:Filiform corrosion

Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided unless absence of an adverse effect has been proven by field experience.

Cavitation damage

Figure-19:Cavitation damage

` Cavitation damage is a special form of erosion corrosion caused by the formation of vapour bubbles and their collapse in the liquid near a metal surface. This form of damage occurs in hydraulic turbines, pump impellers, and other surfaces that are in contact with high-velocity liquid flow along with high pressures.

Erosion corrosion

Figure-20: Erosion corrosion

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities. Erosion corrosion can be controlled by the use of harder alloys (including flame-sprayed or welded hard facings) or by using a more corrosion resistant alloy.

Concentration cell corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. Concentration cell corrosion is associated with gaskets, joints, scale, debris, loose protective films, etc.

Figure-21: Concentration cell corrosion

Corrosion attack is accelerated, where the oxygen concentration is least. Metal at the area of low oxygen availability becomes anodic to other areas. As the cathodic area is large compared to the anodic area, the intensity of attack is usually more severe on surrounding areas of the same surface. This condition can be eliminated by sealing the faying surfaces in a

manner to exclude moisture. Proper protective coating application with inorganic zinc primers is also effective in reducing faying surface corrosion.

Corrosion fatigue

Figure-22:Corrosion fatigue

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment. Control of corrosion fatigue can be accomplished by either lowering the cyclic stresses or by corrosion control by using protection methods.

Direct chemical corrosion (or) dry corrosion

This type of corrosion occurs mainly through the direct chemical action of environment/atmospheric gases such as oxygen, halogens, hydrogen sulphide, nitrogen or anhydrous liquid sulphur dioxide with metal surface in immediate proximity. The extent of corrosion depends upon the following factors

- Chemical affinity between the corrosive environment and solid metals and
- Ability of reaction product on metal surface to form a protective film.

FACTORS AFFECTING RATE OF CORROSION

Nature of the metal

Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum, silver. Whereas metal with lower electrode potentials, readily undergo corrosion. e.g., metals like zinc, magnesium, aluminium. When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion. For e.g., the potential difference between the iron and copper is 0.78V which is more than that between iron and tin is 0.30V. Therefore, iron corrodes faster when in contact with copper than that with tin. On this account, the use of dissimilar metals should be avoided wherever possible. For example, bolt and nut or screw and washer should made by the same metal (or alloy) to avoid galvanic corrosion.

Ratio of cathodic to anodic region

The rate of corrosion is influenced by relative size of cathodic to anodic area. If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio decreases corrosion rate further increases. This is because at anode electrons are liberated. Which are consumed at cathodicregion. If cathodic region is larger the liberated electrons are rapidly consumed at cathode. This further enhances, the anodic reactions leading to increase in overall rate of corrosion. When two dissimilar metals are in contact, Corrosion is more rapid and severe, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank), If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode. An intense localized corrosion occurs at the exposed small anodic surface. On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas Nature of the corrosion product

The corrosion product formed like metal oxide may act as protective film, if it is stable, insoluble, and non-porous. If it acts as protective film it prevents further corrosion by acting as barrier between metal surface and corrosion medium. On the other hand if corrosion

product is Unstable, porous, and soluble, it further enhances corrosion in oxidizing environments, metals like aluminium, chromium, titanium, etc., are highly passive as their oxides as corrosion products form protective films on the metal surface, preventing further corrosion. Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments pH of the medium

In general rate of corrosion is higher in acidic pH than in neutral and alkaline pH.In case of iron, at very high pH protective coating of iron oxide is formed which prevents corrosion. Where as at low pH, severe corrosion takes place. But for metals like aluminium, corrosion rate is high even at high pH.

Temperature

The rate of corrosion increases with increasing temperature. This is due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

Effect of oxygen

Oxygen plays an important corroding medium. If the metal is exposed to different concentration of oxygen, differential aeration corrosion takes place. The region which is less 0exposed to oxygen acts as anode hence undergoes corrosion and region exposed to high oxygen concentration acts cathode hence doesn't undergo corrosion.

Hydrogen over voltage

The metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. Since at lower hydrogen over voltage, the liberation of hydrogen gas is easy. Therefore cathodic reaction is very fast, which in turn makes anodic reaction very fast. Thus increasing the rate of corrosion. Higher the over voltage lesser is the corrosion.

PREVENTION OF CORROSION

Rust and other corrosion forms can lead to safety issues and ruin the integrity of your equipment and supplies. Even routine maintenance to remove and repair corrosion can drive up costs. Fortunately, there are a variety of measures you can take to minimize corrosion. Here we‟ll highlight four of these methods based on cost and effectiveness.

Figure-23: prevention of corrosion

Barrier coatings

One of the easiest and cheapest ways to prevent corrosion is to use barrier coatings like paint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film. Plastic and waxes are often sprayed onto metal surfaces. Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds. Today's paint systems are actually a combination of different paint layers that serve different functions. The primer coat acts as an inhibitor, the intermediate coat adds to the paint overall thickness, and the finish coat provides resistance to the environmental factors.

The biggest drawback with coatings is that they often need to be stripped and reapplied. Coatings that aren't applied properly can quickly failand lead to increased levels of corrosion. Coatings may also contain volatile organic compounds, which can make them vulnerable to corrosion.

Hot-dip galvanization

This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection.

The process has been around for more than 250 years and has been used for corrosion protection of things like artistic sculptures and playground equipment. Compared to other corrosion prevention methods, galvanization is known for lower initial costs, sustainability, and versatility. Unfortunately, galvanization can't be done on-site, meaning companies have to pull equipment out of work to be treated. Some equipment may simply be too large for the process, forcing companies to abandon the idea all together. In addition, if the process isn't done properly, the zinc can chip or peel. And high exposure to environmental elements can speed up the process of zinc wear, leading to increased maintenance check-ups. Lastly, the zinc fumes that release from the galvanizing process are toxic.

Alloyed steel

Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product. Corrosion-resistant nickel, for example, combined with oxidation-resistant chromium results in an alloy that can be used in oxidized and reduced chemical environments. Different alloys provide resistance to different conditions, giving companies greater flexibility. Despite its effectiveness, alloyed steel is very expensive. Companies with limited financial resources will likely have to turn to other methods. Monitoring surface conditions are critical, as cracks or scratches can result in an increase of corrosion. Companies also need to make sure the agents used in maintenance don't include corrosion properties.

Cathodic protection

Cathodic protection protects against galvanic corrosion, which occurs when two different metals are put together and exposed to a corrosive electrolyte. To prevent this, the active sites on the metal surface need to be converted to passive sites by providing electrons

from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

While cathodic protection is highly effective, anodes need to be checked often which can drive up costs of maintenance. They also increase the weight on the attached structure and aren't always effective in high-resistivity environments. Finally, anodes lead to increased water flow on ships and other underwater equipment.

Coatings provide physical barriers that do not allow corrosive materials to come in contact with the structure that is being protected. Mainly, coatings are used on the exterior of pipelines to protect from external factors and are not used to directly protect the pipeline from CO_2 corrosion. The most common type of coatings are painting and platting which both provide effective corrosion protection and aesthetic appearance. Painting: Painting is an effective way to protect pipelines from external environmental factors. Although when looking at CO_2 corrosion on the interior of the pipeline, it is not ideal because painting the inside of a pipeline is impractical. The paint will breakdown over time, either through chemical reactions with the flowing fluid or the erosion due to turbulent or transient flow. Once the coating has broken down it leaves unprotected sections of the pipe when fluid induced localized corrosion occurs.

Plating

Plating involves using electric currents to coat a metal with a thin layer of another metal that acts as a protective barrier. Plating an entire pipeline is very uncommon as it is expensive; however, it can be done when dealing with high pressures and high amounts of H_2S and CO_2. One draw back of plating is if the plating fails in a small section (either an imperfection or a scratch) then highly localized corrosion occurs. Another factor to consider is if the plating is more noble than the pipeline (for example, chromium on steel), the steel will act as a sacrificial anode for the chromium. This causes the exposed area to corrode much more rapidly than an un- plated surface would.

CORROSION INHIBITORS

An inhibitor is a chemical substance or combination of substances which when added in very low concentrations in a corrosive environment effectively prevents or reduces corrosion without significant reaction with the components of the environment. Concentrations of corrosion inhibitors can vary from 1 to 15,000 ppm (0.0001 to 1.5 wt %). Corrosion inhibitors can be solids, liquids and gases, and can be used in solid, liquid and gaseous media. Solid media can be concrete, coal slurries or organic coatings (paints). Liquids may be water, aqueous solutions or organic solvents. A gaseous medium is an atmosphere or water vapor. Corrosion inhibitors are selected on the basis of solubility or dispersiability in fluids which are to be inhibited. For instance, in a hydrocarbon system, a corrosion inhibitor soluble in hydrocarbon is used. Two phase system composed of both hydrocarbons and water is utilized as oil soluble water- dispersible inhibitor.

Corrosion inhibitors have been found to be effective and flexible means of corrosion mitigation. The use of chemical inhibitors to decrease the rate of corrosion processes is quite variable. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment and product additive industries. In the oil extraction, processing and chemical industries, corrosion inhibitors have always been considered to be the first line of defense. A great number of scientific studies have been devoted to the subject of corrosion inhibitors.

Inhibitors find major use in closed environmental systems that have good circulation so that an adequate and controlled concentration of inhibitor is ensured. Such conditions can be met, for instance in cooling water recirculation systems, oil production, oil refining, and acid pickling of steel components. One of the more recognizable applications for inhibitors is in antifreeze for automobile radiators. The application of inhibitors must be viewed with caution by the user because inhibitors may afford excellent protection for one metal in a specific system but can aggravate corrosion for other metals in the same system. Inhibitors can be organic or inorganic compounds and they are usually dissolved in aqueous environments. Some of the most effective inorganic inhibitors are chromates, nitrites, silicates, carbonates, phosphates and arsenates. The organic inhibitors include amines, heterocyclic nitrogen compounds, sulfur compounds such as thioethers, thioalcohols,

thioamides, thiourea and hydrazine. Chromates and zinc salts are used increasingly less due to their toxicity and are nowadays largely replaced by organic inhibitors. Thus practical criteria for the selection of corrosion inhibitors from the great variety of inorganic and organic substances with inhibiting properties are not only their inhibition efficiency but also safety of use, economic constraints and compatibility with other chemicals in the system, and environmental concerns.

In order to avoid or reduce the corrosion of metallic materials, inhibitors used in cooling system must satisfy the following criteria.

- It must give good corrosion protection at a very low concentration of inhibitor.
- It must protect all exposed materials from the attack of corrosion.
- It must remain efficient in extreme operating conditions (higher temperature and velocity).
- In case of an under or over dosage of inhibitor, corrosion rate should not increase drastically.
- The inhibitor or reaction products of the inhibitor should not form any deposits on the metal surface particularly at locations where heat transfer takes place.
- It should suppress both uniform and localized corrosion.
- It should have long range effectiveness.
- It should not cause toxicity and pollution problems.

CLASSIFICATION OF CORROSION INHIBITORS

A common classification of inhibitors is based on their effects on the electrochemical reactions involved in the corrosion process.

Passivating inhibitors

Passivating inhibitors cause a large anodic shift of the corrosion potential forcing the metallic surface into the passivation range. There are two types of passivating inhibitors.

- The oxidizing anions such as chromates, nitrites and nitrates that can passivate steel in the absence of oxygen.

- The non-oxidizing ions such as phosphates, tungstates and molybdates that require the presence of oxygen to passivate steel.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential to monitor the inhibitor concentration.

Volatile inhibitors

Volatile corrosion inhibitors (VCIs) also called vapor phase inhibitors (VPIs) are compounds transferred in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing the acidic carbon dioxide or by shifting the surface pH towards less acidic. If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors.

If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors. Liquid phase inhibitors (LPIs)

LPIs are in wide scale use to combat CO_2 corrosion in pipelines. The inhibitor is that is injected into the pipeline is transported in low concentrations and adsorbs onto the surface of the steel. Because the inhibitor is in the liquid phase only the interior of the pipeline needs to be in contact with the liquid either continuously or semi-continuously. One of the main

benefits in using inhibitors to protect from CO_2 corrosion is that it can continuously be added to the flow to provide continuous protection.

Cathodic inhibitors

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. For example, calcium, magnesium and zinc ions will precipitate as hydroxides on cathodic sites as the local environment becomes more alkaline due to the reduction reaction at these sites. cathodic inhibitors are effective when they slow down the cathodic reaction rate. Arsenic, bismuth and antimony which are referred to as cathodic poisons reduce the hydrogen reduction reaction rate and thus lower the overall corrosion rate. Other cathodic inhibitors remove reducible species from the environment. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through

- the use of oxygen scavengers such as sodium sulfite and hydrazine which react with the oxygen and remove it from the solution
- vacuum de-aeration
- boiling to lower the dissolved oxygen concentrations.

Anodic inhibitors

Anodic inhibitors such as chromates, phosphates, tungstates and other ions of transition elements with high oxygen content are those that stifle the corrosion reaction occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface forming a protective film or barrier, thereby reducing the corrosion rate. Anodic inhibitors build a thin protective film along the anode and increasing their potential and thus slow down the corrosion reaction. Chromates, nitrates, tungstate and molybdates are some examples of anodic inhibitors. Although, this type of control is affected, yet it may be dangerous since severe local attack can occur, if certain areas are left unprotected by depletion of the inhibitors.

Mixed inhibitors

Some substances inhibit corrosion by reducing simultaneously the rate of anodic and cathodic reactions involved in the corrosion process and are therefore called mixed inhibitors. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. Anodic inhibitors are, for the most part, dangerous inhibitors, especially if their concentrations are too less. But cathodic inhibitors are generally safe. Mixed inhibitors are less dangerous than pure anodic inhibitors, and in number of cases they may not increase the corrosion intensity. The most common inhibitors of this category are the silicates and the phosphates.

Synergistic inhibitors

It is very rare that a single inhibitor is used in systems such as cooling water systems. More often, a combination of inhibitors (anodic and cathodic) is used to obtain better corrosion protection properties. The blends which are produced by mixing of multi-inhibitors are called synergistic blends. Examples include chromate-phosphates, polyphosphate-silicate, zinc-tannins, and zinc-phosphates.

Precipitation inhibitors

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust. In aerated hot water systems, sodium silicate protects steel, copper and brass.

GREEN CORROSION INHIBITORS

Extracts of plant materials contain a wide variety of organic compounds. Most of them contain heteroatoms such as P, N, S and O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented.

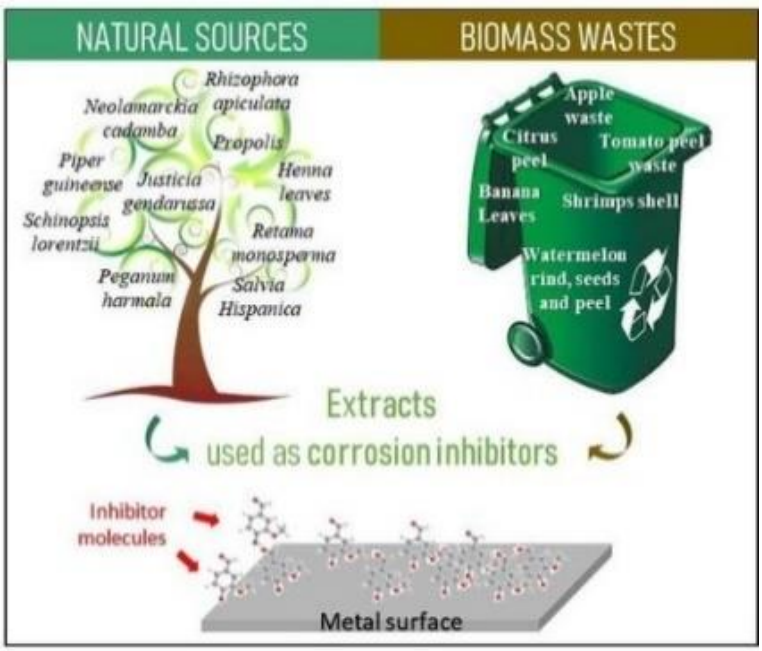

Figure-24:Migrating corrosion inhibitors

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of “inhibitors”, “green inhibitors” can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

Organic green inhibitors

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from natural sources like plants. It also includes synthetic compounds with negligible toxicity. Some of the notable developments on organic green inhibitors especially plant extracts are discussed here.

Plant extracts

The authors have so far investigated the application of plant extracts, as well as other organic inhibitors against corrosion of steel in acidic fluids. Loto had reported the application of the extract of *Mangifera indica* leaves and bark for corrosion of mild steel in diluted sulphuric acid (H_2SO_4) medium. The weight loss measurements and electrochemical impedance spectroscopic studies were used to determine the inhibition efficiency of the inhibitors. Though the extract of leaves and bark showed a significant effect on the corrosion rate separately, the combination of these two extracts exhibited rather higher efficiency.

The inhibitive effect of *Zenthoxylum alatum* fruit extract was reported for corrosion of mild steel in phosphoric acid medium at temperatures ranging from 50–80^{0}C. The surface analysis using X-ray photoelectron spectroscopy (XPS) revealed the layer formation of the plant extract on the surface of mild steel. And the results were indicated the possible formation of iron phosphate that was catalyzed by the formation of the iron-plant extract organo-metallic complex.

Satapathy et al studied the methanol extract of *Justicia gendarussa* leaves for corrosion inhibition of mild steel in hydrochloric acid medium. The authors have made an attempt to characterize the organic compounds present in the methanol extract by means of gas chromatography- mass spectrometric technique. The results showed that the compounds present in the methanol extract were difficult to separate, since the retention times of majority of the compounds were close to each other. The electron spectroscopy for chemical analysis and atomic force microscopy were employed to obtain the information about the film formation on the surface of the mild steel specimen.

Inorganic Green Inhibitor

A number of inorganic elements (minerals) are essential for the growth of living things. Mineral elements in wide variety are present in trace amounts in almost all foodstuffs. The higher concentrations of many metals cause toxicity to all forms of lives. Chromates are among the most common substances used as inhibitors or incorporated in anticorrosive pretreatments of aluminums alloys. The corrosion of galvanized steel was inhibited by the formation of cerium rich film. The film contains Ce^{4+}which was formed by the cerium oxides and hydroxide.

IMPORTANCE OF GREEN INHIBITOR

- Inhibitors are a great method of preventing corrosion and are easy to apply. Has application in a wide range of sectors. The knowledge of the method of the action, facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects.
- It is important in the choice of inhibitor, ascertain the subsequent effects of this towards the environment.
- The search for environmental friendly inhibitors has shown excellent results, out performing conventional inhibitors.
- Reference organic inhibitors newly developed. Inhibitors play a vital role in providing protection against corrosion.
- The selection of the inhibitor is important for environmental protection not all inhibitors are eco-friendly.

CHAPTER-II

AIM AND SCOPE OF THE PRESENT WORK

Green compounds represent a potential class of corrosion inhibitors. There is a wide range of studies regarding corrosion inhibition by hetero atoms containing green compounds. Green compounds containing lot of hetero atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulfur. The corrosion-inhibiting property of these compounds is attributed to their molecular structure.

Acid solutions are widely used in industries for pickling, acid cleaning of boilers, rescaling and oil well as acidizing. Corrosion inhibitors are widely used in order to control the corrosion of metallic materials by cleaning acids. 1.0 M H_2SO_4 is employed in such purposes. Most of the earlier studies on inhibition of corrosion of metals in acids have been related to the performance of organic compounds containing hetero groups.

Recently, environmental friendly inhibitors have attracted several researchers. Natural products are non-toxic, biodegradable and readily available. They have been widely used as inhibitors. Corrosion inhibition of mild steel by various types of plant extracts have been studied.

Investigation of natural inhibitors is particularly interesting because they are non expensive, ecologically friendly, acceptable and possess no threat to the environment. The present work in undertaken:

1. To evaluate the inhibition efficiency of an aqueous leaves extract of *Cosmos sulphureus* in controlling the corrosion of mild steel in 1.0 M H_2SO_4 medium.

2. To analyze the best fit isotherm for corrosion inhibition.

3. To understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization and impedance analysis.

4. To propose a suitable mechanism for corrosion inhibition.

CHAPTER-III

EXPERIMENTAL METHOD

The experimental studies related to the inhibition action of *Cosmos sulphureus* leaves extract on mild steel in 1.0 M H_2SO_4 have been present here. Such studies include weight loss, polarization and impedance studies.

Cosmos sulphureus

Cosmos sulphureus is also known as sulfur cosmos and yellow cosmos. it is native to Mexico , central America, Asia and Australia. This species of cosmos is considered a half-hardy annual, although plants may re-appear via self-sowing for several years. Its foliage is opposite and pinnately divided. The plant height varies from1-7 feet (30-210cm). The original and its cultivars appear in shades of yellow, orange and red. It is especially popular in Korea and Japan, where it is often seen in mass plantings along roadsides.

Figure-25: *Cosmos sulphureus*

PROPERTIES

Botanical name : *Cosmos sulphureus*

Family : Compositae (Daisy family)

Kingdom : Plantae

Order : Asterales

Genus : Cosmos

Division : Magnoliopsida

Common name :Yellow cosmos

Anti-malarial

An botanical study showed cosmos sulphureus to have activity against plasmodium.

Antioxidant

Butein has been isolated from cosmos sulfureus. Butein has been reported to be a powerful antioxidant lipid and LDL peroxidation and has also exhibited anti-inflammatory activities.

Mosquito repellent

Study of petroleum based extract of crushed plant extract of yellow cosmos was effective in the repulsive of mosquitoes.

Dye

Flower yields a yellow dye with sunlight fastness when used on wool.

Collection of the plant material

The leaves were collected from the area Manapparai, Trichy (DT), Tamilnadu. Fresh leaves were authenticated and identified by Dr. John Britto, The Rapinat Herbarium and centre for Modular systematics, St. Joseph's College, Trichirappalli, Tamilnadu, India.

Preparation of extract

The leaves were collected, shade dried and powdered. An aqueous extract was prepared by refluxing 10 gm of powdered *Cosmos sulphureus* leaves in double distilled H_2O. The extract was cooled, filtered and made up to 100 ml with distilled water. From that, various distributions were prepared.

Preparation of the specimens

Mild steel specimen (0.026%-S, 0.06%-P, 0.4%-Mn, 0.1%-C and the rest iron) of the dimensions 1x5x0.2 cm were polished to mirror finished. They are decreased with acetone and used for the weight loss method, polarization and impedance studies.

Materials and chemicals used

For polarization, cylindrical mild steel rod embedded in Teflon with an exposed area of 1 cm^2 was used. The electrodes were polished with emery papers of 0/0, 2/0, 3/0, and 4/0 grades and degreased with acetone, dried and used

Acid: H_2SO_4 was used of G.R. Grade (MERCK CHEMICALS)

Table- 1

Phytochemical screening of aqueous extract of *Cosmos sulphureus* leaves extract

Phytochemical constituents	**Chemical test**	**Aqueous extract**
Carbohydrates	Benedict's test	-
Proteins	Million's test	-
Amino acids	Tyrosine test	-
Fats and oils	Filter paper test	+
Steroids	Libermann-burchard test	-
Glycosides	Libermann's test	-
Flavonoids	lead acetate solution test	+
Alkaloids	Tannic acid test	-

(Note: + : Presence; - : Absence)

Weight loss method

Weight loss measurements were performed in 1.0 M H_2SO_4 medium with and without the presence of different volumes of inhibitor by using the formula, inhibition efficiency were calculated.

Inhibition efficiency (%) = W_0-W_i/W_0*100

where

W_0= Weight loss in plain acid

W_i = Weight loss in inhibited acid

Potentiodynamic polarization studies

Potentiodynamic polarization studies were performed for mild steel specimen in the presence and the absence of the inhibitors. Polarization measurements were performed to evaluate the corrosion current, corrosion potential and the Tafel‟s slope.

The electrode used was a mild steel rod of the same composition embedded in araldite and with an exposed area of $1cm^2$. The polarization cells contain a three electrode assembly. A rectangular foil was used as the counter or auxiliary electrode. The area of the counter electrode is much larger compared to the area of the working electrode. This will exert a uniform potential field on the working electrode. The reference electrode is $Hg/HgCl_2$/1N H_2SO_4 for HCl solution.

A solution quantity of 100 ml of the test solution was taken in a polarization cell. The working electrode was polished with 0/0, 1/0, 2/0, 3/0, and 4/0 emery papers successively and degreased with acetone. The working electrode, reference and auxiliary platinum electrodes were assembled and connections were made.

Stirring was provided to the test solutions to avoid for the system the volume polarization before start of experiment. A time interval of about 15 minutes was given for the system to attain steady state and open circuit potential was recorded.

Polarization measurements were made from mild steel specimens in 1.0 M H_2SO_4 in the presence and absence of the inhibitor. Current in mA and potential in mV were plotted. From the graph, the Tafel slope (in mV/decade) and the corrosion potential (in mV/decade) were calculated.

Impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell setup was the same as that used for polarization measurements.

The real part and imaginary part of the cell impedance were measured in ohms at varies frequencies. The value of charge transfer resistance, R_t , and the double layer capacitance, C_{dl} were calculated.

CHAPTER-IV

RESULTS AND DISCUSSION

It is a well known fact that research activities leading to the development of corrosion inhibitors based on natural products have immense scope in several industries, because of their non-toxicity, biodegradable nature and are also easily available. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly and possess no threat to the environment.

The efficiency of an extract as a corrosion inhibitor can be attributed to the number of mobile electron pairs present, π-orbital character of free electrons and the electron density around the hetero atoms. In the present study, inhibition efficiency of *Cosmos sulphureus* leaves extract in 1.0 M H_2SO_4 medium has been evaluated using weight loss measurements and its potentiodynamic polarization and impedance studies. The effect of this extract on the extent of inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by this extract can be explained in terms of its adsorption on the metal surface. This extract gets adsorbed on the metal surface by means of, when mild steel is immersed in the acid solution the phyto-components diffuses from the bulk of solution towards the metal surface.

The inhibitive influence of *Cosmos sulphureus* on the corrosion of mild steel in 1.0 M H_2SO_4 leaves was studied by weight loss method, polarization and impedance measurements. The inhibition efficiency values determined by these techniques showed closed agreement. The maximum inhibition efficiency was found to be 91.2%.

The corrosion decreased with increase in addition of *Cosmos sulphureus* probably due to the progressive adsorption of the inhibitor on the metal surface.

The percentage of inhibition efficiency increases with increase in the inhibitor volume. The corrosion inhibition by *Cosmos sulphureus* leaves extract is attributed to the adsorption of the additive onto the mild steel surface.

The values obtained from the weight loss technique for the studied inhibitor fit well into the Temkin and El-awady adsorption isotherm. The values of free adsorption process indicate that both physisorption and chemisorption studied for the mild steel surface.

The leaves of *Cosmos sulphureus* prevent the corrosion due to the presence of any of the phytochemical components shifting the corroded metal into the noble. The polarization study also shown an agreement with inhibitor efficiency obtained from weight loss studies.

Weight loss studies

Table-2 gives the inhibition efficiency of different volume of *Cosmos sulphureus* 1.0 M H_2SO_4 medium. The inhibition depends upon the nature and mode of adsorption of the metal surface. The adsorption is assumed to be quasi-substitution process between the water molecules on the surface and any of the natural components present in the inhibitor.

The inhibition of heterocyclic compound present in the plant extract with the metal surface may occur through any of the phyto-components present in the inhibitor and also to the interaction of π-electrons of ring with metal surface, thereby enabling the compound to get adsorbed on the metal surface.

Adsorption isotherm

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Temkin, Flory-Huggins, Frumkin, and the recently formulated thermodynamic/kinetic model of El-awady et al. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clue to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs as the interaction energy between molecules and metal surface is higher than that between the H_2O molecules and the metal surface.

Langmuir adsorption isotherm

Adsorption isotherms are very important to determine the mechanism of phyto-electrochemical reaction. The adsorption isotherm values are shown in **table-3**.

Langmuir adsorption isotherm is

$$\Theta = K_{ads}. C/1 + K_{ads} C$$

$$\Theta (1+K_{ads}.C) = K_{ads} .C$$

$$\Theta = K_{ads}. C - K_{ads} .C/\Theta$$

$$\Theta = (1-\Theta) K_{ads} .C$$

$$\Theta/1-\Theta = K_{ads} .C$$

The plot **of 3+ logs (Θ/1-Θ)** against **3+logC** is a straight line as shown in **figure-26**. Thus the Langmuir isotherm is valid for the inhibitor.

Temkin adsorption isotherm

It is given by the expression;

$$\mathbf{\Theta = -2.303 \log K/2a.-2.303 \log C/2a}$$

where "K" is the adsorption equilibrium constant, "a" is the lateral interaction parameter.The plot of Θ against log C is shown in **figure-27**. The linear plot indicates that Temkin adsorption isotherm was obeyed and negative, value of "a" indicated repulsion exist in the adsorption layer. The results are shown in **table -4.**

Florry-Huggins adsorption isotherm

It is given by the expression

$$\log \Theta/C = \log K + x \log (1-\Theta)$$

where "x" is the size parameter and it is a measure of the number of adsorbed water molecules substituted by an inhibitor molecule. The adsorption parameter is shown, in **table-5.** The plot of **log Θ/C against log (1-Θ)** is linear as shown in **figure-28.**

El-awady isotherm

It is given by the expression:

$$\log (\Theta/1-\Theta) = \log K + y \log C$$

Here K_{ads} the equilibrium constant of adsorption process is calculated by the relationship, K_{ads} = 1/k. A plot of **2 + log (1-Θ) Vs. 2+ logC** is linear as shown in **figure-29**. The calculated K_{ads} and 1/y values are given. The adsorption isotherm values are shown in **table-6.**

Frumkin isotherm

$$K_{ads}\, C = (\ /1-\Theta)e^{-2a}$$

Take logarithm on both sides of the equation, it can be rearranged as given below.

$$\log K_{ads} + 2a = \log(\ /(1-\Theta)C)$$

where, K_{ads} is the adsorption desorption equilibrium constant, V is the inhibition volume and "a" is the interaction parameter describing the lateral interaction among inhibitor molecular in the absorbed layer on the metal surface. Linear plots of **log(/(1- Θ)C)** Vs. **Θ** is

shown in **figure-30** obtained. The values for the Frumkin adsorption parameters are shown in **table-7.**

Free energy change

The free energy of absorbtion (ΔG^0_{ads}) of inhibitor on mild steel surfaces related to the constant of the adsorption according to equation.

$$\mathbf{\Delta G^0_{ads} = -2.303RTlog\ (K_{ads} \times 55.5)}$$

From the results, shown in **table-8**, most of the values of ΔG^0_{ads} were found to be negative and were below the threshold value of -40 kJ/mole indicating that the adsorption of *Cosmos sulphureus* leaves extract, on mild steel susrface is spontaneous and that mechanism of physical adsorption is applicable.

Potentiodynamic polarization studies

Table-9 and **figure**s **31, 32, 33, & 34** gives the values of potentiodynamic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}) and the cathodic Tafel slopes (b_c and b_a) for the different volume shown in the green inhibitor understudy. It can be seen that the phyto-components diffuse from the bulk of the solution and gets absorbed on metal surface.

AC impedance study

Table-10 and **figures 35, 36, 37 & 38** shows the AC impedance value for different volume of the inhibitor. The R_t value increases and C_{dl} value decreases with inhibitor volume. This implies the formation of protective film on the metal surface. It can be also seen from **table-11** that there is a close agreement between the values of inhibition efficiencies obtained from weight loss measurements, polarization and impedance studies.

TABLE-2

Inhibition effect on corrosion of mild steel in 1.0 M H_2SO_4 medium by

***Cosmos sulphureus* leaves extract using weight loss method**

Inhibitor concentration (%), v/v	**Weight loss, g**	**Rate of corrosion, (mdd)**	**Inhibition efficiency (%)**
2	0.002	0.00083	37.50
4	0.009	0.00037	71.87
6	0.007	0.00029	78.10
8	0.006	0.00025	81.20
10	0.003	0.00012	90.60

TABLE-3

Langmuir adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M extract H_2SO_4 medium by *Cosmos sulphureus* leaves aqueous extract

Concentration (%), v/v	**Ɵ**	**C/ Ɵ**
2	0.375	5.3
4	0.719	5.5
6	0.781	7.6
8	0.812	9.8
10	0.906	11.0

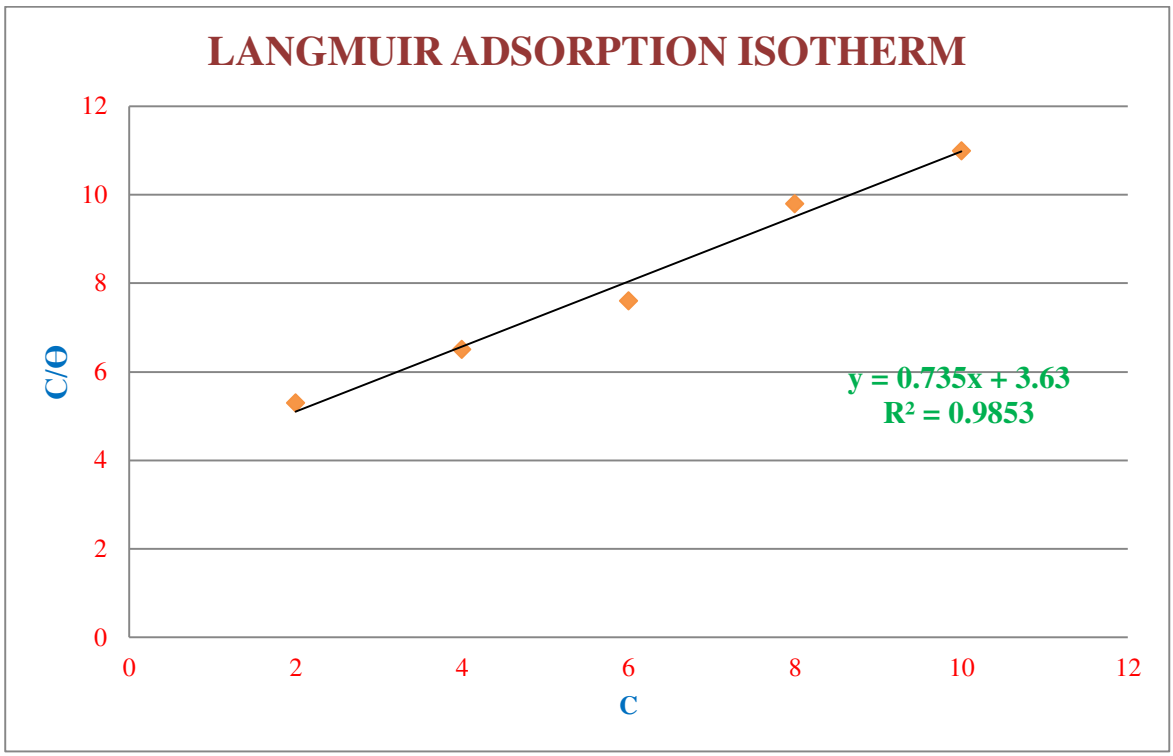

Figure -26: Langmuir adsorption isotherm for the inhibition of corrosion mild steel in 1.0 M H_2SO_4 medium using *Cosmos sulphureus* leaves aqueous extract.

Calculation:

Intercept	= 3.63
Kads	=0.2754
ΔG^{o}_{ads}	= -6.8725
Slope	=0.735
R^2	=0.985
1/y	= 1.3605

TABLE-4

Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cosmos sulphureus* leaves aqueous extract

Concentration(%), v/v	log C	2+log C	Ɵ
2	0.3010	2.301	0.375
4	0.6020	2.602	0.719
6	0.7781	2.778	0.781
8	0.9030	2.903	0.812
10	1	3	0.906

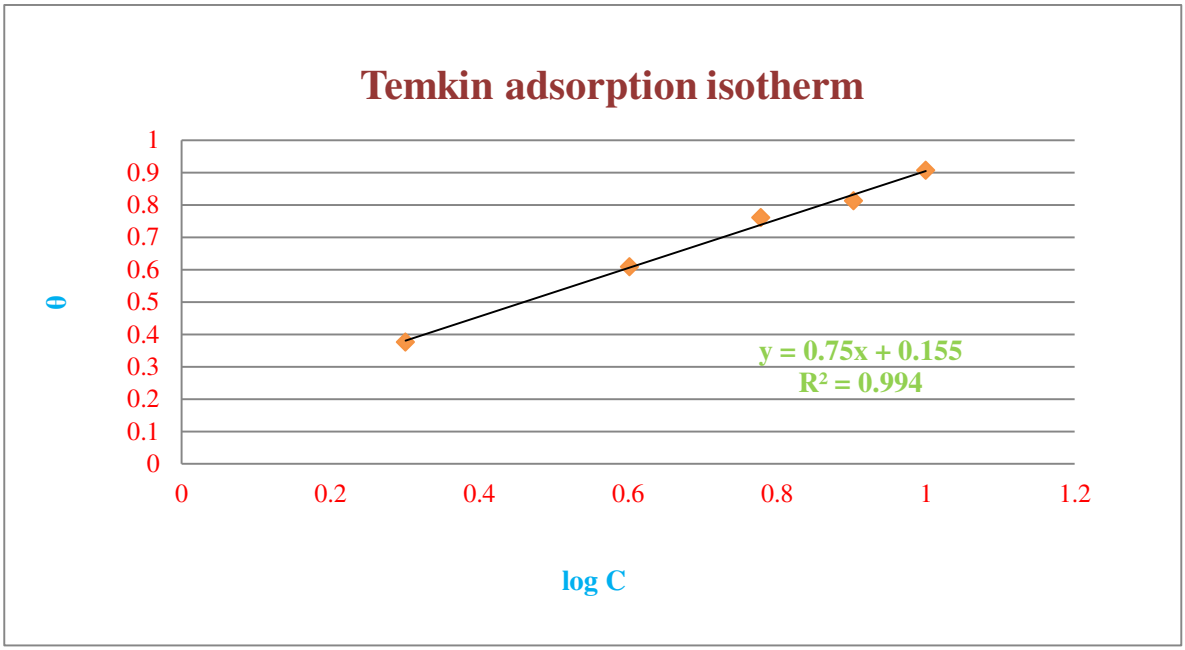

Figure- 27: Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium using *Cosmos sulphureus* leaves aqueous extract.

Calculation:

Intercept = 0.155

Kads =1.6091

ΔG^o_{ads} = -11.3203

Slope = 0.735

R^2 = 0.994

1/y = 1.333

TABLE-5

Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cosmos sulphureus* leaves aqueous extract

Concentration (%), v/v	Θ	log Θ/C	log (1- Θ)
2	0.375	-0.7269	-0.2041
4	0.719	-0.7454	-0.5512
6	0.781	-0.8857	-0.6595
8	0.812	-0.9935	-0.7258
10	0.906	-1.0428	-1.0268

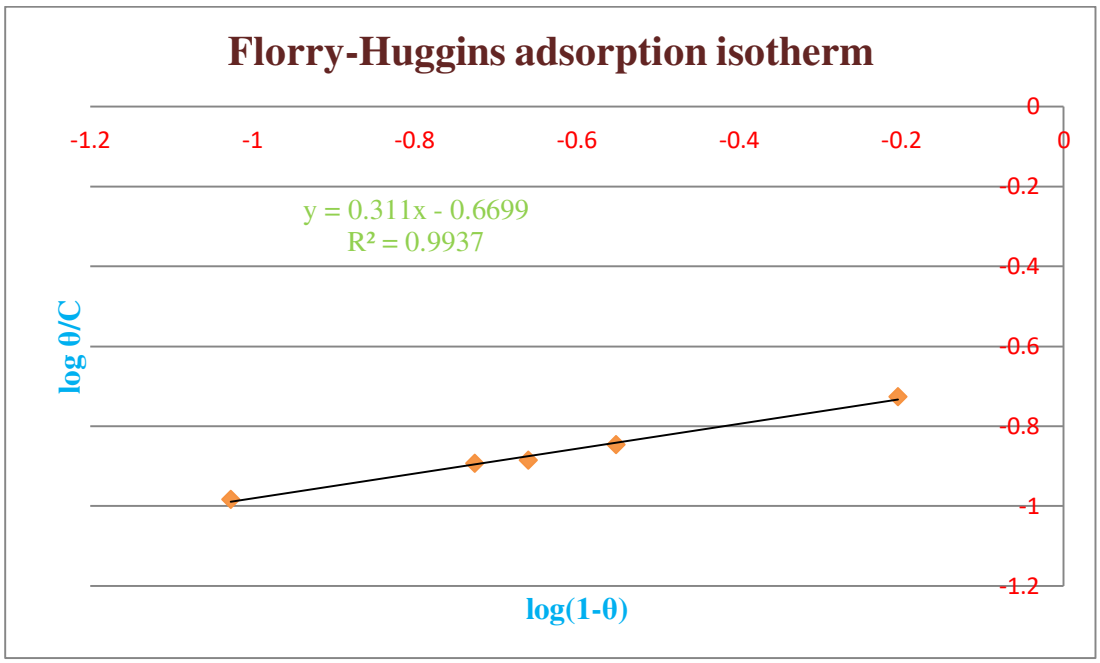

Figure 28: Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium using *Cosmos sulphureus* leaves aqueous extract.

Calculation:

Intercept =0.669

Kads =0.2142

ΔG^o_{ads} =-6.239

Slope = 0.311

R^2 = 0.993

1/y = 3.2154

TABLE – 6

El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cosmos sulphureus* leaves aqueous extract

Concentration (%), v/v	2+log C	Θ	1-Θ	Θ /(1- Θ)	2+logΘ/1-Θ
2	2.301	0.375	0.625	0.5216	1.7173
4	2.602	0.719	0.281	2.5587	2.4080
6	2.778	0.781	0.219	3.5662	2.5520
8	2.903	0.812	0.188	4.3191	2.6353
10	3	0.906	0.094	9.6382	2.9839

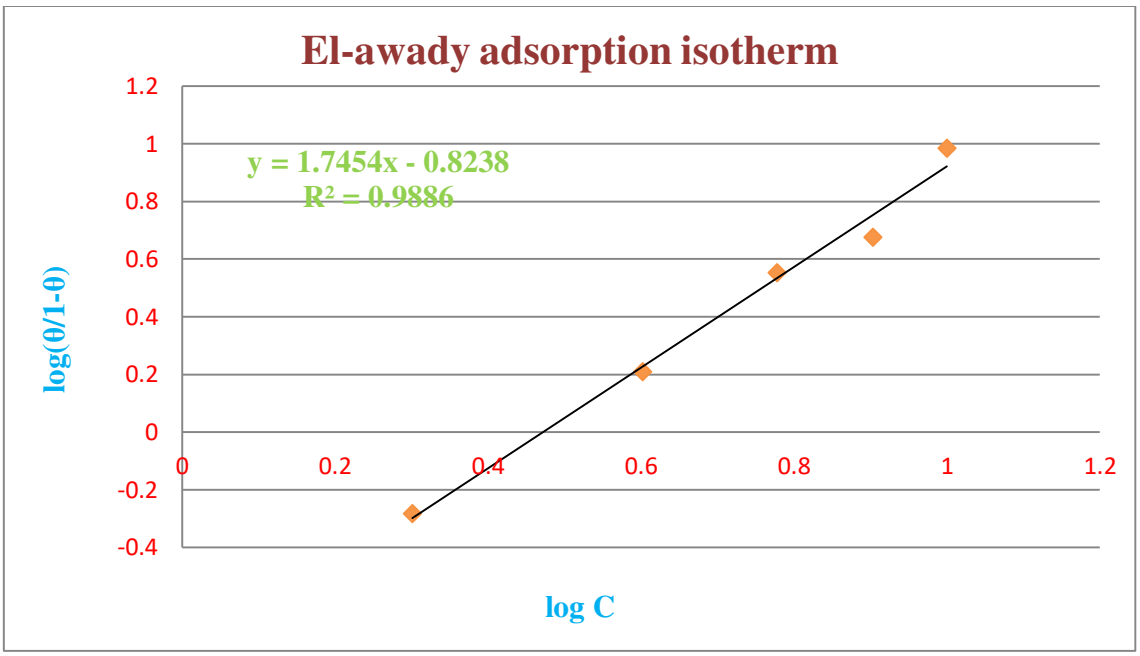

Figure 29: El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 using *Cosmos sulphureus* leaves aqueous extract.

Calculation:

Intercept = -0.823

K_{ads} = 0.3375

ΔG^o_{ads} = -7.3851

Slope = 1.745

R^2 = 0.988

1/y = 0.5730

TABLE – 7

Frumkin adsorption isotherm for the inhibition of mild steel in 1.0 M H_2SO_4 medium by *Cosmos sulphureus* leaves aqueous extract

Concentration (%), v/v	**Θ**	**(1-Θ)**	**log Θ**	**log Θ/(1-Θ)C**
2	0.375	0.625	-0.4259	-0.5229
4	0.719	0.281	-0.14327	-0.1945
6	0.781	0.219	-0.1073	-0.2259
8	0.812	0.188	-0.00904	-0.2677
10	0.906	0.094	-0.0428	-0.01601

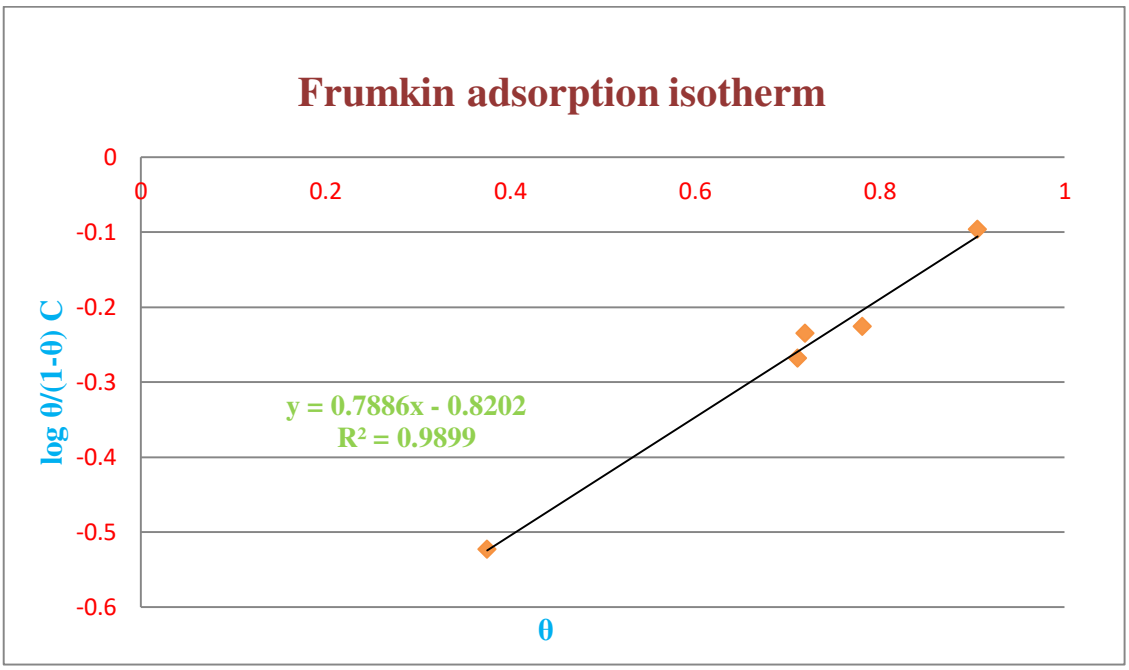

Figure 30: Frumkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 using *Cosmos sulphureus* leaves aqueous extract.

Calculation:

Intercept =-0.820

K_{ads} = 0.1513

ΔG^o_{ads} = -5.36356

Slope =0.788

R^2 =0.9891

1/y =1.2690

a =0.394

TABLE – 8

Adsorption isotherm parameters for the inhibition of the corrosion of mild steel in 1.0 M H_2SO_4 by *Cosmos sulphureus* leave aqueous extract

Isotherm	ΔG^o_{ads}	Slope	R^2	a	1/y
Langmuir Isotherm	-6872.55	0.735	0.995	-	1.3605
Temkin Isotherm	-11320.39	0.750	0.994	1.535	1.333
Florry-Huggins Isotherm	-6239.60	0.311	0.993	-	3.2154
El-awady Isotherm	-7385.12	1.745	0.988	-	0.5730
Frumkin Isotherm	-5363.56	0.788	0.989	0.394	1.2690

The R^2 value shows that **Langmuir, Florry-Huggins & Temkin** are the best fit isotherms compare to the other isotherms.

TABLE – 9

Corrosion parameters obtained from polarization curves for mild steel in 1.0 M H_2SO_4 medium in the presence and absence of inhibitor

SYSTEM	[Inhibitor] (%,) v/v	$I_{corr.}$, mV	$-E_{corr.}$, mV	b_a, mV dec^{-1}	b_c, mV dec^{-1}	% Inhibition Efficiency
Blank	-	779.758	-49.966	38.249	180.905	-
Cosmos sulphureus leaves aqueous extract	2	485.699	-456.222	41.177	208.572	37
	6	215.353	-462.941	49.209	221.358	72.38
	10	140.924	-469.333	90.836	292.475	81.92

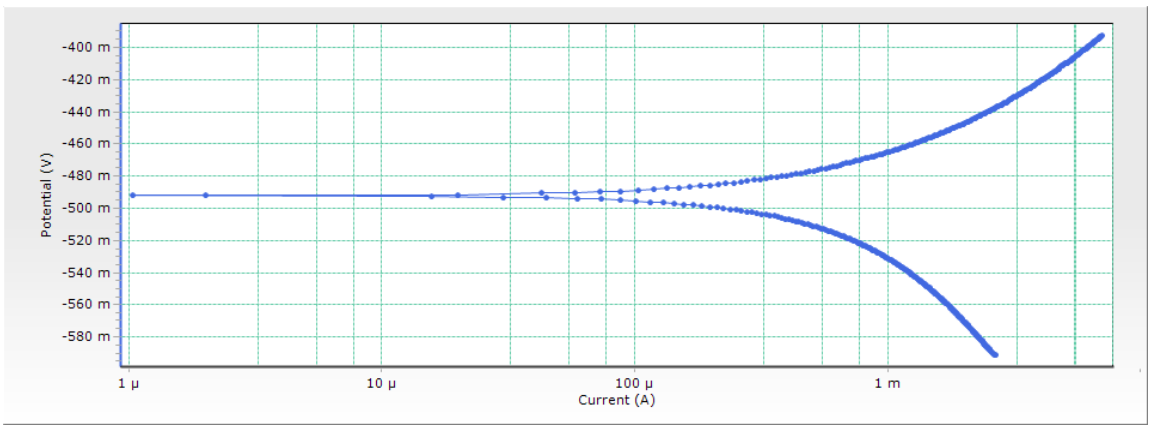

Figure 31: Potentiodynamic polarisation curve for mild steel in 1.0 M H_2SO_4

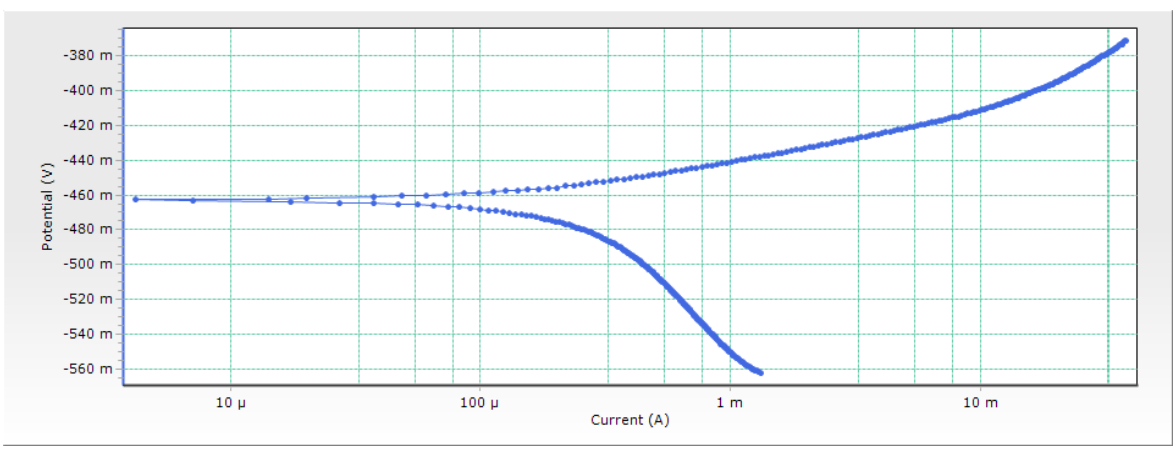

Figure 32:Potentiodynamic polarisation curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 2% of *Cosmos sulphureus* leaves aqueous extract

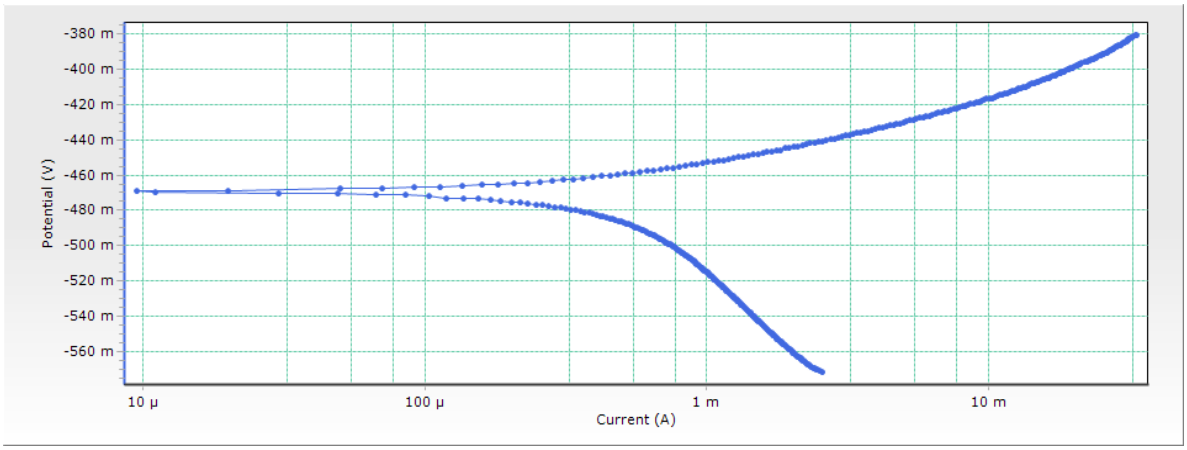

Figure 33:Potentiodynamic polarisation curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 6% of *Cosmos sulphureus* leaves aqueous extract

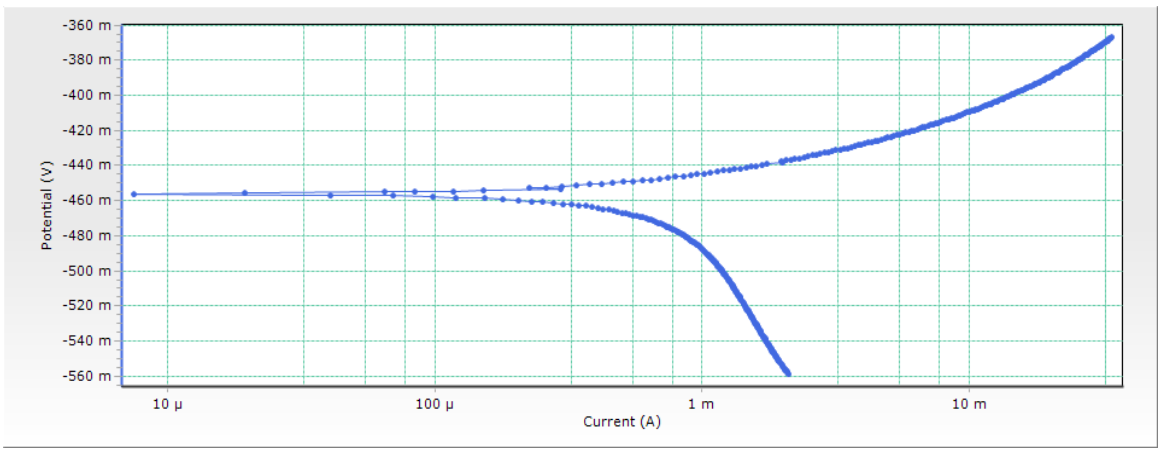

Figure 34:Potentiodynamic polarisation curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 10% of *Cosmos sulphureus* leaves aqueous extract

TABLE-10

Corrosion parameters obtained from impedance curve for mild steel in the presence and absence of inhibitor in 1.0 M H_2SO_4 medium

[Inhibitor] (%), v/v	**R_t, Ohm.cm^2**	**C_{dl}, F/cm^2**	**Inhibition efficiency (%)**
Blank	60	0.000274	-
2	32	0.0001826	33.3
6	38	0.000136	71.2
10	45	0.000095	82.2

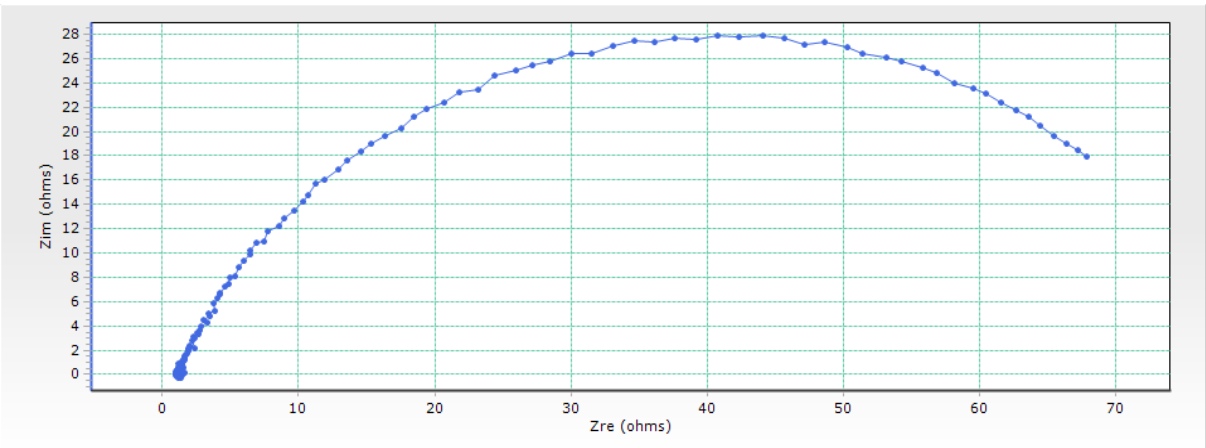

Figure 35:Impedance diagram for mild steel in 1.0 M H_2SO_4

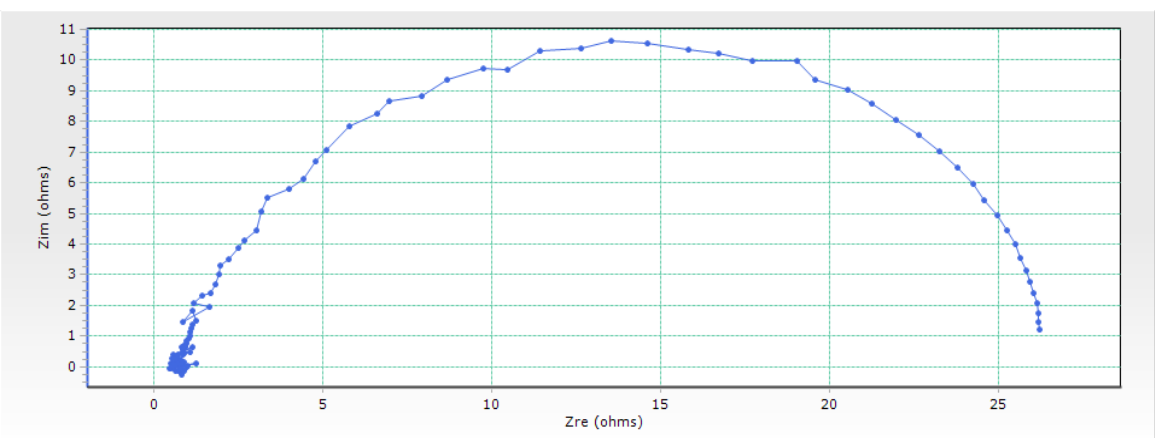

Figure 36: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 2% of *Cosmos sulphureus* leaves aqueous extract

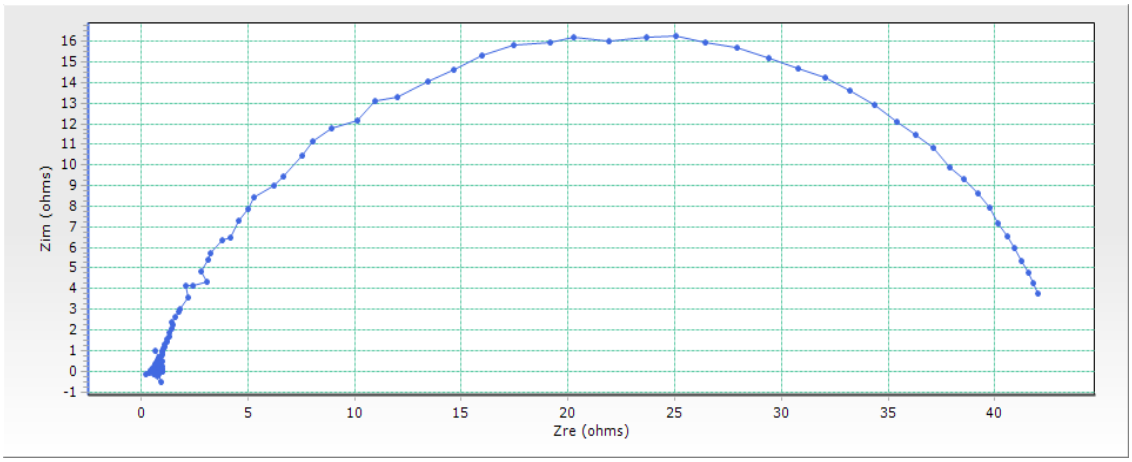

Figure 37: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 6% of *Cosmos sulphureus* leaves aqueous extract

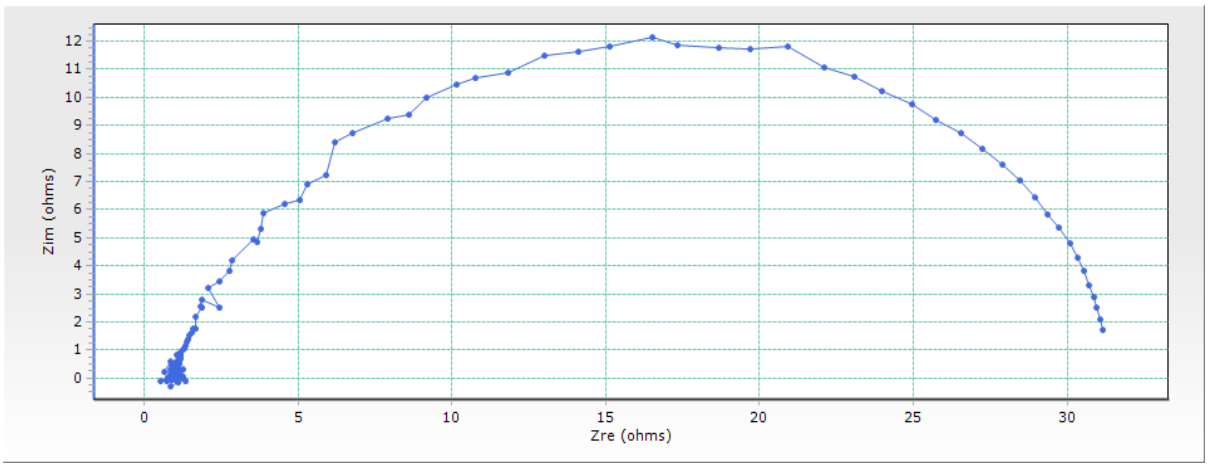

Figure 38: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 10% of *Cosmos sulphureus* leaves aqueous extract

TABLE-11

Comparison of inhibition efficiency measured by Weight loss, Polarization method and Impedance method

[Inhibitor] (%), (v/v)	Inhibition efficiency (%)		
	Weight loss studies	Polarization studies	Impedance studies
Blank	-	-	-
2	37	37	33
6	78	72	71
10	90	81	82

CHAPTER-V

SUMMARY AND CONCLUSION

The inhibitive influence of leaves of *Cosmos sulphureus* on the corrosion of mild steel in 1.0 M H_2SO_4 medium was studied by weight loss method, polarization and impedance measurements. The corrosion is decreased with increase in the addition of *Cosmos sulphureus* leaves extract probably due to the progressive adsorption of the inhibitor on the metal surface. The maximum inhibition efficiency was found to be 90.60%

- The corrosion of mild steel in 1.0 M H_2SO_4 solution is inhibited by the addition of leaves extract of *Cosmos sulphureus.* The percentage of inhibition efficiency increases with increase of the inhibitor concentration.

- The corrosion of mild steel inhibited by leaves extract of *Cosmos sulphureus* is attributed to the adsorption of phytochemical components present in the inhibitor onto the mild steel surface.

- The values obtained from the weight loss technique for the studied inhibitor fit well into the Languir,Temkin&florry-huggins adsorption isotherm. The values of free energy for the adsorption process indicate that the adsorption of the inhibitor on the mild steel surface occurs spontaneously. It suggests that the inhibition is followed by physisorption of the inhibitor on the metal surface.

- The leaves of *Cosmos sulphureus* prevent the corrosion of mild steel due to the presence of phytochemical components shifting the corrosion into the noble.

- The polarization and impedance study also shows an agreement with inhibitor efficiency obtained from weight loss studies And it indicates the corrosion inhibition by investigated inhibitor act as mixed type of inhibitor .

The results obtained suggest that the *Cosmos sulphureus* leaves extract is a good corrosion inhibitor for mild steel in 1.0 M H_2SO_4 medium and it can be preferentially used to replace toxic and non-biodegradable inhibitor.

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Post Graduate Project 2

Corrosion Inhibition Performance of Aqueous Extract of *Chrysanthemum Indicum* on Mild Steel in 1.0 M HCl

Name of the Guide: Dr. A. SamsathBegum
Name of the Candidate: D. Mythili

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CHAPTER-I

INTRODUCTION

CORROSION

Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Both the type of metal and the environmental conditions, particularly gasses that are in contact with the metal, determine the form and rate of deterioration.

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment.

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, Sulphate and Nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different medium.

Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its location. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media.

DEFINITION OF CORROSION

Corrosion is the irreversible damage or destruction of living tissue or material due to a chemical or electrochemical reaction. A prime example of corrosion is of iron or steel.

- Corrosion is a natural process, which converts refined metal to a more chemically stable form, such as its oxide, hydroxide or sulfide. It is the gradual destruction of materials (usually metals) by chemical or electro chemical reaction with their environment.
- Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminolog corrosion processes involve reaction of metals with environmental species.
- Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment.
- Corrosion is the destructive attack on a metal through interaction.

THEORIES OF CORROSION

- **Homogeneous theory**

A corroding metal irrespective of the presence or absence on its surface of any micro heterogeneity can be regarded as single electrode on which reactions take place. Metal becomes unstable due to the charge transfer reaction taking place at the interface. Hence, it is necessary that the potential difference across the interface be more negative than the equilibrium potential for the metal dissolution (anodic) reaction or more positive than the equilibrium potential for the electronation (cathodic) reaction.

- **Heterogeneous theory**

According to this theory, corrosion is caused by local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity. Corroding metal consists of an electron sink area, where de-electronation reaction occurs. b. an electron source area, where electronation reaction occurs in an ionic conductor to keep the current flowing.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I cor. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

The most common and important electrochemical reactions in the corrosion of iron are

thus

Anodic reaction (corrosion)

$$Fe \longrightarrow Fe^{2+} + 2e^{-}$$

Cathodic reactions (simplified)

$$2H^{+} + 2\,e \longrightarrow H_2$$

$$H_2O + 1/2\ O_2 + 2e \longrightarrow 2\ OH^{-}$$

This reaction is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

MECHANISM OF CORROSION

Although several mechanisms have been proposed for the corrosion process, corrosion is mainly electrochemical in nature and hence in this chapter, the electrochemical mechanistic aspects have been discussed. According to this approach, the corrosion reaction can be considered as taking place by two simultaneous reactions; the oxidation of a metal at an anode (a corroded end releasing electrons) and the reduction of a substance at a cathode (a protected end receiving electrons). In order for the reaction to occur, the following conditions must exist:

- A chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition).
- An electrolyte must be present to provide solution conductivity and act as a source of material to be reduced at the cathode.
- An electrical path through the metal or between metals must be available to permit electron flow.

The below diagram illustrates the typical electrochemical corrosion of iron in contact with water.

In a nearly neutral or slightly acid environment, the water is dissociated into hydrogen ions (H^+) and hydroxyl ions (OH^-) as

$$H_2O \rightleftarrows H^+ + OH^-$$

When metal is placed in contact with a liquid, surface ionization occurs, because of the electric charge difference at the solid-liquid interface. For example, iron dissolves in water in the form of positively charged ferrous ions (Fe^{++})

$$Fe \rightleftarrows Fe^{++} + 2e^-$$

Electrochemically, a chemical substance is “oxidized”, when it loses electrons to a second substance. The electrode at which the oxidation takes place is called as the “anode”. A chemical substance is “reduced”, when it acquires electrons. The electrode at which reduction takes place is called the “cathode”. Hence, oxidation reaction results in the formation of positive charge ferrous ions at the anode. Ferrous ions moving away from the metal surface are further oxidized to ferric ions (Fe^{++}) as follows

$$Fe^{++} \rightleftarrows Fe^{+++} + e^-$$

The positively charged ferric ions are attracted to the negatively charged hydroxyl ions and form the corrosion product $Fe(OH)_3$

$$Fe^{+++} + 3(OH)^- \rightleftarrows Fe(OH)_3$$

The rust consists of iron hydroxide or iron oxide hydrates in various states, depending on the degree of oxidation and dehydration.

The reduction reaction at the cathode must take place concurrently in order to continue the corrosion process. Several reactions are possible and the one that occurs is determined by the

environment. Without the presence of air or oxygen, hydrogen ions can be reduced by the excess of electrons at the cathode surface and evolve as molecular hydrogen by

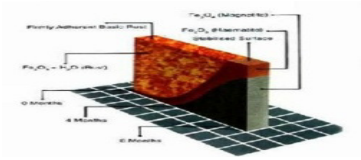
$$2H^+ + 2e^- \rightleftharpoons H_2$$

If hydrogen is not removed from the surface, the cathodic reaction decreases and the corrosion rate is reduced. With the presence of air, the more likely reaction is the reduction of oxygen. Two possible reactions occur:

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4(OH)^-$$

Hydrogen evolution or oxygen reduction with the formation of water is likely to occur in acid media. On the other hand, oxygen reduction with the formation of hydroxyl ions is more dominant in a neutral or alkaline environment. In either case, there is an increase in the alkalinity of the solution at the cathode.



In summary, corrosion occurs when metal atoms detach themselves from the metal surface at the anode and enter the solution as ions, leaving behind electrons in the metal. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen ions that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In solutions, where hydrogen tends to evolve too slowly, oxygen is reduced and combines with hydrogen ions or water to form hydroxyl ions.

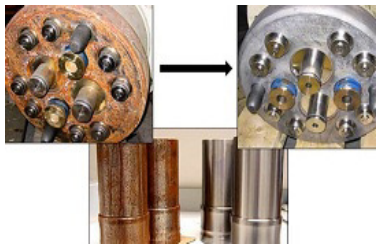
TYPES OF CORROSION

They are many different types of corrosion, each of which can be classified by the cause of the metals chemical deterioration.

The metal corrodes at the same rate over the entire surface for the former and only small areas are affected in localized corrosion. Classification by appearance is manifested by the morphology of the corrosion attack and this can be visualized either by naked eye or magnification. The schematic in the given below diagram illustrates some of the most common forms of corrosion

General attack corrosion

It is also known as uniform attack corrosion. General attack corrosion is the most common type of corrosion and is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal. Ultimately, the metal deteriorates to the point of failure.



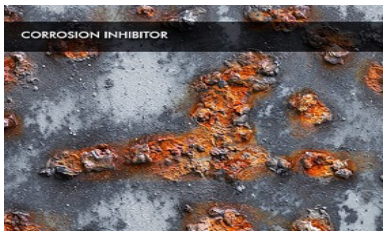
General attack corrosion accounts for the greatest amount of metal destruction by corrosion but is considered as a safe form of corrosion, due to the fact that it is predictable, manageable and often preventable.

Localized Corrosion

Unlike general attack corrosion, localized corrosion specifically targets one area of the metal structure. Localized corrosion is classified as one of three types:

Pitting: Pitting results when a small hole, or cavity, forms in the metal, usually as a result of de-passivation of a small area. This area becomes anodic, while part of the remaining metal

becomes cathodic, producing a localized galvanic reaction. The deterioration of this small area penetrates Crevice corrosion: Similar to pitting, crevice corrosion occurs at a specific location. This type of corrosion is often associated with a stagnant micro-environment, like those found under gaskets and washers and clamps. Acidic conditions or a depletion of oxygen in a crevice can lead to crevice corrosion.

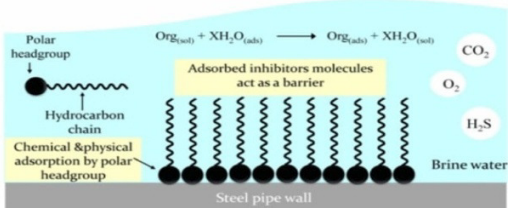


Filiform corrosion

Occurring under painted or plated surfaces when water breaches thecoating, filiform corrosion begins at small defects in the coating and spreads to cause structure.This form of corrosion is often difficult to detect due to the fact that it is usually relatively small and may be covered and hidden by corrosion produced compounds.

Galvanic corrosion

Galvanic corrosion or dissimilar metal corrosion, occurs when two different metals are located together in a corrosive electrolyte. A galvanic couple forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly.

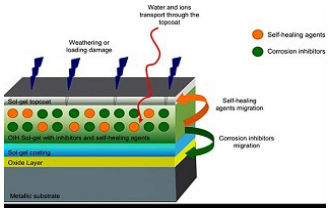


Three conditions must exist for galvanic corrosion to occur:

- Electrochemically dissimilar metals must be present
- The metals must be in electrical contact
- The metals must be exposed to an electrolyte

Environmental cracking

Environmental cracking is a corrosion process that can result from a combination of environmental conditions affecting the metal. Chemical, temperature and stress-related conditions can result in the following types of environmental corrosion:



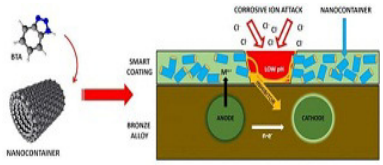
Flow-Assisted corrosion (FAC)

Flow-assisted corrosion, or flow-accelerated corrosion, results when a protective layer of oxide on a metal surface is dissolved or removed by wind or water, exposing the underlying metal to further corroding and deteriorate

- Erosion-assisted corrosion
- Impingement
- Cavitation

Intergranular corrosion

Intergranular corrosion is a chemical or electrochemical attack on the grain boundaries of a metal. It often occurs due to impurities in the metal, which tend to be present in higher contents near grain boundaries. These boundaries can be more vulnerable to corrosion than the bulk of the metal.



De-Alloying

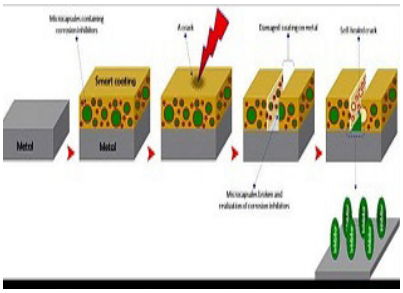
De-alloying, or selective leaching, is the selective corrosion of a specific element in an alloy. The most common type of de-alloying is de-zincification of unstabilized brass. The result of corrosion in such cases is a deteriorated and porous copper.

It is the removal of one solid element from alloy by corrosion processes. De alloying corrosion is also called de-zincification.

The most common example is de-zincification which is selecti removal of zinc in brass alloy. Similar processes occur in other alloy systems in which aluminium, Iron, Cobalt, Chromium and other elements are removed**.**

Fretting corrosion

Fretting corrosion occurs as a result of repeated wearing, weight and/or vibration on an uneven, rough surface. Corrosion, resulting in pits and grooves, occurs on the surface.



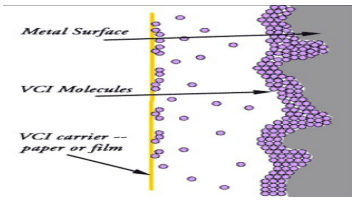
Fretting corrosion is often found in rotation and impact machinery, bolted assemblies and bearings, as well as to surfaces exposed to vibration during transportation.

High-Temperature corrosion

High-temperature corrosion is a mechanism of corrosion that takes place in gasturbines, diesel engines, furnaces or other machinery coming in contact with hot gas containing

certain contaminants. Fuel sometimes contains vanadium compounds or sulfates which can form compounds during combustion having a low melting point. These liquid melted salts are strongly corrosive for stainless steel and other alloys normally inert against the corrosion and high temperatures. Other high-temperature corrosions include high-temperature oxidation, sulfidation and carbonization**.**

Crevice corrosion

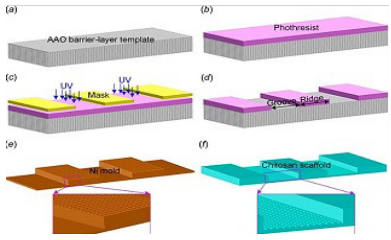


Crevice corrosion is also a localized form of corrosion and usually results from a stagnant microenvironment in which there is a difference in the concentration of ions between two areas of a metal.

Crevice corrosion occurs in shielded areas such as those under washers, bolt heads, gaskets, etc. where oxygen is restricted. These smaller areas allow for a corrosive agent to enter but do not allow enough circulation within, depleting the oxygen content, which prevents re-passivation. As a stagnant solution builds, pH shifts away from neutral. This growing imbalance between the crevice (micro environment) and the external surface (bulk environment) contributes to higher rates of corrosion. Crevice corrosion can often occur at lower temperatures than pitting. Proper joint design helps to minimize crevice corrosion.

Stress corrosion cracking (SCC)

Stress corrosion cracking (SCC) is a result of the combination of tensile stress and a corrosive environment, often at elevated temperatures. Stress corrosion may result from external stress such as actual tensile loads on the metal or expansion/contraction due to rapid temperature changes.

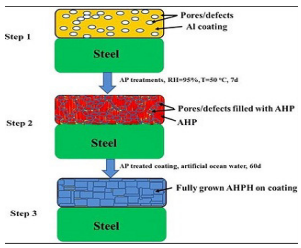


Caustic agent corrosion

Caustic agent corrosion occurs when impure gas, liquids, or solids wear a material down. Although most impure gases do not damage metal in dry form, when exposed to moisture they dissolve to form harmful corrosive droplets. Hydrogen sulfide is an example of one such caustic agent.

Microbial corrosion

Microbial corrosion, commonly referred to as microbiologically influenced corrosion (MIC) is caused by microorganisms. It applies to both metallic and non-metallic materials with or without oxygen. When oxygen is absent, sulfate-reducing bacteria are active and produce hydrogen sulfide causing sulfide stress cracking. When oxygen is present, some bacteria may directly oxidize iron to iron oxides and hydroxides. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.



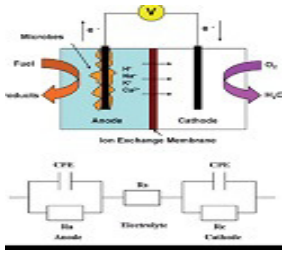
Filiform corrosion

Filiform corrosion: It is basically a special type of crevice corrosion, sometimes termed as “under film” corrosion. This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating.

Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided unless absence of an adverse effect has been proven by field experience.

Cavitation damage

Cavitation damage is a special form of erosion corrosion caused by the formation of vapour bubbles and their collapse in the liquid near a metal surface. This form of damage occurs in hydraulic turbines, pump impellers, and other surfaces that are in contact with high-velocity liquid flow along with high pressures.



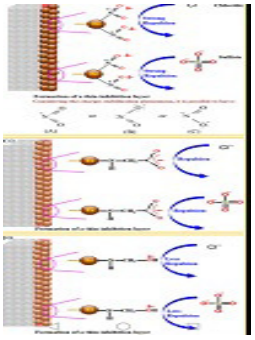
Erosion corrosion

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities. Erosion corrosion can be controlled by the use of harder alloys (including flame-sprayed or welded hard facings) or by using a more corrosion resistant alloy

Concentration cell corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. Concentration cell corrosion is associated with gaskets, joints, scale, debris, loose protective films, etc.

Corrosion attack is accelerated, where the oxygen concentration is least. Metal at the area of low oxygen availability becomes anodic to other areas. As the cathodic area is large compared to the anodic area, the intensity of attack is usually more severe on surrounding areas of the same surface. This condition can be eliminated by sealing the faying surfaces in a manner

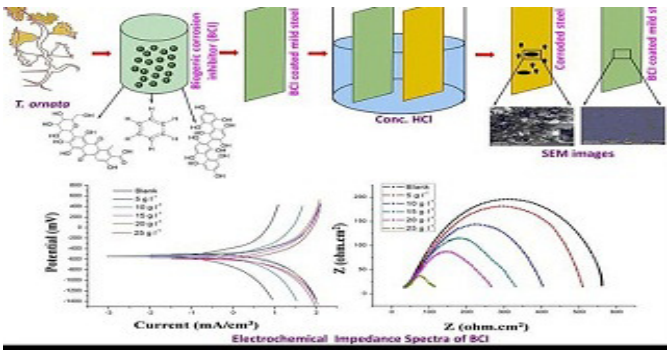


Corrosion fatigue

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment. Control of corrosion fatigue can be accomplished by either lowering the cyclic stresses or by corrosion control by using protection methods.

Direct chemical corrosion (or) dry corrosion

This type of corrosion occurs mainly through the direct chemical action of environment/atmospheric gases such as oxygen, halogens, hydrogen sulphide, nitrogen or anhydrous liquid sulphur dioxide with metal surface in immediate proximity. The extent of corrosion depends upon the following factors:



FACTORS AFFECTING RATE OF CORROSION

Nature of the metal

Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum, silver. Whereas metal with lower electrode potentials, readily undergo corrosion. e.g., metals like zinc, magnesium, aluminium. When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion. For e.g., the potential difference between the iron and copper is 0.78V which is more than that between iron and tin is 0.30V. Therefore, iron corrodes faster when in contact with copper than that with tin. On this account, the use of dissimilar metals should be avoided wherever possible. For example, bolt and nut or screw and washer should made by the same metal (or alloy) to avoid galvanic corrosion.

Ratio of cathodic to anodic region

The rate of corrosion is influenced by relative size of cathodic to anodic area. If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio decreases corrosion rate further increases. This is because at anode electrons are liberated. Which are consumed at cathodic region. If cathodic region is larger the liberated electrons are rapidly consumed at cathode. This futher enhances, the anodic reactions leading to increase in overall rate of corrosion. When two dissimilar metals are in contact, Corrosion is more rapid and severe, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank), If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode. An intense localized corrosion occurs at the exposed small anodic surface. On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas.

Nature of the corrosion product

The corrosion product formed like metal oxide may act as protective film, if it is stable, insoluble, and non-porous. If it acts as protective film it prevents further corrosion by acting as barrier between metal surface and corrosion medium. On the other hand if corrosion product is Unstable, porous, and soluble, it further enhances corrosion in oxidizing environments, metals like aluminium, chromium, titanium, etc., are highly passive as their oxides as corrosion products form protective films on the metal surface, preventing further corrosion. Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments

pH of the medium

In general rate of corrosion is higher in acidic pH than in neutral and alkaline pH.In case of iron, at very high pH protective coating of iron oxide is formed which prevents corrosion. Where as at low pH, severe corrosion takes place. But for metals like aluminium, corrosion rate is high even at high pH.

Temperature

The rate of corrosion increases with increasing temperature. This is due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

Effect of oxygen

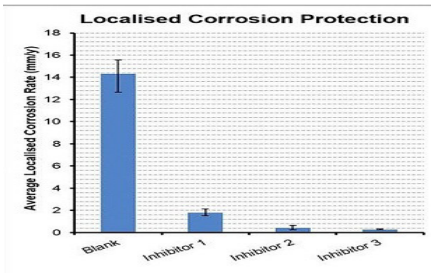
Oxygen plays an important corroding medium. If the metal is exposed to different concentration of oxygen, differential aeration corrosion takes place. The region which is less 0exposed to oxygen acts as anode hence undergoes corrosion and region exposed to high oxygen concentration acts cathode hence doesn‟t undergo corrosion.

Hydrogen over voltage

The metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. Since at lower hydrogen over voltage, the liberation of hydrogen gas is easy. Therefore cathodic reaction is very fast, which in turn makes anodic reaction very fast. Thus increasing the rate of corrosion. Higher the over voltage lesser is the corrosion.

PREVENTION OF CORROSION

Rust and other corrosion forms can lead to safety issues and ruin the integrity of your equipment and supplies. Even routine maintenance to remove and repair corrosion can drive up costs. Fortunately, there are a variety of measures you can take to minimize corrosion. Herewe‟ll highlight four of these methods based on cost and effectiveness.

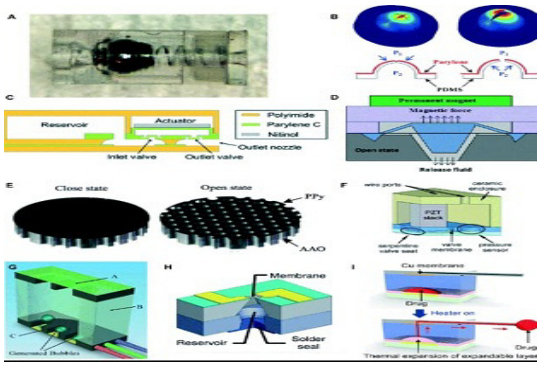


Barrier coatings

One of the easiest and cheapest ways to prevent corrosion is to use barrier coatings likepaint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film. Plastic and waxes are often sprayed onto metal surfaces. Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds. Today‟s paint systemsare actually a combination of different paint layers that serve different functions. The primer coat acts as an inhibitor, the intermediate coat adds to the paint‟s overall thickness, and the finish coat provides resistance to the environmental factors.

The biggest drawback with coatings is that they often need to be stripped and reapplied.

Coatings that aren‟t applied properly can quickly fail andlead to increased levels of corrosion.Coatings may also contain volatile organic compounds, which can make them vulnerable to corrosion.



Hot-Dip galvanization

This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection.

The process has been around for more than 250 years and has been used for corrosion protection of things like artistic sculptures and playground equipment. Compared to other corrosion prevention methods, galvanization is known for lower initial costs, sustainability, and versatility. Unfortunately, galvanization can‟t be done on-site, meaning companies have to pull equipment out of work to be treated. Some equipment may simply be too large for the process, forcing companies to abandon the idea altogether. In addition, if the process isn‟t done properly, the zinc can chip or peel. And high exposure to environmental elements can speed up the process of zinc wear, leading to increased maintenance check-ups. Lastly, the zinc fumes that release from the galvanizing process are toxic.

Alloyed steel (Stainless)

Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product. Corrosion-resistant nickel, for example, combined with oxidation-resistant chromium results in an alloy that can be used in oxidized and reduced chemical environments. Different alloys provide resistance to different conditions, giving companies greater flexibility.

Despite its effectiveness, alloyed steel is very expensive. Companies with limited financial resources will likely have to turn to other methods. Monitoring surface conditions arecritical, as cracks or scratches can result in an increase of corrosion. Companies also need to make sure the agents used in maintenance don‟t include corrosion properties.

Cathodic protection

Cathodic protection protects against galvanic corrosion, which occurs when two different metals are put together and exposed to a corrosive electrolyte. To prevent this, the active sites on the metal surface need to be converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

While cathodic protection is highly effective, anodes need to be checked often which can drive up costs of maintenance. They also increase the weight on the attached structure and aren‟t always effective in high-resistivity environments. Finally, anodes lead to increased water flow on ships and other underwater equipment.

Coatings

Coatings provide physical barriers that do not allow corrosive materials to come in contact with the structure that is being protected. Mainly, coatings are used on the exterior of pipelines to protect from external factors and are not used to directly protect the pipeline from CO_2 corrosion. The most common type of coatings are painting and platting which both provide effective corrosion protection and aesthetic appearance. Painting: Painting is an effective way to protect pipelines from external environmental factors. Although when looking at CO_2 corrosion on the interior of the pipeline, it is not ideal because painting the inside of a pipeline is impractical. The paint will breakdown over time, either through chemical reactions with the flowing fluid or the erosion due to turbulent or transient flow. Once the coating has broken down it leaves unprotected sections of the pipe when fluid induced localized corrosion occurs.

Plating

Plating involves using electric currents to coat a metal with a thin layer of another metal that acts as a protective barrier. Plating an entire pipeline is very uncommon as it is expensive; however, it can be done when dealing with high pressures and high amounts of H_2S and CO_2. One draw back of plating is if the plating fails in a small section (either an imperfection or a scratch) then highly localized corrosion occurs. Another factor to consider is if the plating is more noble than the pipeline (for example, chromium on steel), the steel will act as a sacrificial anode for the chromium. This causes the exposed area to corrode much more rapidly than an un-plated surface would.

CORROSION INHIBITORS

An inhibitor is a chemical substance or combination of substances which when added in very low concentrations in a corrosive environment effectively prevents or reduces corrosion without significant reaction with the components of the environment. Concentrations of corrosion inhibitors can vary from 1 to 15,000 ppm (0.0001 to 1.5 wt %). Corrosion inhibitors can be solids, liquids and gases, and can be used in solid, liquid and gaseous media. Solid media can be concrete, coal slurries or organic coatings (paints). Liquids may be water, aqueous solutions or organic solvents. A gaseous medium is an atmosphere or water vapor. Corrosion inhibitors are selected on the basis of solubility or dispersibility in fluids which are to be inhibited. For instance, in a hydrocarbon system, a corrosion inhibitor soluble in hydrocarbon is used. Two phase system composed of both hydrocarbons and water is utilized as oil soluble water- dispersible inhibitor.

Corrosion inhibitors have been found to be effective and flexible means of corrosion mitigation. The use of chemical inhibitors to decrease the rate of corrosion processes is quite variable. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment and product additive industries. In the oil extraction, processing and chemical industries, corrosion inhibitors have always been considered to be the first line of defense. A great number of scientific studies have been devoted to the subject of corrosion inhibitors.

Inhibitors find major use in closed environmental systems that have good circulation so that an adequate and controlled concentration of inhibitor is ensured. Such conditions can be met, for instance in cooling water recirculation systems, oil production, oil refining, and acid pickling of steel components. One of the more recognizable applications for inhibitors is in antifreeze for automobile radiators. The application of inhibitors must be viewed with caution by the user because inhibitors may afford excellent protection for one metal in a specific system but can aggravate corrosion for other metals in the same system. Inhibitors can be organic or inorganic compounds and they are usually dissolved in aqueous environments. Some of the most effective inorganic inhibitors are chromates, nitrites, silicates, carbonates, phosphates and arsenates. The organic inhibitors include amines, heterocyclic nitrogen compounds, sulfur compounds such as thioethers, thioalcohols, thioamides, thiourea and hydrazine. Chromates and zinc salts are used increasingly less due to their toxicity and are nowadays largely replaced by organic inhibitors. Thus practical criteria for the selection of corrosion inhibitors from the great variety of inorganic and organic substances with inhibiting properties are not only their inhibition efficiency but also safety of use, economic constraints and compatibility with other chemicals in the system, and environmental concerns.

In order to avoid or reduce the corrosion of metallic materials, inhibitors used in cooling system must satisfy the following criteria.

- It must give good corrosion protection at a very low concentration of inhibitor.
- It must protect all exposed materials from the attack of corrosion.
- It must remain efficient in extreme operating conditions (higher temperature and velocity)
- In case of an under or over dosage of inhibitor, corrosion rate should not increase drastically.
- The inhibitor or reaction products of the inhibitor should not form any deposits on the metal surface particularly at locations where heat transfertakes place.
- It should suppress both uniform and localized corrosion.
- It should have long range effectiveness.It should not cause toxicity and pollution problems.

CLASSIFICATION OF CORROSION INHIBITORS

A common classification of inhibitors is based on their effects on the electrochemical reactions involved in the corrosion process.

Passivating inhibitors

Passivating inhibitors cause a large anodic shift of the corrosion potential forcing the metallic surface into the passivation range. There are two types of passivating inhibitors.

- ❖ The oxidizing anions such as chromates, nitrites and nitrates that can passivate steel in the absence of oxygen.
- ❖ The non-oxidizing ions such as phosphates, tungstates and molybdates that require the presence of oxygen to passivate steel.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential to monitor the inhibitor concentration.

Volatile inhibitors

Volatile corrosion inhibitors (VCIs) also called vapor phase inhibitors (VPIs) are compounds transferred in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing the acidic carbon dioxide or by shifting the surface pH towards less acidic. If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors.

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Liquid phase inhibitors (LPIs)

LPIs are in wide scale use to combat CO_2 corrosion in pipelines. The inhibitor is that is injected into the pipeline is transported in low concentrations and adsorbs onto the surface of the steel. Because the inhibitor is in the liquid phase only the interior of the pipeline needs to be in contact with the liquid either continuously or semi-continuously. One of the main benefits in using inhibitors to protect from CO_2 corrosion is that it can continuously be added to the flow to provide continuous protection.

Cathodic inhibitors

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. For example, calcium, magnesium and zinc ions will precipitate as hydroxides on cathodic sites as the local environment becomes more alkaline due to the reduction reaction at these sites. cathodic inhibitors are effective when they slow down the cathodic reaction rate. Arsenic, bismuth and antimony which are referred to as cathodic poisons reduce the hydrogen reduction reaction rate and thus lower the overall corrosion rate. Other cathodic inhibitors remove reducible species from the environment. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through

- the use of oxygen scavengers such as sodium sulfite and hydrazine which react with the oxygen and remove it from the solution
- vacuum de-aeration or
- boiling to lower the dissolved oxygen concentrations.

Anodic inhibitors

Anodic inhibitors such as chromates, phosphates, tungstates and other ions of transition elements with high oxygen content are those that stifle the corrosion reaction occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface forming a protective film or barrier, thereby reducing the corrosion rate. Anodic inhibitors build a thin protective film along the anode and increasing their potential and thus slow down the corrosion reaction. Chromates, nitrates, tungstate and molybdates are some examples of anodic inhibitors. Although, this type of control is affected, yet it may be dangerous since severe local attack can occur, if certain areas are left unprotected by depletion of the inhibitors.

Mixed inhibitors

Some substances inhibit corrosion by reducing simultaneously the rate of anodic and cathodic reactions involved in the corrosion process and are therefore called mixed inhibitors. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. Anodic inhibitors are, for the most part, dangerous inhibitors, especially if their concentrations are too less. But cathodic inhibitors are generally safe. Mixed inhibitors are less dangerous than pure anodic inhibitors, and in number of cases they may not increase the corrosion intensity. The most common inhibitors of this category are the silicates and the phosphates.

Synergistic inhibitors

It is very rare that a single inhibitor is used in systems such as cooling water systems. More often, a combination of inhibitors (anodic and cathodic) is used to obtain better corrosion protection properties. The blends which are produced by mixing of multi-inhibitors are called synergistic blends. Examples include chromate-phosphates, polyphosphate-silicate, zinc-tannins, and zinc-phosphates.

Precipitation inhibitors

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust. In aerated hot water systems, sodium silicate protects steel, copper and brass.

GREEN CORROSION INHIBITORS

Extracts of plant materials contain a wide variety of organic compounds. Most of them contain heteroatoms such as P, N, S, O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented.

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of “inhibitors”, “green inhibitors” can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

Organic green inhibitors

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from natural sources like plants. It also includes synthetic compounds with negligible toxicity. Some of the notable developments on organic green inhibitors especially plant extracts are discussed here.

Plant extracts

The authors have so far investigated the application of plant extracts, as well as other organic inhibitors against corrosion of steel in acidic fluids. Loto had reported the application of the extract of Mangifera indica (Common name: mango, indigenous area: India and other tropical regions) leaves and bark for corrosion of mild steel in diluted sulphuric acid (H_2SO_4) medium. The weight loss measurements and electrochemical impedance spectroscopic studies were used to determine the inhibition efficiency of the inhibitors. Though the extract of leaves and bark showed a significant effect on the corrosion rate separately, the combination of these two extracts exhibited rather higher efficiency.

The inhibitive effect of Zenthoxylum alatum (Winged Prickly Ash, East and South Asian Countries) fruit extract was reported for corrosion of mild steel in phosphoric acid medium at temperatures ranging from 50–80^{0}C. The surface analysis using X-ray photoelectron spectroscopy (XPS) revealed the layer formation of the plant extract on the surface of mild steel. And the results were indicated the possible formation of iron phosphate that was catalyzed by the formation of the iron-plant extract organo-metallic complex.

Satapathy et al studied the methanol extract of Justicia gendarussa (Willow-leaved justicia, India, Indonesia) leaves for corrosion inhibition of mild steel in hydrochloric acid medium (HCl). The authors have made an attempt to characterize the organic compounds present in the methanol extract by means of gas chromatography- mass spectrometric technique. The results showed that the compounds present in the methanol extract were difficult to separate, since the retention times of majority of the compounds were close to each other. The electron spectroscopy for chemical analysis and atomic force microscopywere employed to obtain the information about the film formation on the surface of the mild steel specimen.

Inorganic green inhibitor

A number of inorganic elements (minerals) are essential for the growth of living things. Mineral elements in wide variety are present in trace amounts in almost all foodstuffs. The higher concentrations of many metals cause toxicity to all forms of lives. Chromates are among the most common substances used as inhibitors or incorporated in anticorrosive pretreatments of

aluminums alloys. The corrosion of galvanized steel was inhibited by the formation of cerium-rich film. The film contains Ce^{4+} which was formed by the cerium oxides and hydroxide

IMPORTANCE OF GREEN INHIBITOR

- Inhibitors are a great method of preventing corrosion and are easy to apply. Has application in a wide range of sectors.The knowledge of the method of the action, facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects.
- It is important in the choice of inhibitor, ascertain the subsequent effects of this towards the environment.
- The search for environmental friendly inhibitors has shown excellent results, out performing conventional inhibitors.
- Reference organic inhibitors newly developed. Inhibitors play a vital role in providing protection against corrosion.
- The selection of the inhibitor is important for environmental protection Not all inhibitors are eco-friendly.
- There is a growing trend to use plant extracts and pharmaceutical compounds as corrosion inhibitors. Most of these compounds are environmentally-friendly.

ECO-FRIENDLY INHIBITORS FOR CORROSION CONTROL OF MILD STEEL (MS)

In recent years several researchers have indicated the use of eco-friendly corrosion inhibitors for mild steel in different media. They forms complexes with metal ion onto the metal surface and thus forming a protective coating on the metal surface and protecting them from corrosive agents in different media. Inhibition efficiency of these inhibitors in different media have been evaluated by employing different investigational techniques like weight loss method, electrochemical studies, Raman spectroscopy, gasometric techniques, potentio dynamic polarization, electrochemical impedance, polarization method, SEM, FTIR etc. are being used.

CHAPTER-II

AIM AND SCOPE OF THE PRESENT WORK

Green compounds represent a potential class of corrosion inhibitors. There is a wide range of studies regarding corrosion inhibition by hetero atoms containing green compounds. Green compounds containing lot of hetero atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulfur. The corrosion-inhibiting property of these compounds is attributed to their molecular structure.

Acid solutions are widely used in industries for pickling, acid cleaning of boilers, rescaling and oil well as acidizing. Corrosion inhibitors are widely used in order to control the corrosion of metallic materials by cleaning acids. 1.0 M HCl is employed in such purposes. Most of the earlier studies on inhibition of corrosion of metals in acids have been related to the performance of organic compounds containing hetero groups.

Recently, environmental friendly inhibitors have attracted several researchers. Natural products are non-toxic, biodegradable and readily available. They have been widely used as inhibitors. Corrosion inhibition of mild steel by various types of plant extracts have been studied.

Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly, acceptable and possess no threat to the environment. The present work in undertaken:

1. To evaluate the inhibition efficiency of an aqueous leaves extract of *chrysanthemum indicum* in controlling the corrosion of mild steel in 1.0 M HCl medium.

2. To analyse the best fit isotherm for corrosion inhibition.

3. To understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization and impedance analysis.

4. To propose a suitable mechanism for corrosion inhibition.

CHAPTER-III

EXPERIMENTAL METHOD

The experimental studies related to the inhibition action of *Chrysanthemum indicum* leaves extract on mild steel in 1.0 M HCl have been present here. Such studies include weight loss, polarization and impedance studies.

Chrysanthemum indicum

Chrysanthemum indicum is a monoecious annualvine climbing by means of tendrils.Leaves are palmately lobed, up to 25 cm long. Flowers are unisexual, white, opening at night, with long branching hairs on the margins of the petals. These hairs are curled up in the daytime when the flower is closed, but unfurl at night to form a delicate lacy display Fruits can be up to 200 cm long, deep red at maturity, hanging below the vine.

Chrysanthemum indicum is found in the wild across much of South andSouth east Asia,including India,Bangladesh,Nepal, Pakistan, SriLanka, Indonesia, Malaysia, Myanmar (Burma) and southern China (Guangxi and Yunnan) It is also regarded as native in northern Australia and naturalized in Florida, parts of Africa and on various islands in the Indian and Pacific Oceans.

Chrysanthemum indicum.

Botanical name : Chrysanthemum indicum

Kingdom : plantae

Clade : Anigiosperms

Clade: : Asterids

Order : Asterales

Family : Asteraceae

Genus : Chrysanthemum

Therapeutic uses: The leaves and stems are used for bilious disorders and skin diseases and asan emmenagogue, Snake gourd has been mooted to help lessen the effects of diabetes, Snake gourd extract is one of the best remedies for arterial disorders like palpitation and other conditions like pain and stress on the heart.

Pharmacological action: Anti-inflammatory, antioxidant, anti osteoporatic, anti bacterial activity.

Collection of the plant material: The leaves were collected from the area mandapam,Ramanathapuram (DT), Tamil nadu. Fresh leaves were authenticated and identified by Dr. John Britto, The Rapient Herbarium and centre for Moduler systematics, St. Joseph‟s College,Trichirappalli, Tamilnadu, India.

Preparation of extract

The leaves were collected, shade dried and powdered. An aqueous extract was prepared by refluxing 10 gm of powdered *Chrysanthemum indicum* leaves in double distilled H_2O. The extract was cooled, filtered and made up to 100 ml with distilled water. From that, various distributions were prepared.

Preparation of the specimens

Mild steel specimen (0.026%-S, 0.06%-P, 0.4%-Mn, 0.1%-C and the rest iron) of the dimensions 1x5x0.2 cm were polished to mirror finished. They are decreased with acetone and used for the weight loss method, polarization and impedance studies.

Materials and chemicals used

For polarization, cylindrical mild steel rod embedded in teflon with an exposed area of 1 cm^2 was used. The electrodes were polished with emery papers of 0/0, 2/0, 3/0, and 4/0 grades and degreased with acetone, dried and used.

Acid

HCl was used of G.R. Grade (MERCK CHEMICALS)

Phytochemical screening of aqueous extract of *Chrysanthemum indicum* leaves extract

Phyto-constituents	Chemical Test	Aqueous extract
Alkaloids	Wagners	+
Glycosides	Molisch	+
Tannins	$FeCl_3$	+
Flavonoids	Lead acetate	+
Sterols	Libermann	-
Fats & oils	Stain	-
Phenols	$FeCl_3$	-
Quinones	Alcoholic KOH	-
Lignins	Lignins	+

(Note: + : Presence; - : Absence)

Weight loss method

Weight loss measurements were performed in 1.0 MHCl medium with and without the presence of different volumes of inhibitor by using the formula, inhibition efficiency were calculated.

Inhibition efficiency (%) = W_0-W_i/W_0*100

Where

W_0= Weight loss in plain acid

W_i = Weight loss in inhibited acid

Potentiodynamic polarization studies:

Potentiodynamic polarization studies were performed for mild steel specimen in the presence and the absence of the inhibitors. Polarization measurements were performed to

evaluate the corrosion current, corrosion potential and the Tafel‟s slope.

The electrode used was a mild steel rod of the same composition embedded in araldite and with an exposed area of $1cm^2$. The polarization cells contain a three electrode assembly. A rectangular foil was used as the counter or auxiliary electrode. The area of the counter electrode is much larger compared to the area of the working electrode. This will exert a uniform potential field on the working electrode. The reference electrode is Hg/$HgCl_2$/1N H_2SO_4 for HCl solution.

A solution quantity of 100 ml of the test solution was taken in a polarization cell. The working electrode was polished with 0/0, 1/0, 2/0, 3/0, and 4/0 emery papers successively and degreased with acetone. The working electrode, reference and auxiliary platinum electrodes were assembled and connections were made.

Stirring was provided to the test solutions to avoid for the system the volume polarization before start of experiment. A time interval of about 15 minutes was given for the system to attain steady state and open circuit potential was recorded. Polarization measurements were made carried out from 800mV to 250mV at a constant identical to weight loss measurements.

Polarization measurements were made from mild steel specimens in 1.0 N HCl in the presence and absence of the inhibitor. Current in mA and potential in mV were plotted. From the graph, the Tafel slope (in mV/decade) and the corrosion potential (in mV/decade) were calculated.

Impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell setup was the same as that used for polarization measurements.

The real part and imaginary part of the cell impedance were measured in ohms at varies frequencies. The value of charge transfer resistance, R_t , and the double layer capacitance, C_{dl} were calculated.

CHAPTER-IV

RESULTS AND DISCUSSION

It is a well known fact that research activities leading to the development of corrosion inhibitors based on natural products have immense scope in several industries, because of their non-toxicity, biodegradable nature and are also easily available. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly and possess no threat to the environment.

The efficiency of an extract as a corrosion inhibitor can be attributed to the number of mobile electron pairs present, π-orbital character of free electrons and the electron density around the hetero atoms. In the present study, inhibition efficiency of *Chrysanthemum indicum* leaves extract in 1.0 M HCl medium has been evaluated using weight loss measurements and its potentiodynamic polarization and impedance studies. The effect of this extract on the extent of inhibition of corrosion of mild steel in 1.0 M HCl medium by this extract can be explained in terms of its adsorption on the metal surface. This extract gets adsorbed on the metal surface by means of, when mild steel is immersed in the acid solution the phyto-components diffuses from the bulk of solution towards the metal surface.

The inhibitive influence of *Chrysanthemum indicum* on the corrosion of mild steel in 1.0M HCl leaves was studied by weight loss method, polarization and impedance measurements. The inhibition efficiency values determined by these techniques showed closed agreement. The maximum inhibition efficiency was found to be 93.7%.

The corrosion decreased with increase in addition of *Chrysanthemum indicum* probably due to the progressive adsorption of the inhibitor on the metal surface.

The percentage of inhibition efficiency increases with increase in the inhibitor volume. The corrosion inhibition by *Chrysanthemum indicum* leaves extract is attributed to the adsorption of the additive onto the mild steel surface.

The values obtained from the weight loss technique for the studied inhibitor fit well into the Temkin and El-awady adsorption isotherm. The values of free adsorption process indicate that both physisorption and chemisorption studied for the mild steel surface.

The leaves of *Chrysanthemum indicum* prevent the corrosion due to the presence of any of the phytochemical components shifting the corroded metal into the noble. The polarization study also shown an agreement with inhibitor efficiency obtained from weight loss studies.

Weight loss studies

Table-1 gives the inhibition efficiency of different volume of *Chrysanthemum indicum*in 1.0 M HCl medium. The inhibition depends upon the nature and mode of adsorption of the metal surface. The adsorption is assumed to be quasi-substitution process between the water molecules on the surface and any of the natural components present in the inhibitor.

The inhibition of heterocyclic compound present in the plant extract with the metal surface may occur through any of the phyto-components present in the inhibitor and also to the interaction of π-electrons of ring with metal surface, thereby enabling the compound to getadsorbed on the metal surface.

Adsorption isotherm

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Temkin, Flory-Huggins, Frumkin, and the recently formulated thermodynamic/kinetic model of El-awady et al. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clue to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs as the interaction energy between molecules and metal surface is higher than that between the H_2O molecules and the metal surface.

Langmuir adsorption isotherm

Adsorption isotherms are very important to determine the mechanism of phyto-electrochemical reaction. The adsorption isotherm values are shown in **table-2**.

Langmuir adsorption isotherm is

$$\Theta = K_{ads}.C/1 + K_{ads}.C$$

$$\Theta (1+K_{ads}.C) = K_{ads}.C$$

$$\Theta = K_{ads}.C - K_{ads}.C\Theta$$

$$\Theta = (1-\Theta) K_{ads}.C$$

$$\Theta/1-\Theta = K_{ads}.C$$

The plot of 3+ logs (Θ/1-Θ) against 3+logC is a straight line as shown in **figure-1**. Thus the Langmuir isotherm is valid for the inhibitor.

Temkin adsorption isotherm

It is given by the expression;

$$\Theta = -2.303 \log K/2a. -2.303 \log C/2a$$

Where "K" is the adsorption equilibrium constant, "a" is the lateral interaction parameter. The plot of Θ against log C is shown in**figure-2**. The linear plot indicates that Temkin adsorption isotherm was obeyed and negative, value of "a" indicated repulsion exist in the adsorption layer. The results are shown in **table -3.**

Florry-Huggins adsorption isotherm

It is given by the expression

$$\log \Theta/C = \log K + x \log (1-\Theta)$$

Where „x" is the size parameter and it is a measure of the number of adsorbed water molecules substituted by an inhibitor molecule. The adsorption parameter is shown, in **table-4.**

El-awady isotherm

It is given by the expression:

$$\log (\Theta/1-\Theta) = \log K + y \log C$$

Here K_{ads} the equilibrium constant of adsorption process is calculated by the relationship, K_{ads} = 1/k. A plot of 2 + log(1-Θ) Vs. 2+ logC is linear as shown in **figure-4**. The calculated K_{ads} and 1/y values are given. The adsorption isotherm values are shown in **table-5.**

Frumkin Isotherm

$$K_{ads}\, C = (\ /1-\Theta) e^{-2a}$$

Take logarithm on both sides of the equation, it can be rearranged as given below.

$$\log K_{ads} + 2a = \log(\ /(1-\ )C)$$

where K_{ads} is the adsorption desorption equilibrium constant, V is the inhibition volume and „a" is the interaction parameter describing the lateral interaction among inhibitor molecular in the absorbed layer on the metal surface. Linear plots of **log(/(1-)C)** Vs. **Θ** is shown in **figure -5** obtained.The values for the Frumkin adsorption parameters are shown in **table-6.**

Free energy change

$$\Delta G^{0}_{ads} = -2.303RT\log (K_{ads} x\ 55.5)$$

From the results, shown in **table-7**, most of the values of ΔG^{0}_{ads} were found to be negative and were below the threshold value of -40kJ/mole indicating that the adsorption of *Chrysanthemum indicum* leaves extract, on mild steel susrface is spontaneous and thatmechanism of physical adsorption is applicable.

Potentiodynamic polarization studies

Table-8 and **figure**s **6, 7, 8, & 9** gives the values of potentiodynamic parameters such ascorrosion current (I_{corr}), corrosion potential (E_{corr}) and the cathodic Tafel slopes (b_c and b_a) for the different volume shown in the green inhibitor understudy. It can be seen that the phyto-components diffuse from the bulk of the solution and gets absorbed on metal surface.

AC impedance study:

Table-9 and **figures 10, 11, 12 & 13** shows the AC impedance value for different volumeof the inhibitor. The R_t value increases and C_{dl} value decreases with inhibitor volume. This implies the formation of protective film on the metal surface. It can be also seen from **table-10** that there is a close agreement between the values of inhibition efficiencies obtained from weight loss measurements, polarization and impedance studies.

TABLE-1

Inhibition effect on corrosion of mild steel in 1.0 M HCl medium by

***Chrysanthemum indicum* leaves extract using weight loss method**

.

Concentration ,(%)	Weight loss	I.E(%)	Rate of corrosion
2	0.021	67.1	$8.75X10^{-4}$
4	0.012	81.2	$5X10^{-4}$
6	0.009	85.9	$3.75X10^{-4}$
8	0.008	87.5	$3.33X10^{-4}$
10	0.004	93.7	$1.66X10^{-4}$

TABLE-2 :Langmuir adsorption isotherm for the inhibition of corrosion of mild steel in 1.0M HCl medium by *Chrysanthemum indicum* leaves extract

Concentration (%)	Ɵ	1-Ɵ	Ɵ/1-Ɵ	logƟ/1-Ɵ	3+log Ɵ/1- Ɵ	3+logC
2	0.671	0.329	2.039	0.3094	3.3094	3.301
4	0.812	0.188	4.319	0.6353	3.6353	3.6020
6	0.859	0.141	6.092	0.7847	3.7847	3.7781
8	0.875	0.125	7.000	0.8450	3.8451	3.9030
10	0.937	0.063	14.873	1.1723	4.1723	4.000

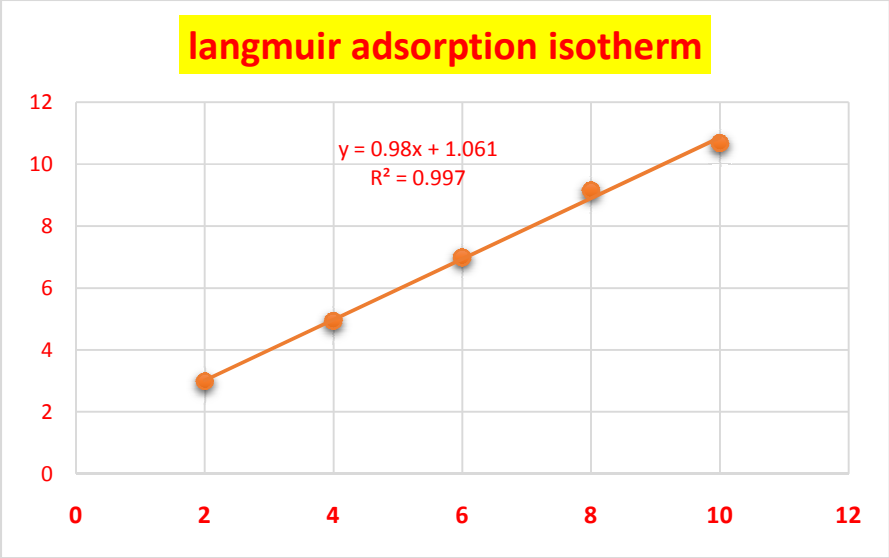

Figure1: Langmuir adsorption isotherm for the inhibition of corrosion mild steel in 1.0 M HCl medium using *Chrysanthemum indicum* leaves extract.

Calculation:

Intercept = 0.0613

K_{ads} = 0.9422

ΔG_{ads} = 9.9717

Slope = 0.98

R^2 = 0.9974

1/y = 1.020

TABLE-3

Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0M HCl medium by *Chrysanthemum indicum* leaves extract

Concentration(%)	logC	2+logC	Ɵ
2	0.3010	2.301	0.671
4	0.6020	2.6020	0.812
6	0.7781	2.778	0.859
8	0.9030	2.903	0.875
10	1	3	0.937

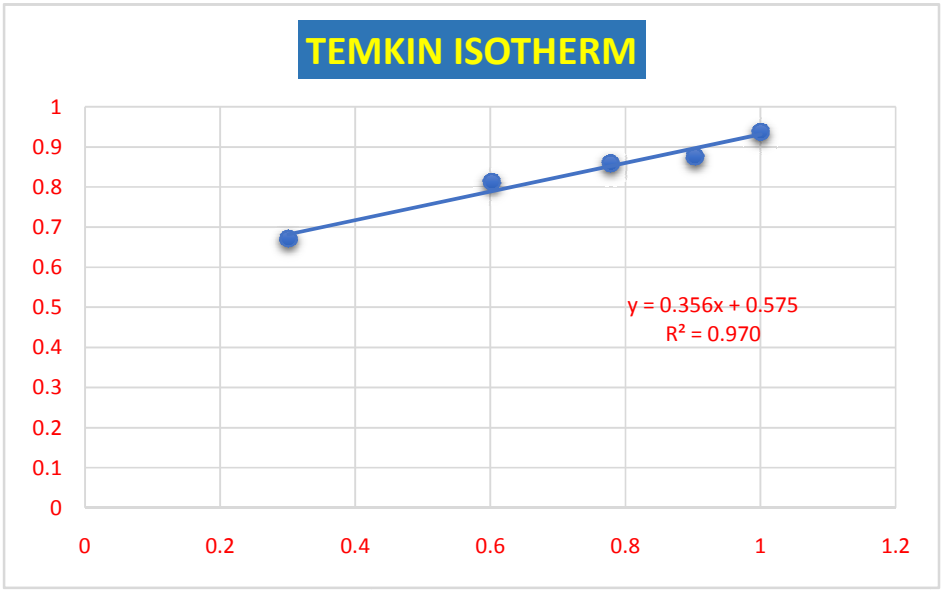

Figure 2: Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0M HCl medium using *Chrysanthemum indicum* leaves extract.

Calculation:

Intercept =0.5752

K_{ads} = 41.059

ΔG_{ads} = 19.4817

Slope = 0.3565

R^2 = 0.9704

1/y = 2.8050

a = 0.178

TABLE-4

Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium by *Chrysanthemum indicum* leaves extract

Concentration (%)	Ɵ	Ɵ/C	logƟ/C	4+logƟ/C	1-Ɵ	log(1-Ɵ)	4+log(1-Ɵ)
2	0.671	0.3355	-0.4743	3.5257	0.329	-0.4828	4.4828
4	0.812	0.203	-0.6925	3.3075	0.188	-0.7258	3.7242
6	0.859	0.1431	-0.8443	3.1557	0.141	-0.8507	3.1493
8	0.875	0.1093	-0.9613	3.0387	0.125	-.9030	3097
10	0.937	0.0937	-0.1028	2.9718	0.063	-1.2006	2.7994

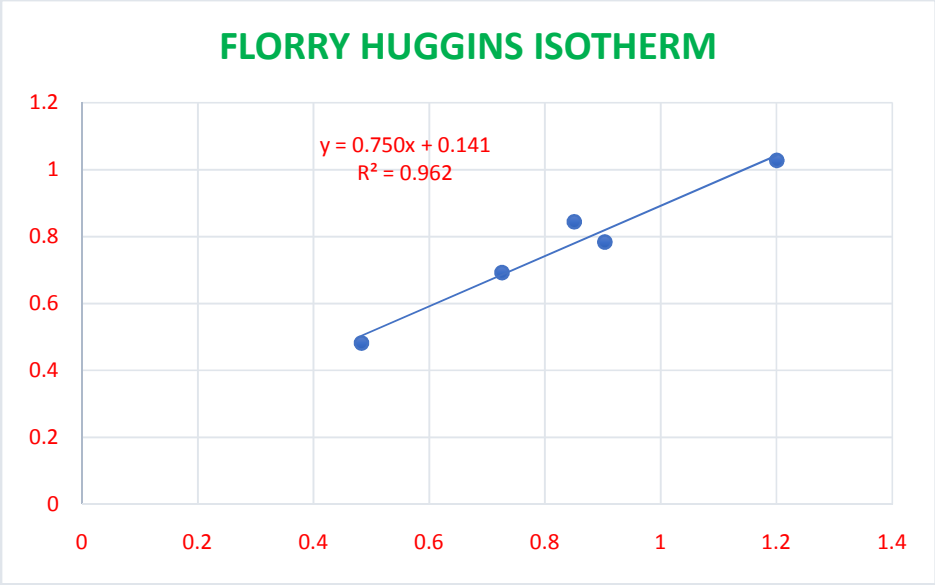

Figure 3: Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium using *Chrysanthemum indicum* leaves extract.

Calculation:

Intercept = 0.1305

K_{ads} = 1.350

ΔG_{ads} = 10.8785

Slope = 0.7617

R^2 = 0.9611

1/y = 1.312

TABLE – 5

El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium by *Chrysanthemum indicum* leaves extracts

Cocentration (%)	2+logC	Ɵ	1-Ɵ	Ɵ/1-Ɵ	2+log(Ɵ/1-Ɵ)
2	2.301	0.671	0.329	2.0395	2.3095
4	2.602	0.812	0.188	4.3191	2.6353
6	2.778	0.859	0.141	6.0921	2.7847
8	2.903	0.125	0.125	7.000	2.8450
10	3	0.063	0.063	14.8730	3.1723

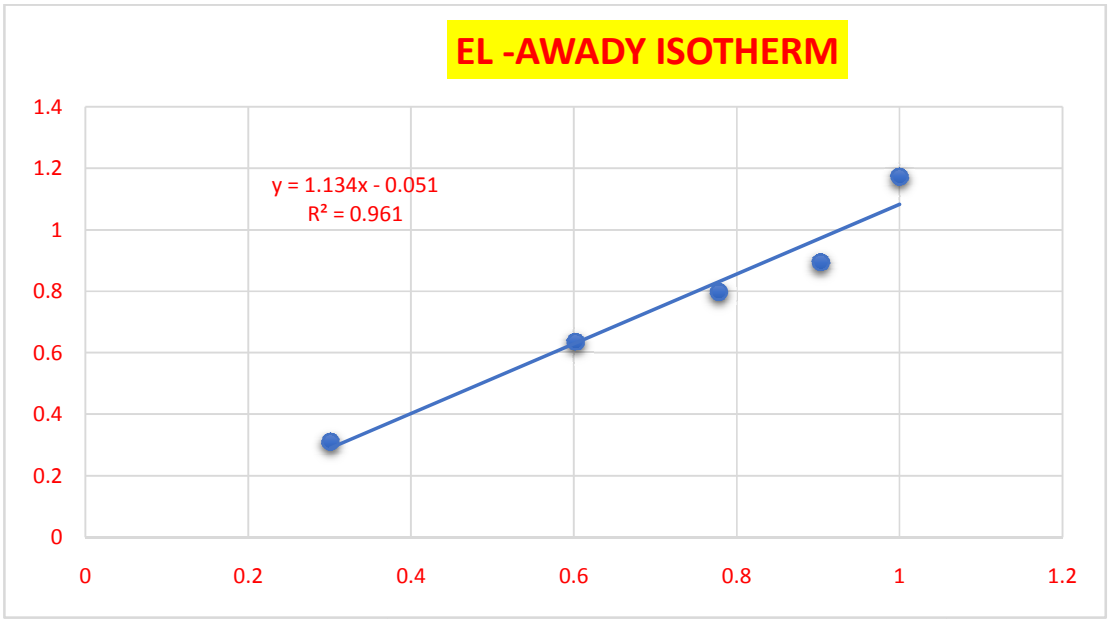

Figure 4: El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl using *Chrysanthemum indicum* leaves extract

Calculation:

Intercept = -0.0514

K_{ads} = 0.9008

ΔG_{ads} = 9.8586

Slope = 1.1343

R^2 = 0.9614

1/y = 0.8816

TABLE – 6

Frumkin adsorption isotherm for the inhibition of mild steel in 1.0 M HCl medium by *Chrysanthemum indicum* leaves extract

.

Ɵ	**(1-Ɵ)C**	**Ɵ/(1-Ɵ)C**	**logƟ/(1-Ɵ)C**
0.0869	0.9131	0.0951	-1.0218
0.1459	1.7082	0.0854	-1.0685
0.2608	2.2176	0.1176	-0.9295
0.3509	2.5964	0.1351	-0.8693
0.4378	2.8112	0.1557	-0.8077
0.5155	2.9072	0.1773	-0.7512
0.6024	2.7832	0.2164	-0.6647
0.7142	2.2864	0.3123	-0.5054
0.8291	1.5381	0.5390	-0.2684
0.9347	0.6531	1.4313	0.1557

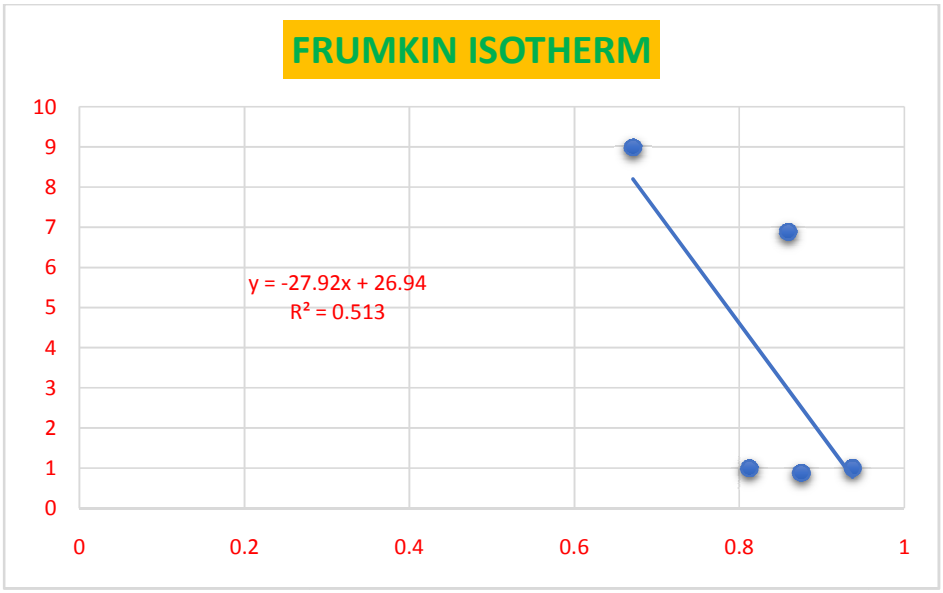

Figure 5: Frumkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl using *Chrysanthemum indicum* leaves extract.

Calculation:

Intercept = 26.9431

K_{ads} = 0.7805

ΔG_{ads} = 15.5928

Slope = -27.92

R^2 = 0.5138

1/y = 0.0358

a = -13.961

TABLE-7

Adsorption isotherm parameters for the inhibition of the corrosion of mild steel in 1.0 M HCl by *Chrysanthemum indicum* leave extract

Isotherm	$-\Delta G^{0}_{ads}$	Slope	R^2	A	1/y
Langmuir Isotherm	9.9717	0.98	0.9974	0.49	1.020
Temkin Isotherm	-19.4817	0.3565	0.9704	0.178	2.8050
Florry-Huggins Isotherm	10.8785	0.7617	0.9611	0.380	1.312
El-awady Isotherm	9.8586	1.1343	0.9614	0.567	0.8816
Frumkin Isotherm	15.5928	-27.922	0.5138	-13.961	-0.0358

The R^2 value shows that **Temkin & Langmuir** are the best fit isotherms.

TABLE-8

Corrosion parameters obtained from polarization curves for mild steel in 1.0 M HCl medium in the presence and absence of inhibitor

SYSTEM	[Inhibitor], (%)	$I_{corr.}$, mV	$-E_{corr.}$, mV	b_a, mV dec^{-1}	b_c, mV dec^{-1}	% Inhibition Efficiency
Blank	-	779.758	-49.996	90.836	180.905	-
***Chrysanthemum* leaves aquous extract**	2	202.353	-467.685	82.875	224.656	74%
	6	160.216	-477.842	94.072	254.078	79.4%
	10	123.518	-476.481	54.509	155.7	84.1%

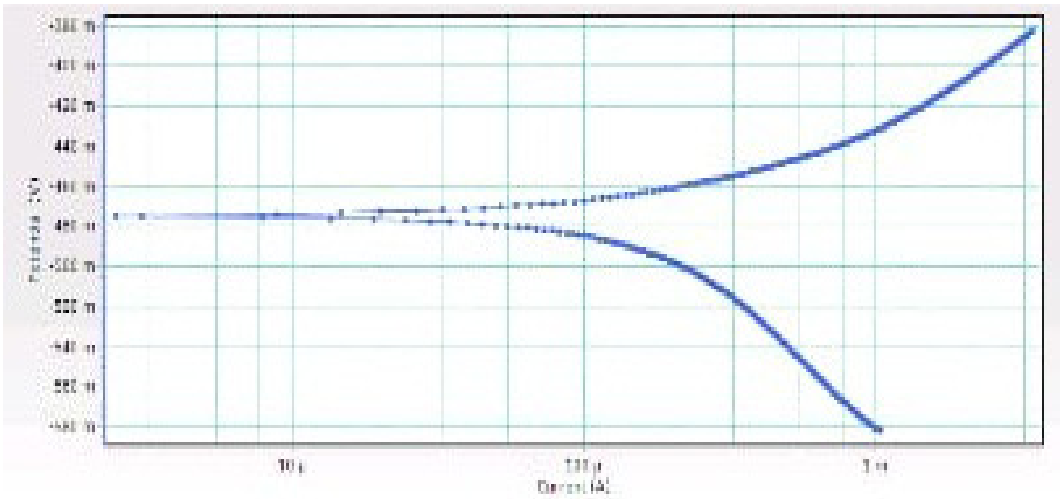

Figure 6: Potentiodynamic polarization curve for mild steel in 1.0M HCl

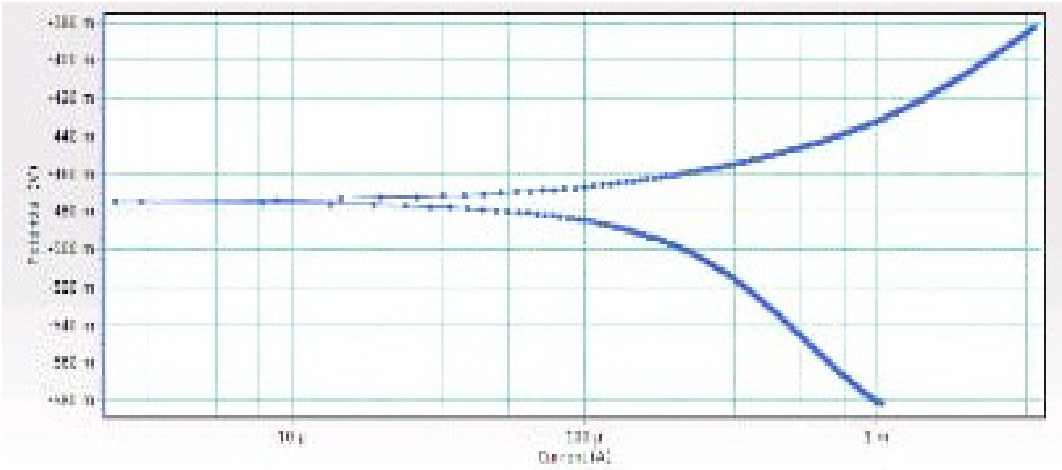

Figure 7: Potentiodynamic polarisation curve for mild steel in 1.0 M HCl solution in the presence of 2 % of *Chrysanthemum indicum* leaves extract

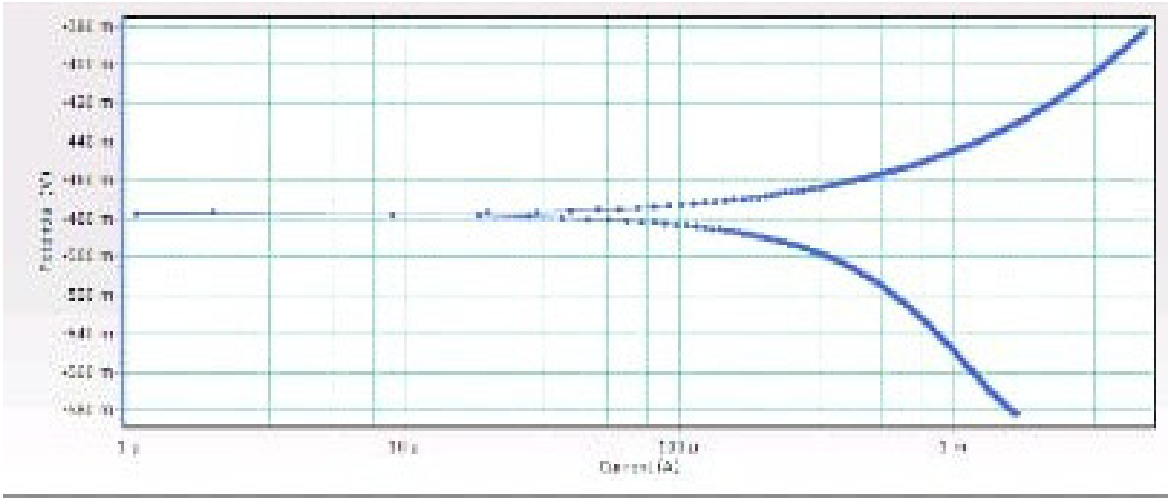

Figure 8: Potentiodynamic polarisation curve for mild steel in 1.0 M HCl solution in the presence of 6 % of *Chrysanthemum indicum* leaves extract

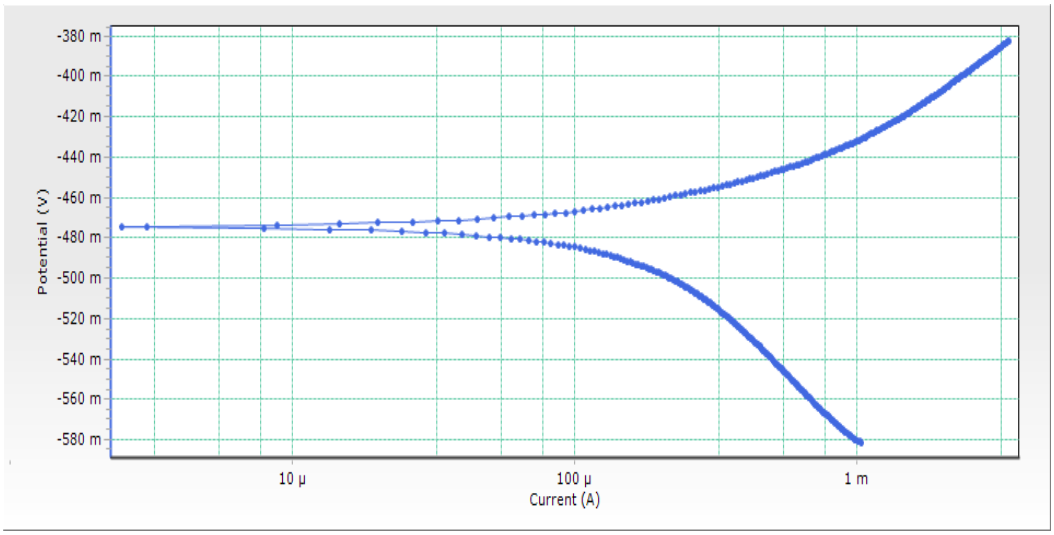

Figure 9:potentiodynamic polarization curve for mild steel in 1.0M H cl solution in the presence of 10 % of Chrysanthemum indicum extract.

TABLE – 9

Corrosion parameters obtained from impedance curve for mild steel in the presence and absence of inhibitor in 1.0 M HCl medium

[Inhibitor], (%)	R_t, Ohm.cm^2	C_{dl}, F/cm^2	Inhibition Efficiency (%)
Blank	60	2.7450×10^{-4}	-
2	163	1.0104×10^{-4}	63.1%
4	30	5.49×10^{-4}	81%
6	32	5.149×10^{-4}	87%

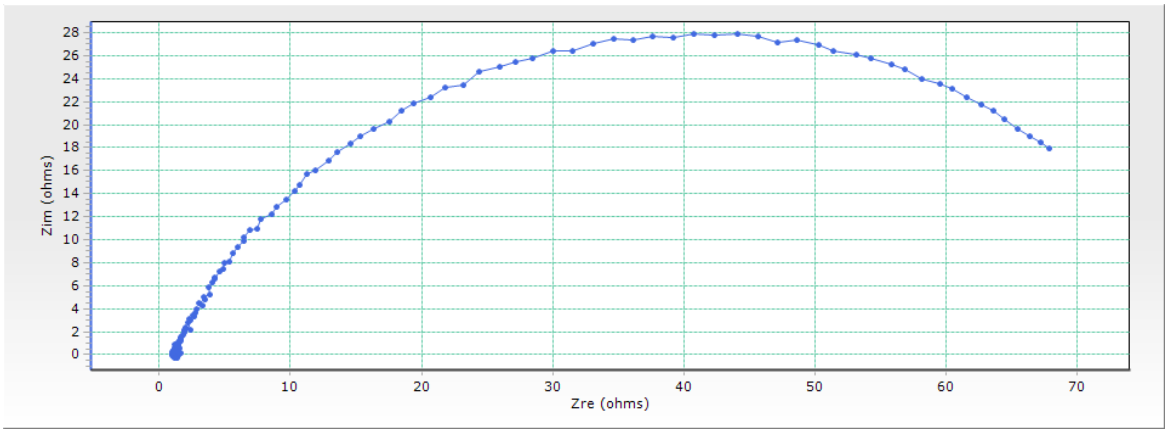

Figure 10; Impedance diagram for mild steel in 1.0M Hcl solution

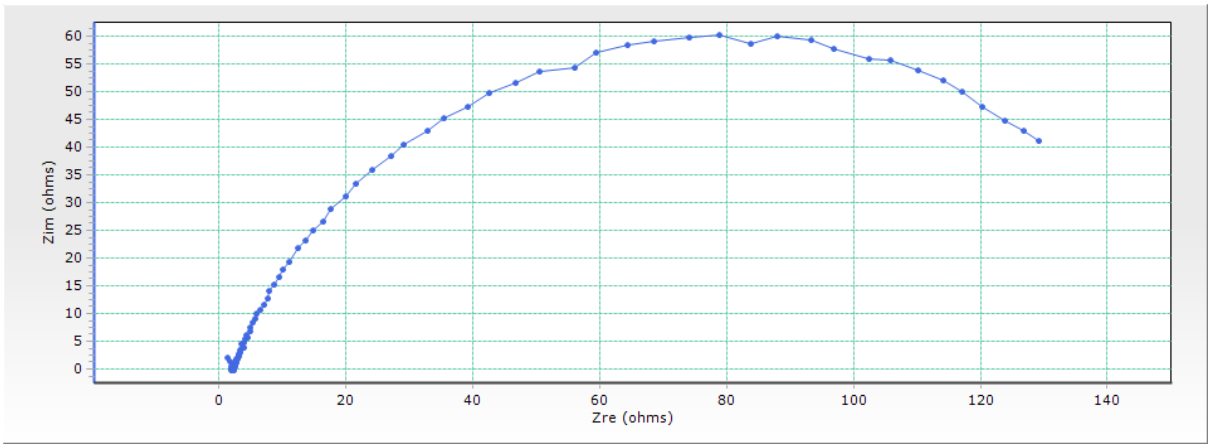

Figure 11: Impedance diagram for mild steel in 1.0 M Hcl solution in the presence of 2% of Chrysanthemum indicum extract.

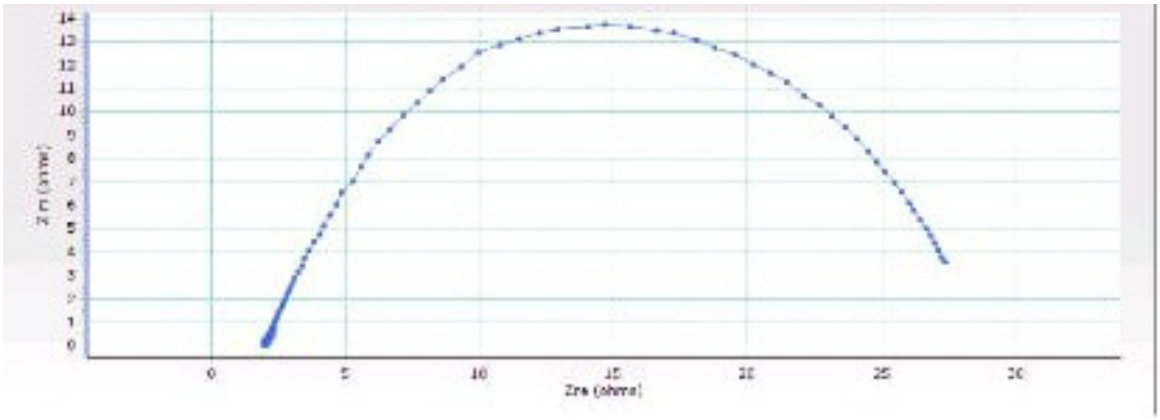

Figure 12: Impedance diagram for mild steel in 1.0 M HCl solution in the presence of 6 % of *Chrysanthemum indicum* leaves extract

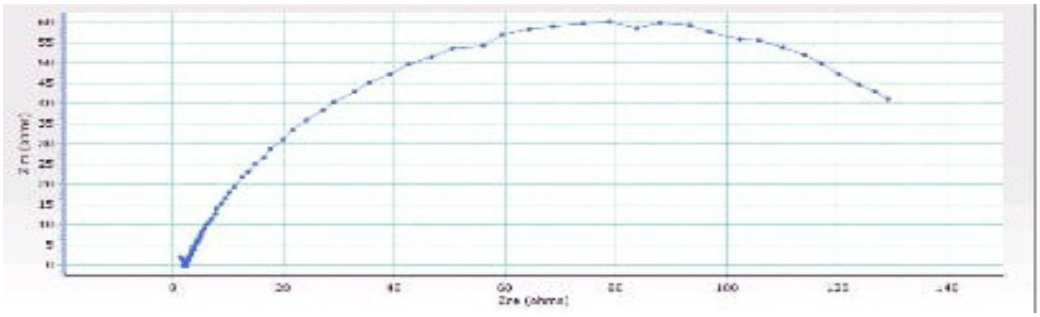

Figure 13 :impedance diagram for mild steel in 1.0 M solution in presence of 10 % of chrysanthemum indicum extract.

TABLE-10

Comparison of inhibition efficiency measured by Weight loss, Polarization method and Impedance method

[Inhibitor], (%)	**Inhibition efficiency**		
	Weight loss Studies	**Polarization studies**	**Impedance Studies**
Blank	-	-	-
2	14.59	14.06	14.80
6	51.55	49.89	50.45
10	93.47	93.85	94.28

CHAPTER-V

SUMMARY AND CONCLUSION

The inhibitive influence of leaves of *Chrysanthemum indicum* on the corrosion of mild steel in 1.0 M HCl medium was studied by weight loss method, polarization and impedance measurements. The corrosion is decreased with increase in the addition of *Chrysanthemum indicum* leaves extract probably due to the progressive adsorption of the inhibitor on themetal surface. The maximum inhibition efficiency was found to be 93.7%

- The corrosion of mild steel in 1.0 M HCl solution is inhibited by the addition of leaves extract of *Chrysanthemum indicum*.
- The percentage of inhibition efficiency increases with increase of the inhibitor concentration.
- The corrosion of mild steel inhibited by leaves extract of *Chrysanthemum indicum* is attributed to the adsorption of phytochemical components present in the inhibitor onto themild steel surface
- The values obtained from the weight loss technique for the studied inhibitor fit well into the Temkin & El-awady adsorption isotherm. The values of free energy for the adsorptionprocess indicate that the adsorption of the inhibitor on the mild steel surface occurs spontaneously.
- The leaves of *Chrysanthemum indicum* prevent the corrosion of mild steel due to the presence of phytochemical components shifting the corrosion into the noble.
- The polarization and impedance study also shows an agreement with inhibitor efficiency obtained from weight loss studies.
- The results obtained suggest that the *Chrysanthemum indicum* leaves extract is a good corrosion inhibitor for mild steel in 1.0 M HCl medium and it can be preferentially used to replace toxic and non-biodegradable inhibitor.

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Post Graduate Project 3

Corrosion Mitigation of Mild Steel in 1.0 M H_2SO_4 Medium with the Aqueous Extract of *Cajanus Cajan* Leaves

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Name of the Candidate: D. Percy

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CHAPTER-1

INTRODUCTION

CORROSION

Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Both the type of metal and the environmental conditions, particularly gasses that are in contact with the metal, determine the form and rate of deterioration.

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment.

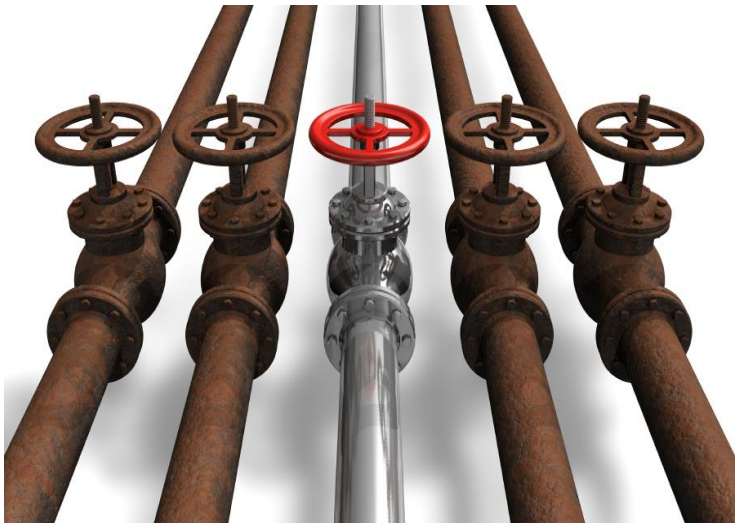


Figure-1: Corrosion

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readilyavailable in plenty. Several investigations have been reported usingsuch

naturally occurring substances as corrosion inhibitor for several metals in different media.

Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its location. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media.

DEFINITION OF CORROSION

- Corrosion is the irreversible damage or destruction of living tissue or material due to a chemical or electrochemical reaction. A prime example of corrosion is rustingof iron or steel.

- Corrosion is a natural process, which converts refined metal to a more chemically stable form, such as its oxide, hydroxide or sulfide. It is the gradual destruction ofmaterials (usually metals) by chemical or electro chemical reaction with their environment.

- Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology,corrosion processes involve reaction of metals with environmental species.

- Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with its environment which results in its consumption or dissolution intothe material of a component of the environment.

- Corrosion is the destructive attack on a metal through interaction.

THEORIES OF CORROSION

- **Homogeneous theory**

A corroding metal irrespective of the presence or absence on its surface of any micro heterogeneity can be regarded as single electrode on which reactions take place. Metal becomes unstable due to the charge transfer reaction taking place at the interface. Hence, it is necessary that the potential difference across the interface be more negative than the equilibrium potential for the metal dissolution (anodic) reaction or more positive than the equilibrium potential for the electronation (cathodic) reaction.

- **Heterogeneous theory**

According to this theory, corrosion is caused by local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity. Corroding metal consists of an electron sink area, where de-electronation reaction occurs. b. an electron source area, where electronation reaction occurs in an ionic conductor to keep the current flowing.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodicreactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I_{cor}. Since thecorrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece ofmetal is described as a "mixed

electrode" since simultaneous anodic and cathodic reactions areproceeding on its surface. The mixed electrode is a complete electrochemical cell on one metalsurface.

The most common and important electrochemical reactions in the corrosion of iron arethus

Anodic reaction (corrosion)

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Cathodic reactions (simplified)

$$2H^+ + 2\,e \longrightarrow H_2$$

$$H_2O + 1/2\,O_2 + 2e \longrightarrow 2\,OH^-$$

This reaction is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

MECHANISM OF CORROSION

Although several mechanisms have been proposed for the corrosion process, corrosion is mainly electrochemical in nature and hence in this chapter, the electrochemical mechanistic aspects have been discussed. According to this approach, the corrosion reaction can be considered as taking place by two simultaneous reactions; the oxidation of a metal at an anode (a corroded end releasing electrons) and the reduction of a substance at a cathode (a protected end receiving electrons). In order for the reaction to occur, the following conditions must exist:

1. A chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition).

2. An electrolyte must be present to provide solution conductivity and act as a source of material to be reduced at the cathode.

3. An electrical path through the metal or between metals must be available to permit electron flow.

The below diagram illustrates the typical electrochemical corrosion of iron in contact with water.

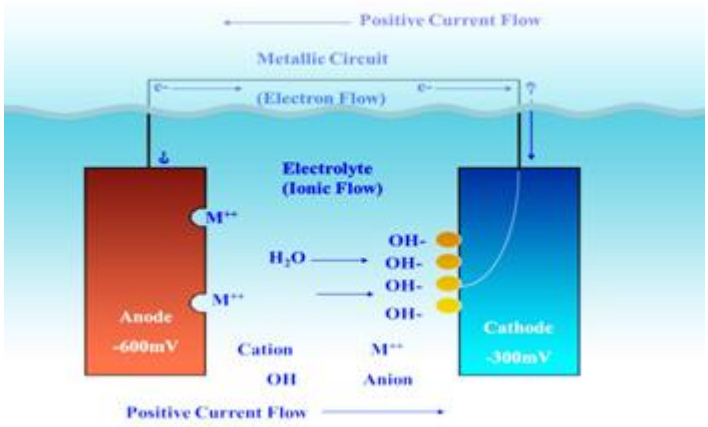


Figure -2: Corrosion cell

In a nearly neutral or slightly acid environment, the water is dissociated into hydrogen ions (H^+) and hydroxyl ions (OH^-) as

$$H_2O \leftrightarrow H^+ + OH^-$$

When metal is placed in contact with a liquid, surface ionization occurs, because of the electric charge difference at the solid-liquid interface. For example, iron dissolves in water in the form of positively charged ferrous ions (Fe^{++}).

$$Fe \leftrightarrow Fe^{++} + 2e^-$$

Electrochemically, a chemical substance is "oxidized", when it loses electrons to a second substance. The electrode at which the oxidation takes place is called as the "anode". A chemical substance is "reduced", when it acquires electrons. The electrode at which reduction takes place is called the "cathode". Hence, oxidation reaction results in the formation of positive charge ferrous ions at the anode. Ferrous ions moving away from the metal surface are further

oxidized to ferric ions (Fe^{++}) as follows

$$Fe^{++} \leftrightarrow Fe^{+++} + e^-$$

The positively charged ferric ions are attracted to the negatively charged hydroxyl ions and form the corrosion product $Fe(OH)_3$

$$Fe^{+++} + 3(OH)^{-} \leftrightarrow Fe(OH)_3$$

The rust consists of iron hydroxide or iron oxide hydrates in various states, depending on the degree of oxidation and dehydration.

The reduction reaction at the cathode must take place concurrently in order to continue the corrosion process. Several reactions are possible and the one that occurs is determined by the environment. Without the presence of air or oxygen, hydrogen ions can be reduced by the excess of electrons at the cathode surface and evolve as molecular hydrogen by

$$2H^{+} + 2e^{-} \leftrightarrow H_2$$

If hydrogen is not removed from the surface, the cathodic reaction decreases and the corrosion rate is reduced. With the presence of air, the more likely reaction is the reduction of oxygen. Two possible reactions occur:

$$O_2 + 4H^{+} + 4e^{-} \leftrightarrow 2H_2O$$

$$O_2 + 2H_2O + 4e^{-} \leftrightarrow 4(OH)^{-}$$

Hydrogen evolution or oxygen reduction with the formation of water is likely to occur in acid media. On the other hand, oxygen reduction with the formation of hydroxyl ions is more dominant in a neutral or alkaline environment. In either case, there is an increase in the alkalinity of the solution at the cathode.

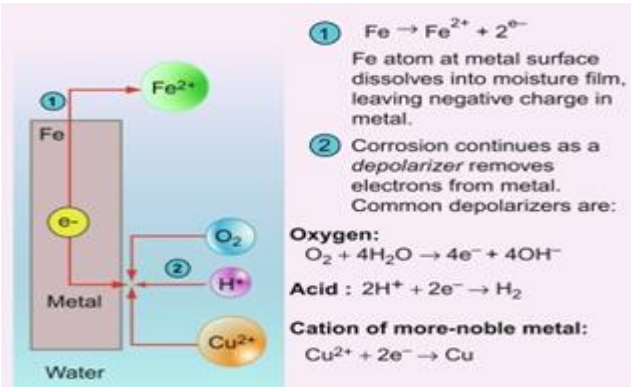


Figure-3: Two-step process corrosion

In summary, corrosion occurs when metal atoms detach themselves from the metal surface at the anode and enter the solution as ions, leaving behind electrons in the metal. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen ions that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In solutions, where hydrogen tends to evolve too slowly, oxygen is reduced and combines with hydrogen ions or water to form hydroxyl ions.

TYPES OF CORROSION

They are many different types of corrosion, each of which can be classified by the cause of the metals chemical deterioration.

The metal corrodes at the same rate over the entire surface for the former and only small areas are affected in localized corrosion. Classification by appearance is manifested by the morphology of the corrosion attack and this can be visualized either by naked eye or magnification. The schematic in the given below diagram illustrates some of the most common forms of corrosion.Schematics of the common forms of corrosion.

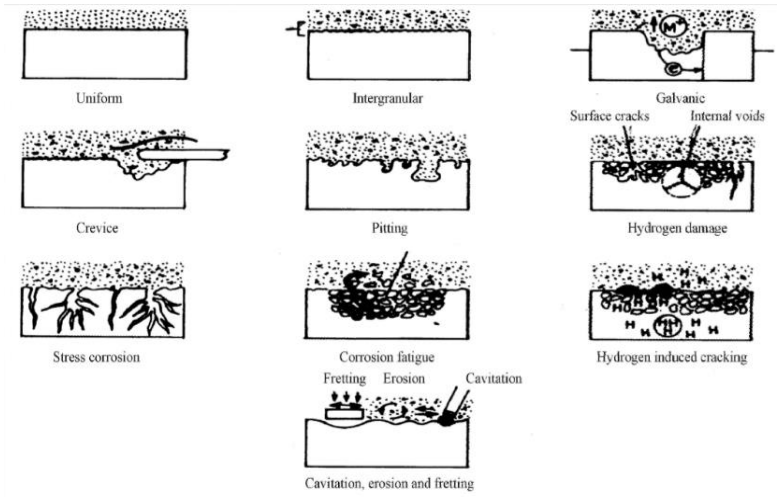


Figure-4: Types of corrosion

General attack corrosion

It is also known as uniform attack corrosion. General attack corrosion is the most common type of corrosion and is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal.

Figure-5: General attack corrosion

Ultimately, the metal deteriorates to the point of failure. General attack corrosion accounts for the greatest amount of metal destruction by corrosion but is considered as a safe form of corrosion, due to the fact that it is predictable, manageable and often preventable.

Localized corrosion

Unlike general attack corrosion, localized corrosion specifically targets one area of the metal structure. Localized corrosion is classified as one of three types:

Pitting corrosion

Pitting results when a small hole, or cavity, forms in the metal, usually as a result of de-passivation of a small area. This area becomes anodic, while part of the remaining metal becomes cathodic, producing a localized galvanic reaction.

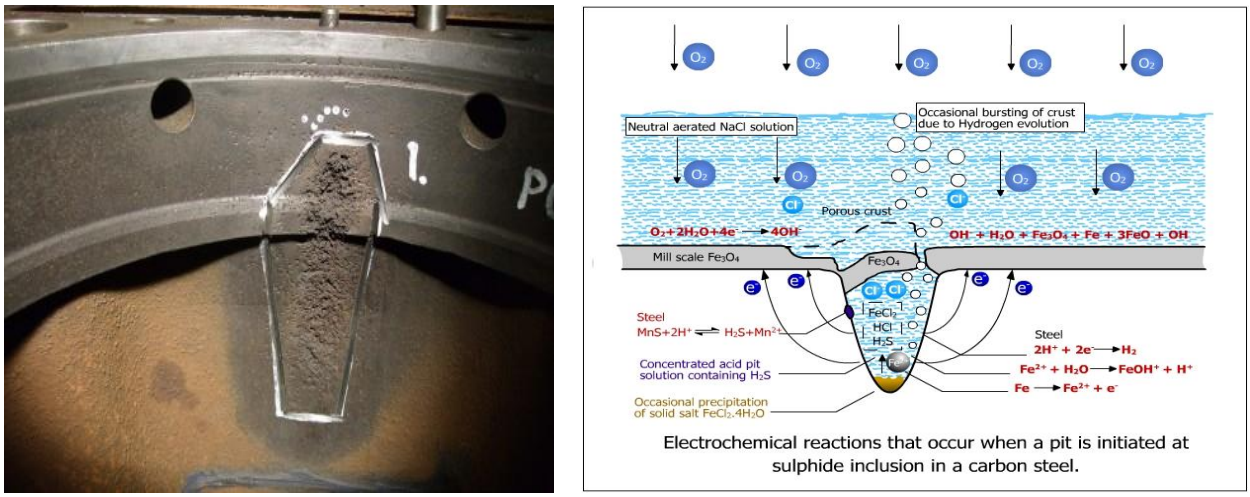


Figure-6: Pitting corrosion

The deterioration of this small area penetrates Crevice corrosion: Similar to pitting, crevice corrosion occurs at a specific location. This type of corrosion is often associated with a stagnant micro-environment, like those found under gaskets and washers and clamps. Acidic conditions or a depletion of oxygen in a crevice can lead to crevice corrosion.

Filiform corrosion

Occurring under painted or plated surfaces when water breaches thecoating, filiform corrosion begins at small defects in the coating and spreads to cause structure.This form of corrosion is often difficult to detect due to the fact that it is usually relatively small and may be covered and hidden by corrosion-produced compounds.

Figure-7: Filiform corrosion

Galvanic corrosion

Galvanic corrosion or dissimilar metal corrosion occurs when two different metals are located together in a corrosive electrolyte. A galvanic couple forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly.

Figure-8: Galvanic corrosion

Three conditions must exist for galvanic corrosion to occur:

- ♣ Electrochemically dissimilar metals must be present
- ♣ The metals must be in electrical contact
- ♣ The metals must be exposed to an electrolyte

Environmental cracking

Environmental cracking is a corrosion process that can result from a combination of environmental conditions affecting the metal. Chemical, temperature and stress-related conditions can result in the following types of environmental corrosion.

Figure-9: Environmental cracking

- ♣ Corrosion cracking
- ♣ Corrosion fatigue
- ♣ Hydrogen-induced racking
- ♣ Liquid metal embrittlement

Flow-assisted corrosion

- ♣ Flow-assisted corrosion, or flow-accelerated corrosion, results when a protective layer of oxide on a metal surface is dissolved or removed by wind or water, exposing the underlying metal to further corroding and deteriorate

Figure-10: Flow-assisted corrosion

- ♣ Erosion-assisted corrosion
- ♣ Impingement
- ♣ Cavitations

Intergranular corrosion

Intergranular corrosion is a chemical or electrochemical attack on the grain boundaries of a metal. It often occurs due to impurities in the metal, which tend to be present in higher contents near grain boundaries. These boundaries can be more vulnerable to corrosion than the bulk of the metal.

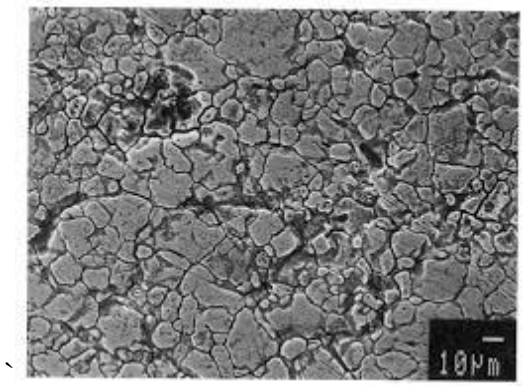


Figure-11: Intergranular corrosion

De-alloying

De-alloying, or selective leaching, is the selective corrosion of a specific element in an alloy. The most common type of de-alloying is de-zincification of unstabilized brass. The result of corrosion in such cases is a deteriorated and porous copper.

It is the removal of one solid element from alloy by corrosion processes. De alloying corrosion is also called de-zincification.

Figure-12: De-alloying

The most common example is de-zincification which is selective removal of zinc in brass alloy. Similar processes occur in other alloy systems in which aluminum, Iron, Cobalt, Chromium and other elements are removed**.**

Fretting corrosion

Fretting corrosion occurs as a result of repeated wearing, weight and/or vibration on an uneven, rough surface. Corrosion, resulting in pits and grooves, occurs on the surface.Fretting corrosion is often found in rotation and impact machinery, bolted assemblies and bearings, as well as to surfaces exposed to vibration during transportation.

Figure-13: Fretting corrosion

High-temperature corrosion

High-temperature corrosion is a mechanism of corrosion that takes place in gas turbines diesel engines, furnaces or other machinery coming in contact with hot gas containing certain contaminants. Fuel sometimes contains vanadium compounds or sulfates which can form compounds during combustion having a low melting point.

Figure-14: High-temperature corrosion

These liquid melted salts are strongly corrosive for stainless steel and other alloys normally inert against the corrosion and high temperatures. Other high-temperature corrosions include high-temperature oxidation, sulfidation and carbonization**.**

Crevice corrosion

Crevice corrosion is also a localized form of corrosion and usually results from a stagnant microenvironment in which there is a difference in the concentration of ions between two areas of a metal.

Figure-15: Crevice corrosion

Crevice corrosion occurs in shielded areas such as those under washers, bolt heads, gaskets, etc. where oxygen is restricted. These smaller areas allow for a corrosive agent to enter but do not allow enough circulation within, depleting the oxygen content, which prevents re-passivation. As a stagnant solution builds, pH shifts away from neutral. This growing imbalance between the crevices

(Micro environment) and the external surface (bulk environment) contributes to higher rates of corrosion. Crevice corrosion can often occur at lower temperatures than pitting. Proper joint design helps to minimize crevice corrosion.

Stress corrosion cracking

Stress corrosion cracking (SCC) is a result of the combination of tensile stress and a corrosive environment, often at elevated temperatures. Stress corrosion may result from external stress such as actual tensile loads on the metal or expansion/contraction due to rapid temperature changes.

It may also result from residual stress imparted during the manufacturing process such as from cold forming, welding, machining, grinding, etc. In stress corrosion, the majority of the surface usually remains intact; however, fine cracks appear in the microstructure, making the corrosion hard to detect.

Figure-16: Stress corrosion cracking

` The cracks typically have a brittle appearance and form and spread in a direction perpendicular to the location of the stress. Selecting proper materials for a given environment (including temperature and management of external loads) can mitigate the potential for catastrophic failure due to SCC.

Caustic agent corrosion

Caustic agent corrosion occurs when impure gas, liquids, or solids wear a material down. Although most impure gases do not damage metal in dry form, when exposed to moisture they dissolve to form harmful corrosive droplets. Hydrogen sulfide is an example of one such caustic agent.

Figure-17: Caustic agent corrosion

Microbial corrosion

Microbial corrosion, commonly referred to as microbiologically influenced corrosion (MIC) is caused by microorganisms. It applies to both metallic and non-metallic materials with or without oxygen. When oxygen is absent, sulfate-reducing bacteria are active and produce hydrogen sulfide causing sulfide stress cracking. When oxygen is present, some bacteria may directly oxidize iron to iron oxides and hydroxides. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

Figure-18: Microbial corrosion

Filiform corrosion

Filiform corrosion: It is basically a special type of crevice corrosion, sometimes termed as “under film” corrosion. This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating.

Figure-19: Filiform corrosion

Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided unless absence of an adverse effect has been proven by field experience.

Cavitation damage

Cavitation damage is a special form of erosion corrosion caused by the formation of vapors bubbles and their collapse in the liquid near a metal surface. This form of damage occurs in hydraulic turbines, pump impellers, and other surfaces that are in contact with high-velocity liquid flow along with high pressures.

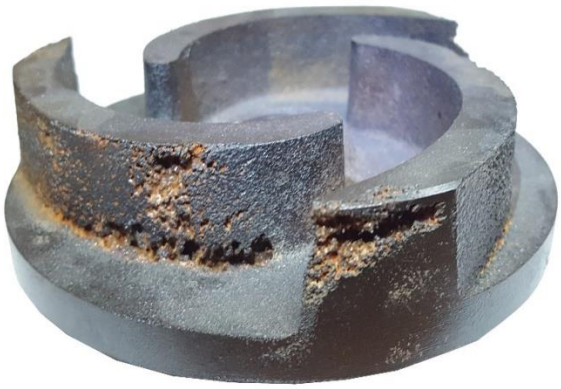


Figure- 20: Cavitation damage

Erosion corrosion

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities. Erosion corrosion can be controlled by the use of harder alloys (including flame-sprayed or welded hard facings) or by using a more corrosion resistant alloy.

:

Figure-21: Erosion corrosion

Concentration cell corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. Concentration cell corrosion is associated with gaskets, joints, scale, debris, loose protective films, etc.

Corrosion attack is accelerated, where the oxygen concentration is least. Metal at the area of low oxygen availability becomes anodic to other areas. As the cathodic area is large compared to the anodic area, the intensity of attack is usually more

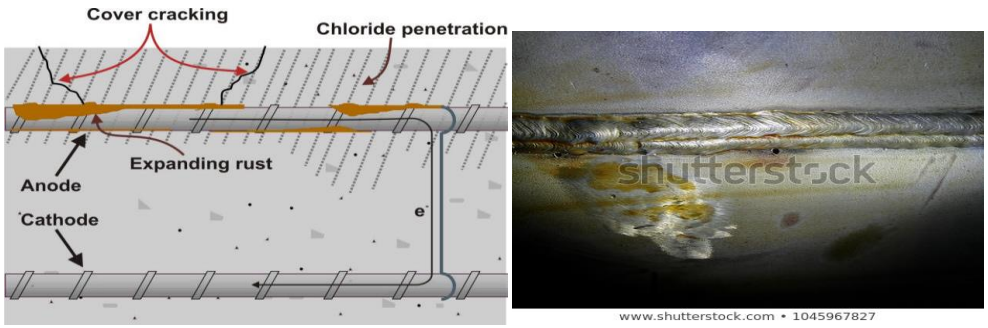


Figure-22: Concentration cell corrosion

Severe on surrounding areas of the same surface. This condition can be eliminated by sealing the faying surfaces in a manner to exclude moisture. Proper protective coating application with inorganic zinc primers is also effective in reducing faying surface corrosion.

Corrosion fatigue

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment.

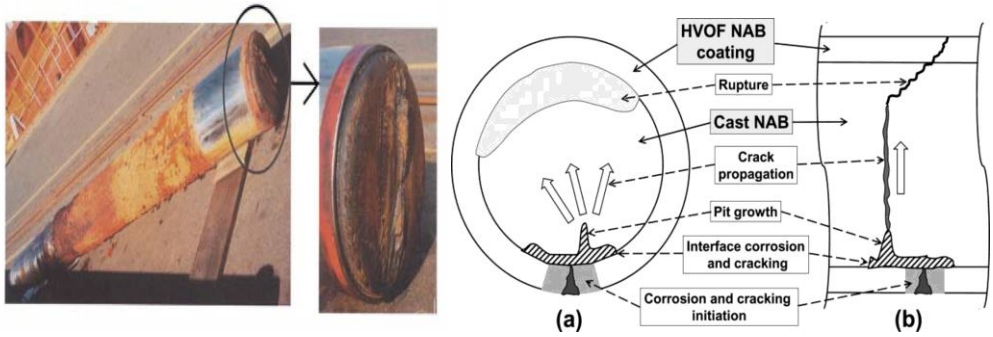


Figure-23: Corrosion fatigue

Control of corrosion fatigue can be accomplished by either lowering the cyclic stresses or by corrosion control by using protection methods.

Direct chemical corrosion

This type of corrosion occurs mainly through the direct chemical action of environment/atmospheric gases such as oxygen, halogens, hydrogen sulfide, nitrogen or anhydrous liquid sulfur dioxide with metal surface in immediate proximity. The extent of corrosion depends upon the following factors

- Chemical affinity between the corrosive environment and solid metals
- Ability of reaction product on metal surface to form a protective film.

Figure-24: Direct chemical corrosion

FACTORS AFFECTING RATE OF CORROSION

- **Nature of the metal**

Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum and silver. Whereas metal with lower electrode potentials, readily undergo corrosion. e.g., metals like zinc, magnesium, aluminium. When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion. For e.g., the potential difference between the iron and copper is 0.78V which is more than that between iron and tin is 0.30V. Therefore, iron corrodes faster when in contact with copper than that with tin. On this account, the use of dissimilar metals should be avoided wherever possible. For example, bolt and nut or screw and washer should made by the same metal (or alloy) to avoid galvanic corrosion.

- **Ratio of cathodic to anodic region**

The rate of corrosion is influenced by relative size of cathodic to anodic area. If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio decreases corrosion rate further increases. This is because at anode electrons are liberated. These are consumed at cathodic region. If cathodic region is larger the liberated electrons are rapidly consumed at cathode. This further enhances, the anodic reactions leading to increase in overall rate of corrosion. When two dissimilar metals are in contact, Corrosion is more rapid and severe, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank), If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode. An intense localized corrosion occurs at the exposed small anodic surface. On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas.

- **Nature of the corrosion product**

The corrosion product formed like metal oxide may act as protective film, if it is stable, insoluble, and non-porous. If it acts as protective film it prevents further

corrosion by acting as barrier between metal surface and corrosion medium. On the other hand if corrosion product is unstable, porous, and soluble, it further enhances corrosion in oxidizing environments, metals like aluminium, chromium, titanium, etc., are highly passive as their oxides as corrosion products form protective films on the metal surface, preventing further corrosion. Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments

- **pH-of the medium**

In general rate of corrosion is higher in acidic pH than in neutral and alkaline pH in case of iron, at very high pH protective coating of iron oxide is formed which prevents corrosion. Whereas at low pH, severe corrosion takes place. But for metals like aluminium, corrosion rate is high even at high pH.

- **Temperature**

The rate of corrosion increases with increasing temperature. This is due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

- **Effect of oxygen**

Oxygen plays an important corroding medium. If the metal is exposed to different concentration of oxygen, differential aeration corrosion takes place. The region which is less 0exposed to oxygen acts as anode hence undergoes corrosion and region exposed to high oxygenconcentration acts cathode hence doesn't undergo corrosion.

- **Hydrogen over voltage**

The metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. Since at lower hydrogen over voltage, the liberation of hydrogen gas is easy. Therefore cathodic

reaction is very fast, which in turn makes anodic reaction very fast. Thus increasing the rate of corrosion. Higher the over voltage lesser is the corrosion.

PREVENTION OF CORROSION

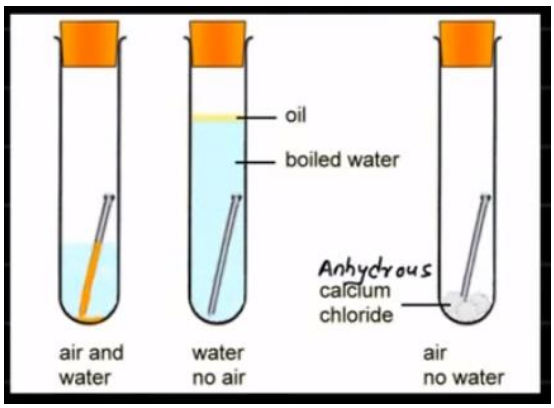


Figure-25: Prevention of corrosion

Rust and other corrosion forms can lead to safety issues and ruin the integrity of your equipment and supplies. Even routine maintenance to remove and repair corrosion can drive up costs. Fortunately, there are a variety of measures you can take to minimize corrosion. Herewe will highlight four of these methods based on cost and effectiveness.

- **Barrier coatings**

One of the easiest and cheapest ways to prevent corrosion is to use barrier coatings likepaint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film. Plastic and waxes are often sprayed onto metal surfaces. Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds. Today's paint systemsare actually a combination of different paint layers that serve different functions. The primer coat acts as an inhibitor, the intermediate coat adds to the paint's overall thickness, and the finish coat provides resistance to the environmental factors.The biggest drawback with coatings is that they often need to be stripped and reapplied.Coatings that aren't applied properly can quickly fail andlead to increased levels of corrosion.Coatings may also contain volatile organic compounds, which can make them vulnerable to corrosion.

- **Hot-dip galvanization**

This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection.

The process has been around for more than 250 years and has been used for corrosion protection of things like artistic sculptures and playground equipment. Compared to other corrosion prevention methods, galvanization is known for lower initial costs, sustainability, and versatility. Unfortunately, galvanization can't be done on-site, meaning companies have to pull equipment out of work to be treated. Some equipment may simply be too large for the process, forcing companies to abandon the idea altogether. In addition, if the process isn't done properly, the zinc can chip or peel. And high exposure to environmental elements can speed up the process of zinc wear, leading to increased maintenance check-ups. Lastly, the zinc fumes that release from the galvanizing process are toxic.

- **Alloyed steel (Stainless)**

Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product. Corrosion-resistant nickel, for example, combined with oxidation-resistant chromium results in an alloy that can be used in oxidized and reduced chemical environments. Different alloys provide resistance to different conditions, giving companies greater flexibility.

Despite its effectiveness, alloyed steel is very expensive. Companies with limited financial resources will likely have to turn to other methods. Monitoring surface conditions arecritical, as cracks or scratches can result in an increase of corrosion. Companies also need tomake sure the agents used in maintenance don't include corrosion properties.

- **Cathodic protection**

Cathodic protection protects against galvanic corrosion, which occurs when two different metals are put together and exposed to a corrosive electrolyte. To prevent this, the active sites on the metal surface need to be converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

While cathodic protection is highly effective, anodes need to be checked often which can drive up costs of maintenance. They also increase the weight on the attached structure and aren't always effective in high-resistivity environments. Finally,anodes lead to increased water flow on ships and other underwater equipment.

- **Coatings**

Coatings provide physical barriers that do not allow corrosive materials to come in contact with the structure that is being protected. Mainly, coatings are used on the exterior of pipelines to protect from external factors and are not used to directly protect the pipeline from CO_2 corrosion. The most common type of coatings are painting and platting which both provide effective corrosion protection and aesthetic appearance. Painting: Painting is an effective way to protect pipelines from external environmental factors. Although when looking at CO_2 corrosion on the interior of the pipeline, it is not ideal because painting the inside of a pipeline is impractical. The paint will breakdown over time, either through chemical reactions with the flowing fluid or the erosion due to turbulent or transient flow. Once the coating has broken down it leaves unprotected sections of the pipe when fluid induced localized corrosion occurs.

- **Plating**

Plating involves using electric currents to coat a metal with a thin layer of another metal that acts as a protective barrier. Plating an entire pipeline is very uncommon as it is expensive; however, it can be done when dealing with high pressures and high amounts of H_2S and CO_2. One drawback of plating is if the plating fails in a small section (either an imperfection or a scratch) then highly localized corrosion occurs. Another factor to consider is if the plating is more noble than the

pipeline (for example, chromium on steel), the steel will act as a sacrificial anode for the chromium. This causes the exposed area to corrode much more rapidly than an un-plated surface would.

CORROSION INHIBITORS

An inhibitor is a chemical substance or combination of substances which when added in very low concentrations in a corrosive environment effectively prevents or reduces corrosion without significant reaction with the components of the environment. Concentrations of corrosion inhibitors can vary from 1 to 15,000 ppm (0.0001 to 1.5 wt %). Corrosion inhibitors can be solids, liquids and gases, and can be used in solid, liquid and gaseous media. Solid media can be concrete, coal slurries or organic coatings (paints). Liquids may be water, aqueous solutions or organic solvents. A gaseous medium is an atmosphere or water vapor. Corrosion inhibitors are selected on the basis of solubility or dispersibility in fluids which are to be inhibited. For instance, in a hydrocarbon system, a corrosion inhibitor soluble in hydrocarbon is used. Two phase system composed of both hydrocarbons and water is utilized as oil soluble water- dispersible inhibitor.

Corrosion inhibitors have been found to be effective and flexible means of corrosion mitigation. The use of chemical inhibitors to decrease the rate of corrosion processes is quite variable. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment and product additive industries. In the oil extraction, processing and chemical industries, corrosion inhibitors have always been considered to be the first line of defense. A great number of scientific studies have been devoted to the subject of corrosion inhibitors.

Inhibitors find major use in closed environmental systems that have good circulation so that an adequate and controlled concentration of inhibitor is ensured. Such conditions can be met, for instance in cooling water recirculation systems, oil production, oil refining, and acid pickling of steel components. One of the more recognizable applications for inhibitors is in antifreeze for automobile radiators. The application of inhibitors must be viewed with caution by the user because inhibitors may afford excellent protection for one metal in a specific system but can aggravate corrosion for other metals in the same system. Inhibitors can be organic or inorganic

compounds and they are usually dissolved in aqueous environments. Some of the most effective inorganic inhibitors are chromates, nitrites, silicates, carbonates, phosphates and arsenates. The organic inhibitors include amines, heterocyclic nitrogen compounds and sulfur compounds such as thioethers, thioalcohols, thioamides, thiourea and hydrazine. Chromates and zinc salts are used increasingly less due to their toxicity and are nowadays largely replaced by organic inhibitors. Thus practical criteria for the selection of corrosion inhibitors from the great variety of inorganic and organic substances with inhibiting properties are not only their inhibition efficiency but also

Safety of use, economic constraints and compatibility with other chemicals in the system, and environmental concerns.

In order to avoid or reduce the corrosion of metallic materials, inhibitors used in cooling system must satisfy the following criteria.

- ♣ It must give good corrosion protection at a very low concentration of inhibitor.
- ♣ It must protect all exposed materials from the attack of corrosion.
- ♣ It must remain efficient in extreme operating conditions (higher temperature and velocity).
- ♣ In case of an under or over dosage of inhibitor, corrosion rate should not increase drastically.
- ♣ The inhibitor or reaction products of the inhibitor should not form any deposits on the metal surface particularly at locations where heat transfer takes place.
- ♣ It should suppress both uniform and localized corrosion.
- ♣ It should have long range effectiveness.
- ♣ It should not cause toxicity and pollution problems

CLASSIFICATION OF CORROSION INHIBITORS

A common classification of inhibitors is based on their effects on the electrochemical reactions involved in the corrosion process.

➢ Passivating inhibitors

Passivating inhibitors cause a large anodic shift of the corrosion potential forcing the metallic surface into the passivation range. There are two types of passivating inhibitors.

- ♣ The oxidizing anions such as chromates, nitrites and nitrates that can passivate steel in the absence of oxygen.
- ♣ The non-oxidizing ions such as phosphates, tungstates and molybdates that require the presence of oxygen to passivate steel.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential to monitor the inhibitor concentration.

- **Volatile inhibitors**

Volatile corrosion inhibitors (VCIs) also called vapor phase inhibitors (VPIs) are compounds transferred in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morph line or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing the acidic carbon dioxide or by shifting the surface pH towards less acidic. If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors.

If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors.

Liquid phase inhibitors

LPIs are in wide scale use to combat CO_2 corrosion in pipelines. The inhibitor is that is injected into the pipeline is transported in low concentrations and adsorbs onto the surface of the steel. Because the inhibitor is in the liquid phase only the interior of the pipeline needs to be in contact with the liquid either continuously or

semi-continuously. One of the main benefits in using inhibitors to protect from CO_2 corrosion is that it can continuously be added to the flow to provide continuous protection.

- **Cathodic inhibitors**

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. For example, calcium, magnesium and zinc ions will precipitate as hydroxides on cathodic sites as the local environment becomes more alkaline due to the reduction reaction at these sites. cathodic inhibitors are effective when they slow down the cathodic reaction rate. Arsenic, bismuth and antimony which are referred to as cathodic poisons reduce the hydrogen reduction reaction rate and thus lower the overall corrosion rate. Other cathodic inhibitors remove reducible species from the environment. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through

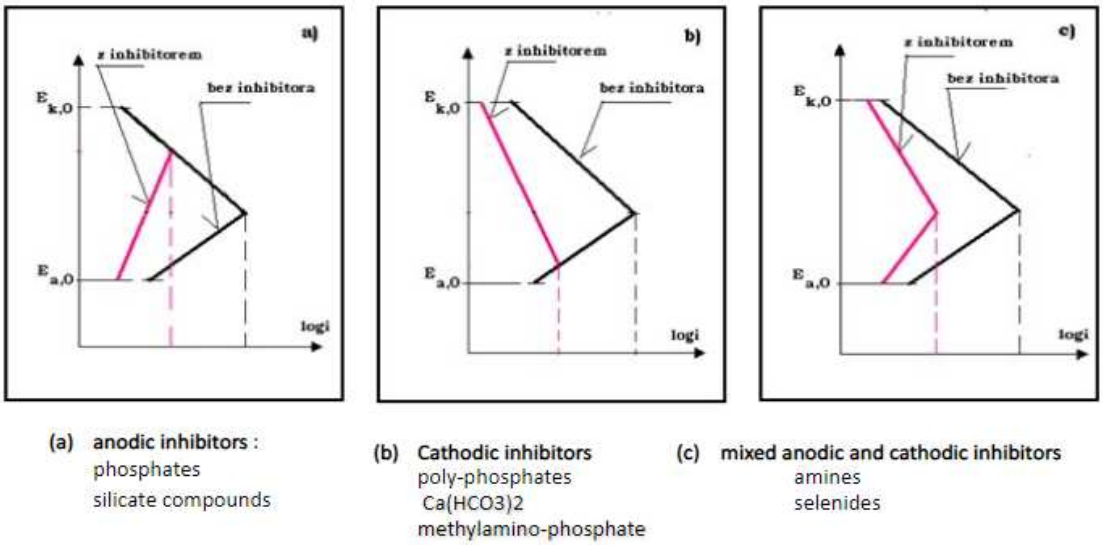
- The use of oxygen scavengers such as sodium sulfite and hydrazine which react with the oxygen and remove it from the solution
- Vacuum de-aeration orBoiling tolower the dissolved oxygen concentrations.

- **Anodic inhibitors**

Anodic inhibitors such as chromates, phosphates, tungstates and other ions of transition elements with high oxygen content are those that stifle the corrosion reaction occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface forming a protective film or barrier, thereby reducing the corrosion rate. Anodic inhibitors build a thin protective film along the anode and increasing their potential and thus slow down the corrosion reaction. Chromates, nitrates, tungstate and molybdates are some examples of anodic inhibitors. Although, this type of control is affected, yet it may be dangerous since severe local attack can occur, if certain areas are left unprotected by depletion of the inhibitors.

➢ Mixed inhibitors

Some substances inhibit corrosion by reducing simultaneously the rate of anodic and cathodic reactions involved in the corrosion process and are therefore called mixed inhibitors. They are typically film forming compounds that cause the formation of precipitates on thesurface blocking both anodic and cathodic sites indirectly. Anodic inhibitors are, for the most part, dangerous inhibitors, especially if their concentrations are too less.



(a) anodic inhibitors :
phosphates
silicate compounds

(b) Cathodic inhibitors
poly-phosphates
$Ca(HCO3)2$
methylamino-phosphate

(c) mixed anodic and cathodic inhibitors
amines
selenides

Figure- 26: Mixed Inhibitors

But cathodic inhibitors are generally safe. Mixed inhibitors are less dangerous than pure anodic inhibitors, and in number of cases they may not increase the corrosion intensity. The most common inhibitors of this category are the silicates and the phosphates.

➢ Synergistic inhibitors

It is very rare that a single inhibitor is used in systems such as cooling water systems. More often, a combination of inhibitors (anodic and cathodic) is used to obtain better corrosion protection properties. The blends which are produced by mixing of multi-inhibitors are called synergistic blends. Examples include chromate-phosphates, polyphosphate-silicate, zinc-tannins, and zinc-phosphates.

- **Precipitation inhibitors**

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust. In aerated hot water systems, sodium silicate protects steel, copper and brass.

GREEN CORROSION INHIBITORS

Extracts of plant materials contain a wide variety of organic compounds. Most of them contain heteroatoms such as P, N, S, O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented.

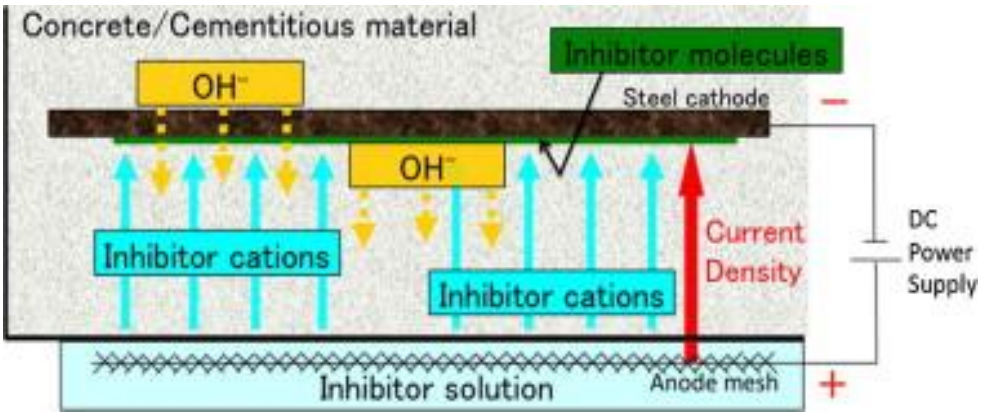


Figure-27: Green corrosion inhibitor

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that have biocompatibility in nature. The inhibitors like plant

extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of 'inhibitors', 'green inhibitors' can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

- **Organic green inhibitors**

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from natural sources like plants. It also includes synthetic compounds with negligible toxicity. Some of the notable developments on organic green inhibitors especially plant extracts are discussed here.

- **Plant extracts**

The authors have so far investigated the application of plant extracts, as well as other organic inhibitors against corrosion of steel in acidic fluids. Lotto had reported the application of the extract of *Mangiferaindica* (Common name: mango, indigenous area: India and other tropical regions) leaves and bark for corrosion of mild steel in diluted sulfuric acid (H_2SO_4) medium. The weight loss measurements and electrochemical impedance spectroscopic studies were used to determine the inhibition efficiency of the inhibitors. Though the extract of leavesand bark showed a significant effect on the corrosion rate separately, the combination of these two extracts exhibited rather higher efficiency.

The inhibitive effect of *Zenthoxylumalatum* (Winged Prickly Ash, East and South Asian Countries) fruit extract was reported for corrosion of mild steel in phosphoric acid medium at temperatures ranging from 50–80^{0}C. The surface analysis using X-ray photoelectron spectroscopy (XPS) revealed the layer formation of the plant extract on the surface of mild steel. And the results were indicated the possible formation of iron phosphate that was catalyzed by the formation of the iron-plant extract organo-metallic complex.

Sat apathy et al studied the methanol extract of *Justiciagendarussa* (Willow-leaved justicia, India, Indonesia) leaves for corrosion inhibition of mild steel in hydrochloric acid medium (HCl). The authors have made an attempt to characterize the organic compounds present in the methanol extract by means of gas chromatography- mass spectrometric technique. The results showed that the compounds present in the methanol extract were difficult to separate, since the

retention times of majority of the compounds were close to each other. The electron spectroscopy for chemical analysis and atomic force microscopy were employed to obtain the information about the film formation on the surface of the mild steel specimen.

- **Inorganic green inhibitor**

A number of inorganic elements (minerals) are essential for the growth of living things. Mineral elements in wide variety are present in trace amounts in almost all foodstuffs. The higher concentrations of many metals cause toxicity to all forms of lives. Chromates are among the most common substances used as inhibitors or incorporated in anticorrosive pretreatments of aluminums alloys. The corrosion of galvanized steel was inhibited by the formation of cerium-rich film. The film contains Ce^{4+} which was formed by the cerium oxides and hydroxide.

IMPORTANCE OF GREEN INHIBITOR

- Inhibitors are a great method of preventing corrosion and are easy to apply. Has application in a wide range of sectors.The knowledge of the method of the action,facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects.
- It is important in the choice of inhibitor, ascertain the subsequent effects of this towards the environment.
- The search for environmental friendly inhibitors has shown excellent results, outperforming conventional inhibitors.Reference organic inhibitors newly developed. Inhibitors play a vital role in providing protection against corrosion.
- The selection of the inhibitor is important for environmental protection Not all inhibitors are eco-friendly.
- There is a growing trend to use plant extracts and pharmaceutical compounds as corrosion inhibitors. Most of these compounds are environmentally-friendly.

CHAPTER-II

AIM AND SCOPE OF THE PRESENT WORK

Green compounds represent a potential class of corrosion inhibitors. There is a wide range of studies regarding corrosion inhibition by hetero atoms containing green compounds. Green compounds containing lot of hetero atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulfur. The corrosion-inhibiting property of these compounds is attributed to their molecular structure.

Acid solutions are widely used in industries for pickling, acid cleaning of boilers, rescaling and oil well as acidizing. Corrosion inhibitors are widely used in order to control the corrosion of metallic materials by cleaning acids. 1.0 M H_2SO_4 is employed in such purposes. Most of the earlier studies on inhibition of corrosion of metals in acids have been related to the performance of organic compounds containing hetero groups.

Recently, environmental friendly inhibitors have attracted several researchers. Natural products are non-toxic, biodegradable and readily available. They have been widely used as inhibitors. Corrosion inhibitions of mild steel by various types of plant extracts have been studied.

Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly and acceptable and possess no threat to the environment. The present work in undertaken:

1. To evaluate the inhibition efficiency of an aqueous leaves extract of *Cajanus cajan* in controlling the corrosion of mild steel in 1.0 M H_2SO_4 medium.
2. To analyses the best fit isotherm for corrosion inhibition.
3. To understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization and impedance analysis.
4. To propose a suitable mechanism for corrosion inhibition.

CHAPTER-III

EXPERIMENTAL METHOD

The experimental studies related to the inhibition action of *Cajanus cajan* leaves extract on mild steel in have been present here. Such studies include weight loss, polarization and impedance studies.

Figure-28: Cajanus cajan

Pigeon pea (*Cajanus cajan*) is one of the most common tropical and subtropical legumes cultivated for its edible seeds. Pigeon pea is fast growing, hardy, widely adaptable, and drought resistant, Because of its drought resistance it can be considered of utmost importance for food security in areas where rainfall is not reliable and droughts are likely to occur. At the end of the dry season, pigeon pea provides green forage of outstanding value when other forages are not available.

Properties

Botanical name : *Cajanus cajan*

Family : Fabaceae (pea family)

Order : Fabales

Genus : Cajanus

Kingdom : Plantae

Tamil name : Thuvarai

Synonyms : Cajanus

Morphology

Pigeon pea is an erect, short-lived perennial leguminous shrub that usually grows to a height of about 1-2 m, but can reach up to 2-5 m high. It quickly develops a deep (2 m depth) poisonous taproot. The stems are woody at the base, angular and branching. The leaves are alternate and trifoliate. The leaflets are oblong and lance late, 5-10 cm long x 2-4 cm wide. Leaves and stems are pubescent. The flowers (5 to 10) are grouped in racemes at the apices or axils of the branches. The flowers are papilionaceous and generally yellow in color. They can also be striated with purple streaks. The corolla is about 2-2.5 cm. The fruit is a flat, straight and pubescent pod, 5-9 cm long x 12-13 mm wide. It contains 2-9 seeds that are brown, red or black in color, small and sometimes hard-coated.

Therapeutic use

The leaves and stems are used for diabetic disorders, constipations and staunch blood, the seed past is used for Energy stimulant. Leaf and stem is used for gingivitis,stomatitis and tooth brush. Fresh leaves are used for nullify effect of intoxication and laxative. Seeds and leaves are used to apply over breast to induce lactation.

Pharmacological action

Anti-inflammatory, anti-oxidant, anti-cancer, anti-bacterial activity and anti-microbial activity.

Collection of the plant material

The leaves were collected from the area Keeranur, Trichy (DT), Tamil nadu. Fresh leaves were authenticated and identified by Dr. John Britto, The Rapient Herbarium and center for Modular systematic, St. Joseph's College, Thiruchirappalli, Tamil nadu, India.

Preparation of extract

The leaves were collected, shade dried and powdered. An aqueous extract was prepared by refluxing 10 gm of powdered *Cajanus cajan* leaves in double distilled H_2O. The extract was cooled, filtered and made up to 100 ml with distilled water. From that, various distributions were prepared.

Preparation of the specimens

Mild steel specimen (0.026%-S, 0.06%-P, 0.4%-Mn, 0.1%-C and the rest iron) of the dimensions 1x5x0.2 cm were polished to mirror finished. They are decreased with acetone and used for the weight loss method, polarization and impedance studies.

Materials and chemicals used

For polarization, cylindrical mild steel rod embedded in Teflon with an exposed area of 1 cm^2 was used. The electrodes were polished with emery papers of 0/0, 2/0, 3/0, and 4/0 grades and degreased with acetone, dried and used.

Acid**:** H_2SO_4 was used of G.R. Grade (MERCK CHEMICALS)

Table: 1

Phytochemical screening of aqueous extract of *Cajanus cajan* leaves aqueous extract

Phyto-constituents	Chemical test	Aqueous extract
Alkaloids	Wagner's	+
Flavonoids	Lead acetate	+
Glycosides	Molisch	+
Sterols	Libermann	+
Phenols	$FeCl_3$	+
Saponin	Sodium bicarbonate test	+
Tannins	$FeCl_3$	+
Quinones	Alcoholic KOH	+
Lignin	Lignin's	+
Terpenoides	Salkowski's test	+
Sugar/Carbohydrates	Molish's test	+
Fats and Fixed Oils	Saponification test	+

Weight loss method

Weight loss measurements were performed in 1.0 M H_2SO_4 medium with and without the presence of different volumes of inhibitor by using the formula, inhibition efficiency and corrosion rate were calculated.

Inhibition efficiency (%) = W_0-W_i/W_0*100; Corrosion rate (mmd) = 53.5× W / a × t

Where

W_0 = Weight loss in plain acid
W_i = Weight loss in inhibited acid
W = Weight loss in grams
a = area of the specimen in cm^2
t = time exposure in hour

Potentiodynamic polarization studies:

Potentiodynamic polarization studies were performed for mild steel specimen in the presence and the absence of the inhibitors. Polarization measurements were performed toevaluate the corrosion current, corrosion potential and the Tafel's slope.

The electrode used was a mild steel rod of the same composition embedded in araldite and with an exposed area of $1cm^2$. The polarization cells contain a three electrode assembly. A rectangular foil was used as the counter or auxiliary electrode. The area of the counter electrode is much larger compared to the area of the working electrode. This will exert a uniform potential field on the working electrode. The reference electrode is $Hg/HgCl_2/1N\ H_2SO_4$ for HCl solution.

A solution quantity of 100 ml of the test solution was taken in a polarization cell. The working electrode was polished with 0/0, 1/0, 2/0, 3/0, and 4/0 emery papers successively and degreased with acetone. The working electrode, reference and auxiliary platinum electrodes were assembled and connections were made.

Stirring was provided to the test solutions to avoid for the system the volume polarization before start of experiment. A time interval of about 15 minutes was given for the system to attain steady state and open circuit potential was recorded. Polarization measurements were made carried out from 800mV to 250mV at a constant identical to weight loss measurements.

Polarization measurements were made from mild steel specimens in 1.0 M H_2SO_4 in the presence and absence of the inhibitor. Current in mA and potential in mV were plotted. From the graph, the Tafel slope (in mV/decade) and the corrosion potential (in mV/decade) were calculated.

Impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell setup was the same as that used for polarization measurements.

The real part and imaginary part of the cell impedance were measured in ohms at varies frequencies. The value of charge transfer resistance, R_t, and the double layer capacitance, C_{dl} were calculated.

CHAPTER-IV

RESULTS AND DISCUSSION

It is a well-known fact that research activities leading to the development of corrosion inhibitors based on natural products have immense scope in several industries, because of their non-toxicity, biodegradable nature and are also easily available. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly and possess no threat to the environment.

The efficiency of an extract as a corrosion inhibitor can be attributed to the number of mobile electron pairs present, π-orbital character of free electrons and the electron density around the hetero atoms. In the present study, inhibition efficiency of *Cajanus cajan* leaves extract in 1.0 M H_2SO_4 medium has been evaluated using weight loss measurements and its potentiodynamicpolarization and impedance studies. The effect of this extract on the extent of inhibition of corrosion of mild steel in 1.0 M H_2SO_4medium by this extract can be explained in terms of its adsorption on the metal surface. This extract gets adsorbed on the metal surface by means of, when mild steel is immersed in the acid solution the phyto-components diffuses from the bulk of solution towards the metal surface.

The inhibitive influence of *Cajanus cajan* on the corrosion of mild steel in 1.0 M H_2SO_4leaves was studied by weight loss method, polarization and impedance measurements. The inhibition efficiency values determined by these techniques showed closed agreement. The maximum inhibition efficiency was found to be 97%.

The corrosion decreased with increase in addition of *Cajanus cajan* probably due to the progressive adsorption of the inhibitor on the metal surface.

The percentage of inhibition efficiency increases with increase in the inhibitor volume. The corrosion inhibition by *Cajanus cajan* leaves extract is attributed to the adsorption of the additive onto the mild steel surface.

The values obtained from the weight loss technique for the studied inhibitor fit well into the **Langmuir, Flory-Huggins** and **Frumkin** isotherm adsorption isotherm.

The values of free adsorption process indicate that both physisorption and chemisorptions studied for the mild steel surface.

The leaves of *Cajanus cajan* prevent the corrosion due to the presence of any of the phytochemical components shifting the corroded metal into the noble. The polarization study also shown an agreement with inhibitor efficiency obtained from weight loss studies.

Weight loss studies

Table-2 gives the inhibition efficiency of different volume of *Cajanus cajan* in 1.0 M H_2SO_4 medium. The inhibition depends upon the nature and mode of adsorption of the metal surface. The adsorption is assumed to be quasi-substitution process between the water molecules on the surface and any of the natural components present in the inhibitor.

The inhibition of heterocyclic compound present in the plant extract with the metal surface may occur through any of the phyto-components present in the inhibitor and also to the interaction of π-electrons of ring with metal surface, thereby enabling the compound to getadsorbed on the metal surface.

Adsorption isotherm

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Temkin, Flory-Huggins, Frumkin, and the recently formulated thermodynamic/kinetic model of El-awady et al. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clue to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs as the interaction energy between molecules and metal surface is higher than that between the H_2O molecules and the metal surface.

Langmuir adsorption isotherm

Adsorption isotherms are very important to determine the mechanism of phyto-electrochemical reaction. The adsorption isotherm values are shown in **table-3**

Langmuir adsorption isotherm is

$$\Theta = K_{ads}.C/1 + K_{ads}.C$$

$$\Theta (1+K_{ads}.C) = K_{ads}.C$$

$$\Theta = K_{ads}.C - K_{ads}.C/\Theta$$

$$\Theta = (1-\Theta) K_{ads}.C$$

$$\Theta/1-\Theta = K_{ads}.C$$

The plot of 3+ log (Θ/1-Θ) against 3+logC is a straight line as shown in **figure-29**. Thus the Langmuir isotherm is valid for the inhibitor.

Temkin adsorption isotherm

It is given by the expression;

$$\Theta = -2.303 \log K/2a.-2.303 \log C/2a$$

Where 'K' is the adsorption equilibrium constant, 'a' is the lateral interaction parameter.

The plot of Θ against log C is shown in **figure-30**. The linear plot indicates that Temkin adsorption isotherm was obeyed and negative, value of 'a' indicated repulsion exist in theadsorption layer. The results are shown in table**- 4.**

Florry-Huggins adsorption isotherm

It is given by the expression

$$\text{Log } \Theta/C=\log K+ x \log (1-\Theta)$$

Where 'x' is the size parameter and it is a measure of the number of adsorbed watermolecules substituted by an inhibitor molecule. The adsorption parameter is shown, in **table-5.** The plot of log Θ/V against log (1-Θ) is linear as shown in **figure-3.**

El-awady isotherm

It is given by the expression:

$$\log (\Theta/1-\Theta) = \log K + y \log C$$

Here K_{ads} the equilibrium constant of adsorption process is calculated by the relationship, K_{ads} = 1/k. A plot of 2 + log(1-Θ) Vs. 2+ log C is linear as shown in **figure-6**. The calculated K_{ads} and 1/y values are given. The adsorption isotherm values are shown in **table-32.**

Frumkin Isotherm

$$K_{ads} C = (/1-\Theta)e^{-2a}$$

Take logarithm on both sides of the equation, it can be rearranged as given below.

$$\log K_{ads} + 2a = \log(\Theta/(1-\Theta)C)$$

where K_{ads} is the adsorption desorption equilibrium constant, V is the inhibition volume and 'a' is the interaction parameter describing the lateral interaction among inhibitor molecular in the absorbed layer on the metal surface. Linear plots of **log(Θ /(1-Θ)C)** Vs. **Θ** is shown in **figure-33** obtained. The values for the Frumkin adsorption parameters are shown in **table-7.**

Free energy change

Inhibitor on mild steel surfaces related to the constant of the adsorption according to equation. The

$$\Delta G^0_{ads} = -2.303RT\log (K_{ads} \times 55.5)$$

From the results, shown in **table-8** most of the values of ΔG^0_{ads} were found to be negative and were below the threshold value of -40 kJ/mole indicating that the

adsorption of *Cajanus cajan* leaves extract, on mild steel surface is spontaneous and that mechanism of physical adsorption is applicable.

Potentiodynamic polarization studies

Table-9 and **figures 34, 35, 36 & 37** gives the values of potentiodynamic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}) and the cathodic Tafel slopes (b_c and b_a) for the different volume shown in the green inhibitor understudy. It can be seen that the phyto-components diffuse from the bulk of the solution and gets absorbed on metal surface.

AC impedance study

Table-10 and **figures 38, 39, 40 & 41**shows the AC impedance value for different volumeof the inhibitor. The R_t value increases and C_{dl} value decreases with inhibitor volume. This implies the formation of protective film on the metal surface. It can be also seen from **table-11** that there is a close agreement between the values of inhibition efficiencies obtained from weight loss measurements, polarization and impedance studies.

TABLE-2

Inhibition effect on corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cajanus cajan* leaves aqueous extract using weight loss method.

Inhibition concentration, (%) v/v	Rate of corrosion, (mdd)	Inhibition efficiency (%)
Blank	-	-
2	3.17×10^{-5}	41
4	2.33×10^{-5}	56
6	2.00×10^{-5}	69
8	1.33×10^{-5}	75
10	2.00×10^{-5}	97

TABLE-3

Langmuir adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cajanus cajan* leaves aqueous extract

Inhibitor concentration, (%) v/v	**θ**	**C/θ**
Blank	-	-
2	0.406	4.9989
4	0.5625	7.0001
6	0.688	7.8949
8	0.750	4.6457
10	0.969	10.9949

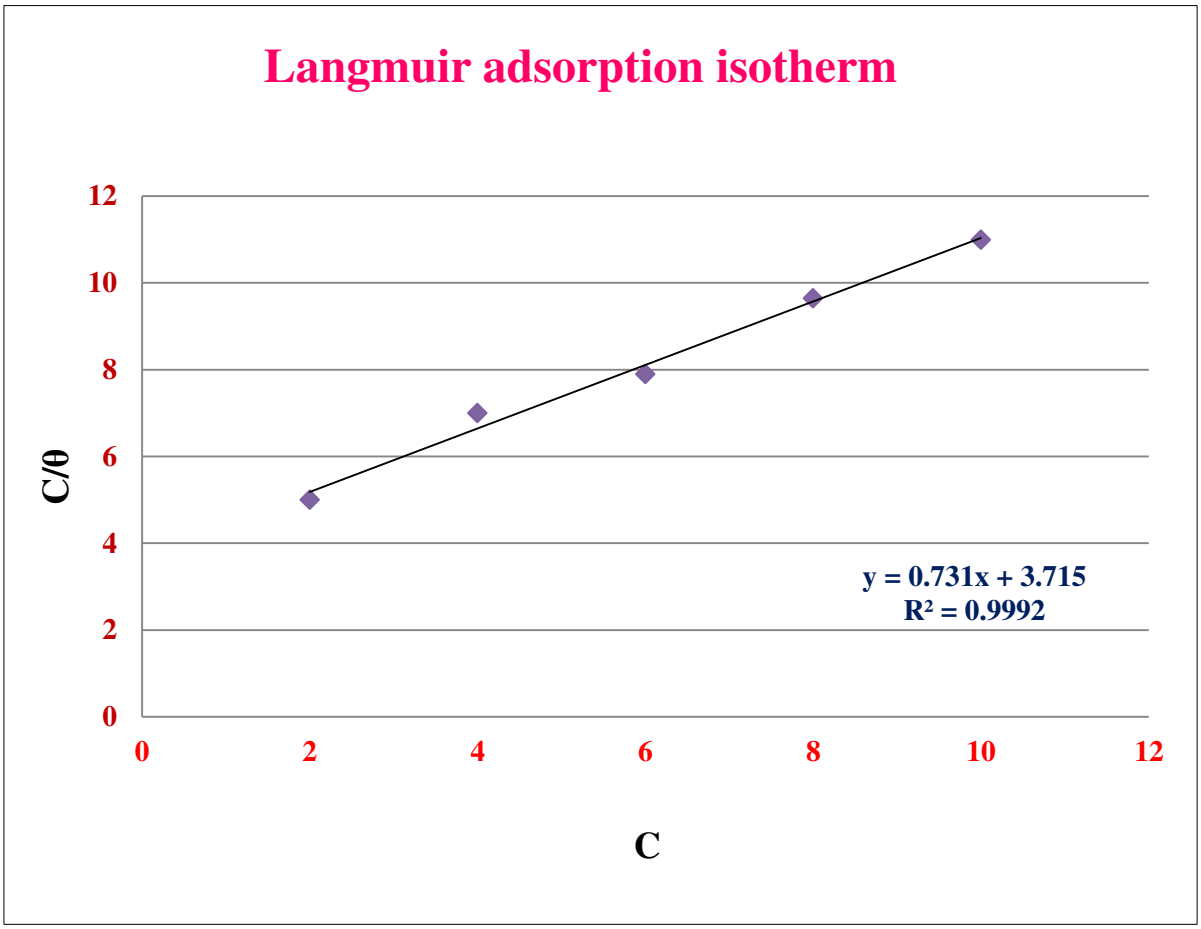


Figure-29: Langmuir adsorption isotherm for the inhibition of corrosion mild steel in 1.0 M H_2SO_4 medium using *Cajanus cajan* leaves aqueous extract.

Calculation:

Intercept	= 3.7156
K_{ads}	= 0.26
ΔG^0_{ads}	= -6.81454
Slope	= 0.7319
R^2	= 0.9902
1/y	= 1.3663

TABLE-4

Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cajanus cajan* leaves aqueous extract.

Inhibitor Concentration, (%) v/v	**θ**	**log C**
Blank	-	-
2	0.406	0.3010
4	0.5625	0.6020
6	0.688	0.7781
8	0.750	0.9030
10	0.969	1.0000

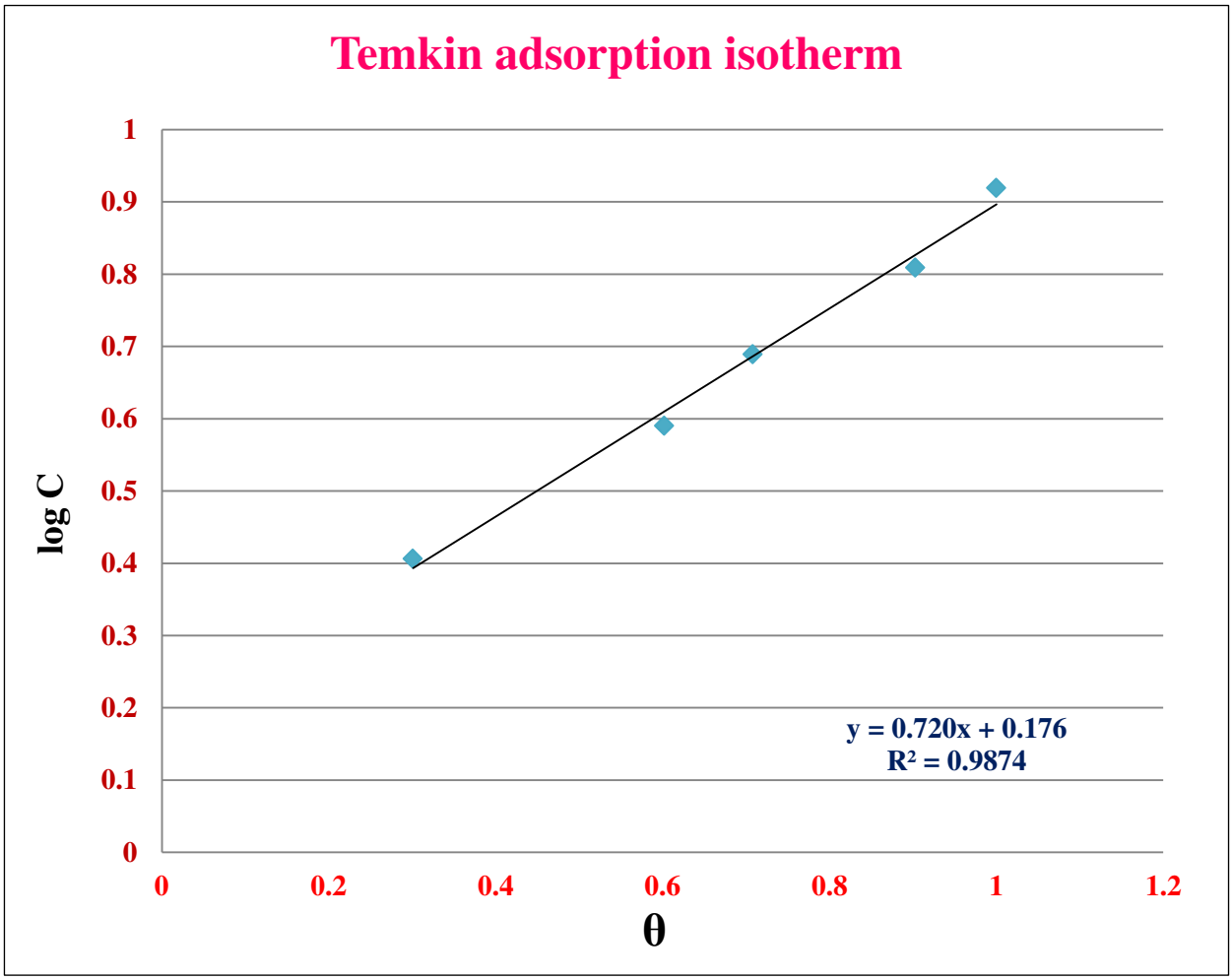


Figure -30: Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium using *Cajanus cajan* leaves aqueous extract.

Calculation:

Intercept = 0.3091

K_{ads} = 303.8070

ΔG^0_{ads} = -24.5249

Slope = 0.1245

R^2 = 0.9874

1/y = 8.0321

a = -9.248

TABLE-5

Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cajanus cajan* leaves aqueous extract.

Inhibitor Concentration, (%) v/v	θ	θ/C	log(θ /C)	(1-θ)	log(1-θ)
Blank	-	-	-	-	-
2	0.406	0.203	- 0.693	0.594	-0.2262
4	0.5625	0.1406	-.8520	0.4375	-0.3590
6	0.688	0.115	-.9393	0.312	-0.5058
8	0.750	0.094	-.0269	0.250	-0.6021
10	0.969	0.097	-.0132	0.031	-1.5086

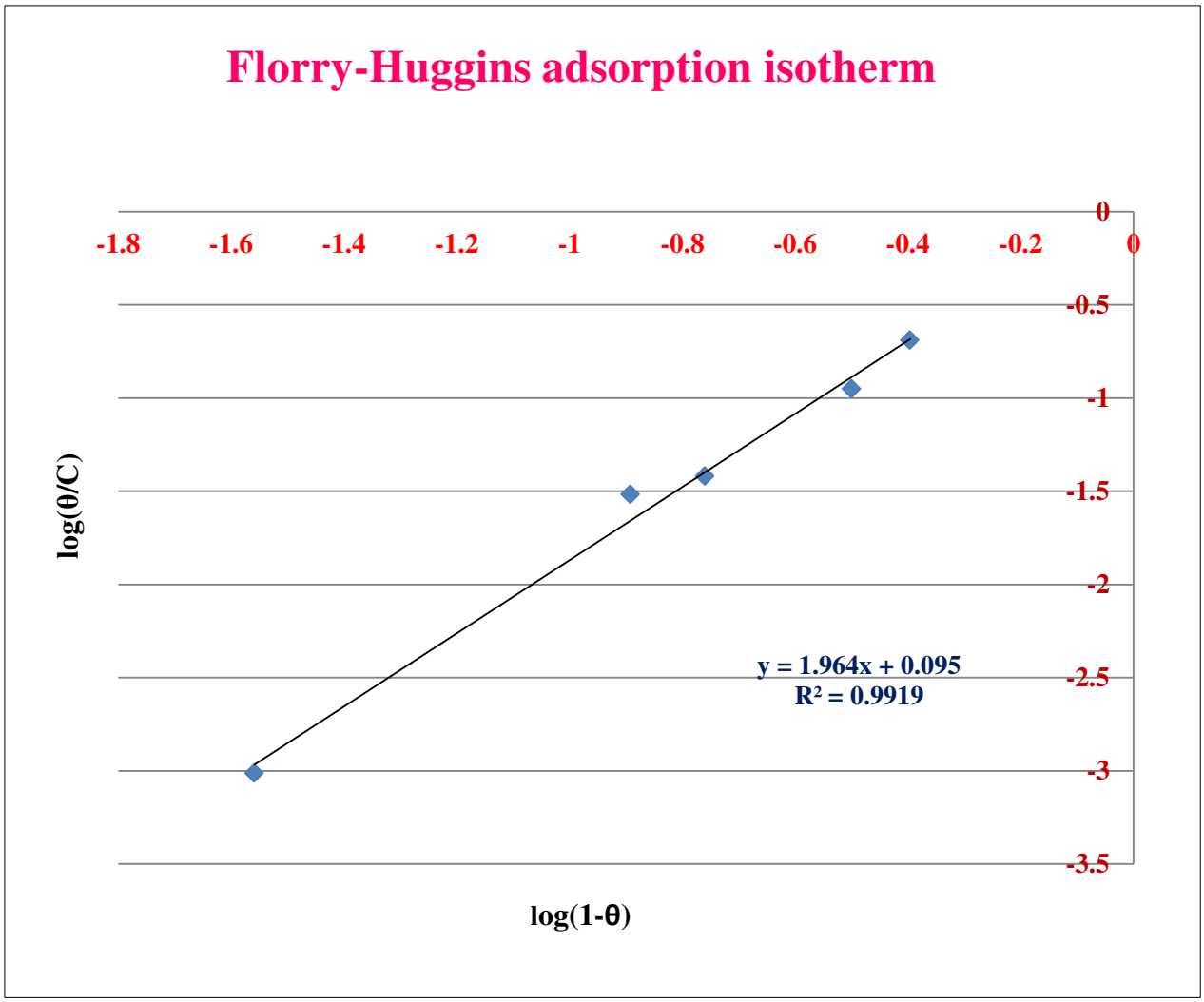


Figure -31: Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium using *Cajanus cajan* leaves aqueous extract.

Calculation:

Intercept = 0.095

K_{ads} = 1.2445

ΔG^0_{ads} = -10.6731

Slope = 1.964

R^2 = 0.9919

1/y = 0.509

TABLE-6

El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Cajanus cajan* leaves aqueous extracts

Inhibitor Concentration, (%) v/v	θ	(1-θ)	θ/(1-θ)	2+logc	2+log θ/(1-θ)
Blank	-	-	-	-	-
2	0.406	0.594	0.6835	2.3010	2.1653
4	0.5625	0.4375	1.2857	2.6020	3.1091
6	0.688	0.312	2.2051	2.7781	4.3434
8	0.750	0.250	3.0000	2.9030	5 .4771
10	0.969	0.031	31.2581	3.0000	33.4949

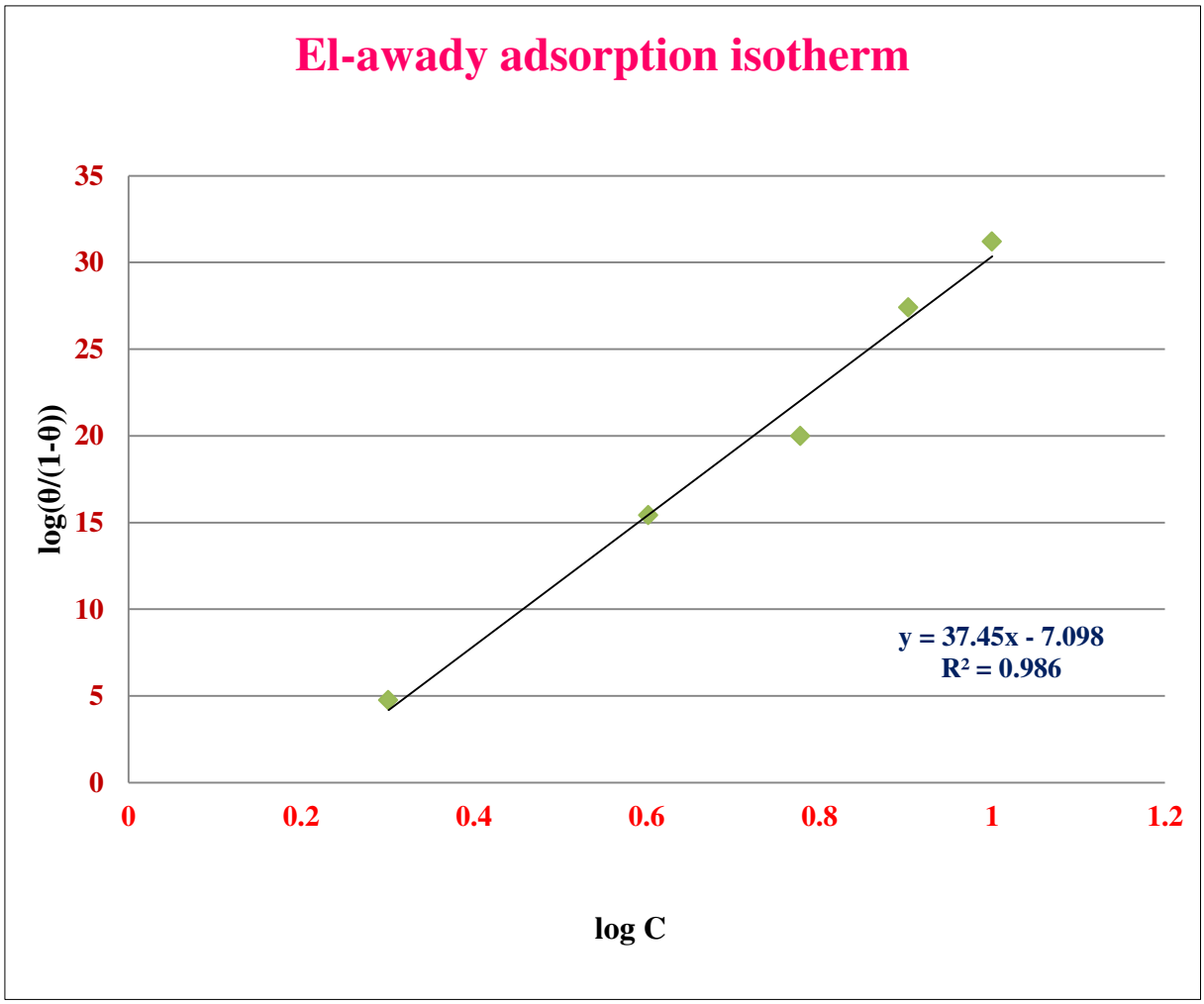


Figure-32: El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium using *Cajanus cajan* leaves aqueous extract.

Calculation:

Intercept = -7.0982

K_{ads} = 0.64742

ΔG^0_{ads} = -9.0265

Slope = 37.454

R^2 = 0.9867

1/y = 0.0267

TABLE-7

Frumkin adsorption isotherm for the inhibition of mild steel in 1.0 M H_2SO_4 medium by *Cajanus cajan* leaves aqueous extract.

Inhibitor concentration, (%) v/v	θ	(1-θ)	θ/(1-θ)	log (θ/(1-θ))	log (θ/(1- θ)c)
Blank	-	-	-	-	-
2	0.406	0.594	0.6835	0.1653	-0.4662
4	0.5625	0.4375	1.2857	0.1091	-0.4529
6	0.688	0.312	2.2051	0.3434	-0.4347
8	0.750	0.250	3.0000	0.4771	-0.4259
10	0.969	0.031	31.2581	1.4949	-0.4201

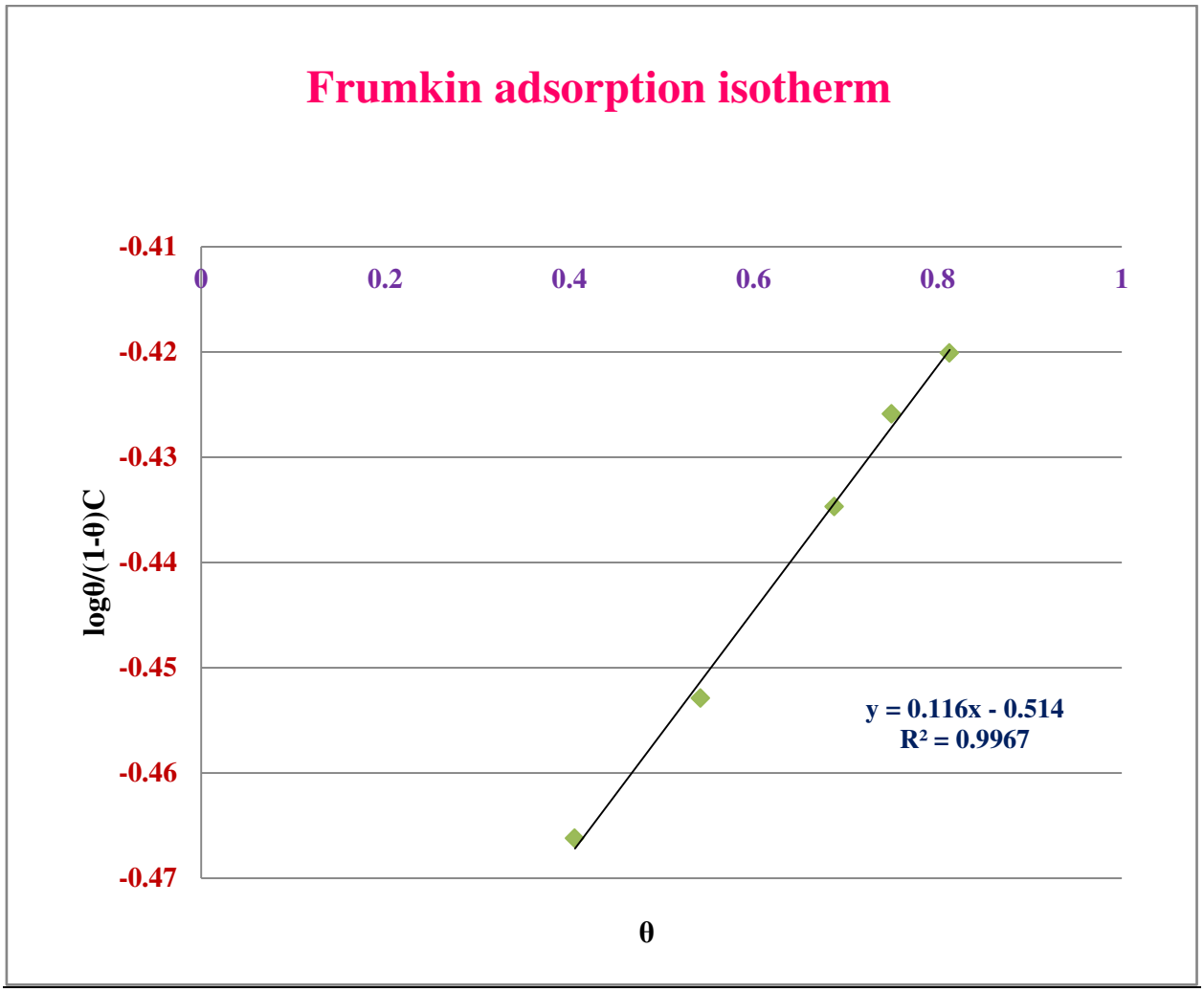


Figure -33: Frumkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium using *Cajanus cajan* leaves aqueous extract.

Calculation:

Intercept = -0.5144

K_{ads} = 0.3059

ΔG^0_{ads} = -7.137

Slope = 0.1164

R^2 = 0.9964

1/y = 8.5910

TABLE-8

Adsorption isotherm parameters for the inhibition of the corrosion of mild steel in 1.0 M H_2SO_4 by *Cajanus cajan* leave aqueous extract.

Isotherm	$-\Delta G^0_{ads}$	Slope	R^2	a	1/Y
Langmuir isotherm	6.81454	0.7319	0.9992	-	1.3663
Temkin isotherm	24.5249	0.1245	0.9874	-9.2489	8.0321
Flory-Huggins isotherm	10.6731	1.964	0.9919	-	0.5092
El-awady isotherm	9.0265	37.454	0.9867	-	0.0267
Frumkin isotherm	7.137	0.1164	0.9964	0.0582	8.5910

The R^2 value shows that **Langmuir, Flory-Huggins** and **Frumkin i**sotherm are the best fit isotherms.

TABLE – 9

Corrosion parameters obtained from polarization curves for mild steel in 1.0 M H_2SO_4 medium in the presence and absence of inhibitor.

System	Inhibitor concentration, (%) v/v	I_{corr} mV	$-E_{corr}$ mV	b_a mV,dec^{-1}	b_c mV,dec^{-1}	Inhibitor efficiency %
Blank	-	779.758	-491.966	52.351	180.905	-
Cajanus cajan Leaves extract	2	425.712	-459.982	56.432	186.211	41.94
	6	275.525	-490.405	73.938	186.914	64.67
	10	2.429	-466.385	90.836	236.425	99.69

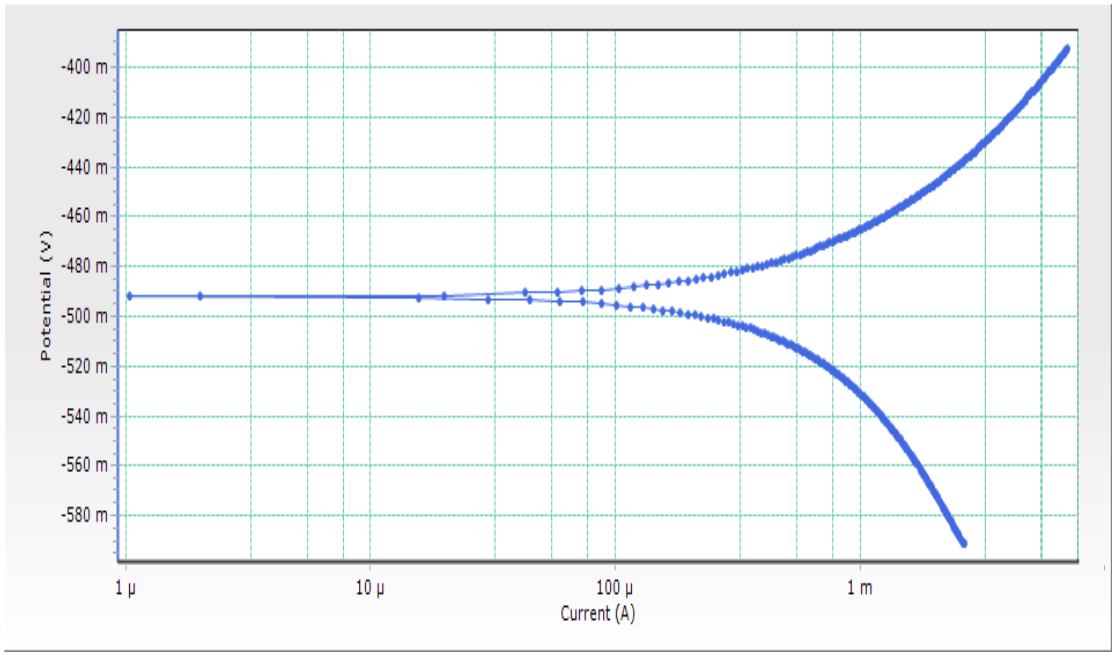


Figure-34: Potentiodynamic polarization curve for mild steel in 1.0 M H_2SO_4

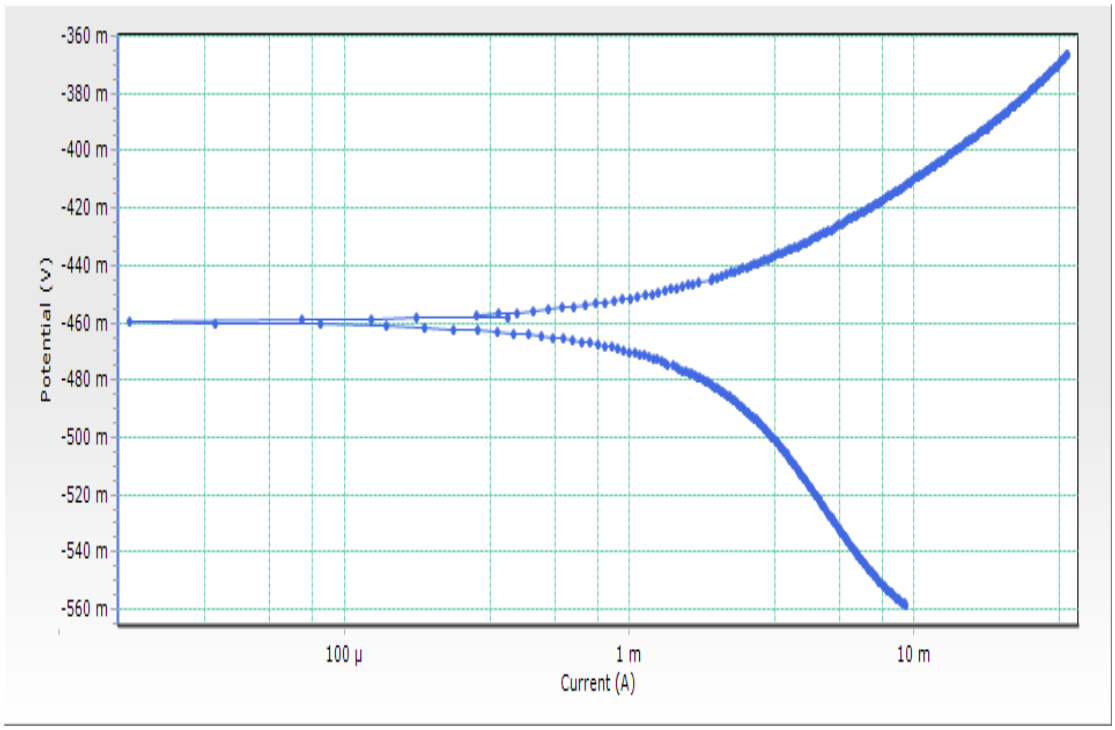


Figure -35: Potentiodynamicpolarization curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 2% of *Cajanus cajan* leaves aqueous extract.

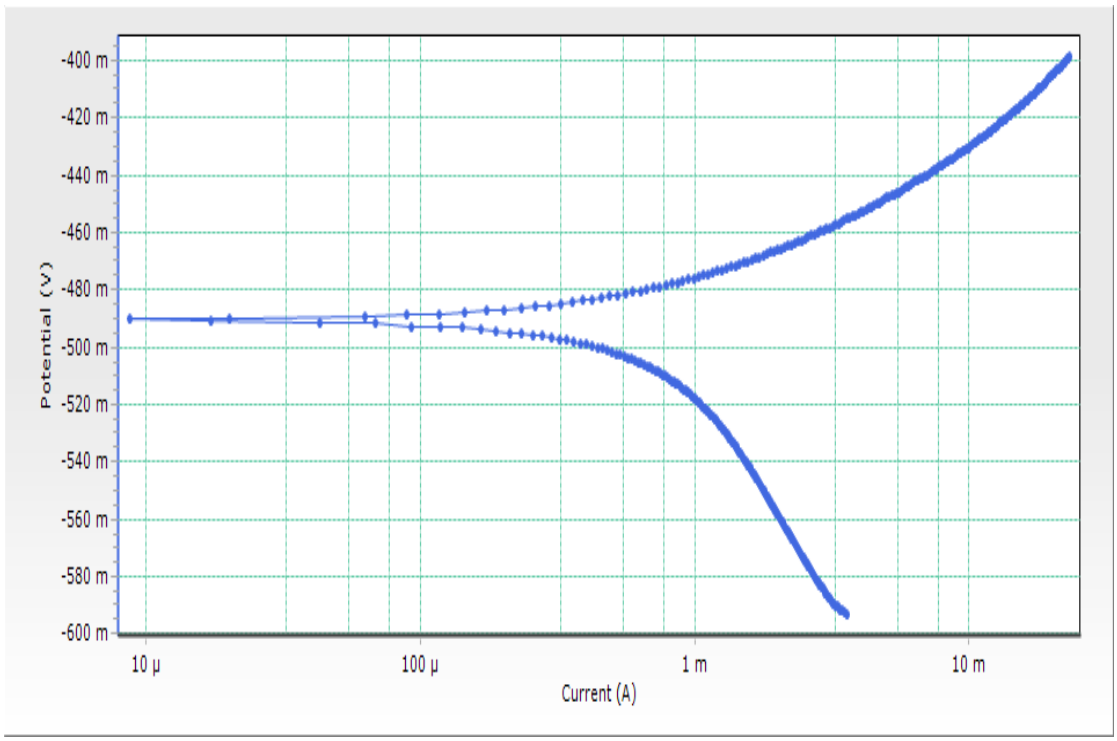


Figure -36: Potentiodynamicpolarization curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 6% of *Cajanus cajan* leaves aqueous extract

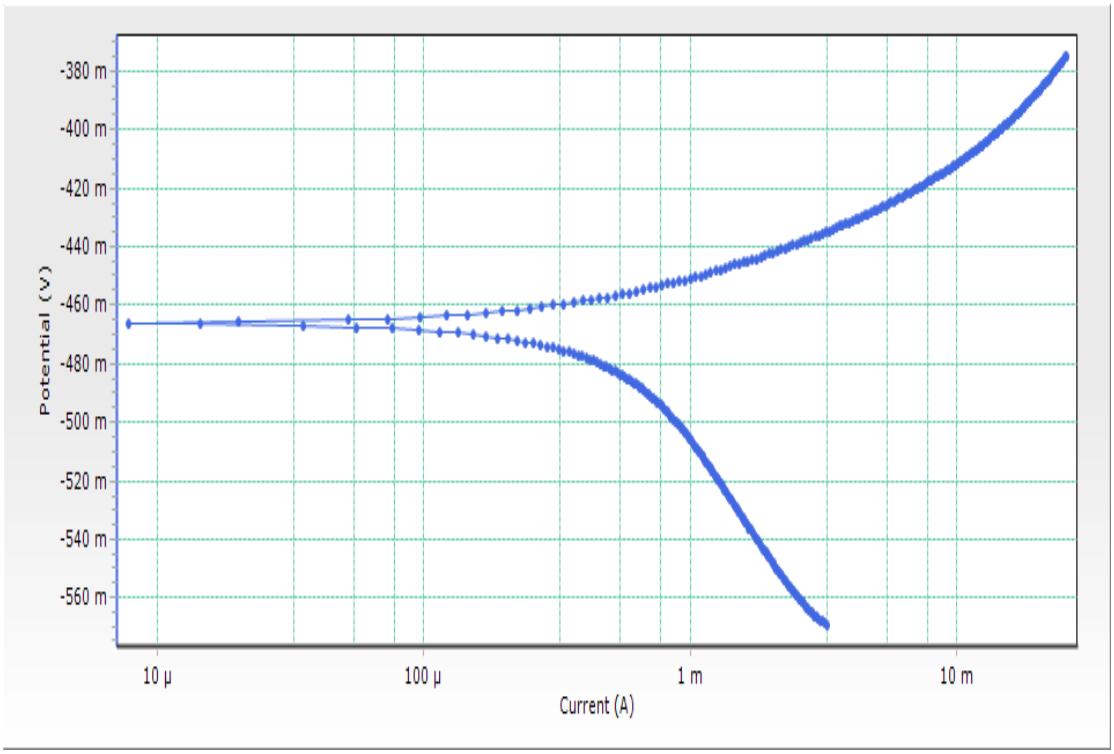


Figure-37: Potentiodynamicpolarization curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 10 % of *Cajanus cajan* leaves aqueous extract

TABLE-10

Corrosion parameters obtained from impedance curve for mild steel in the presence and absence of inhibitor in 1.0 M H_2SO_4 medium.

Inhibitor concentration, (%) v/v	R_t	C_{dl}	Inhibitor efficiency (%)
0	1.25	2.1088	-
2	7.8103	1.1229	46.75
6	14.667	0.7356	65.51
10	22.545	0.0132	99.37

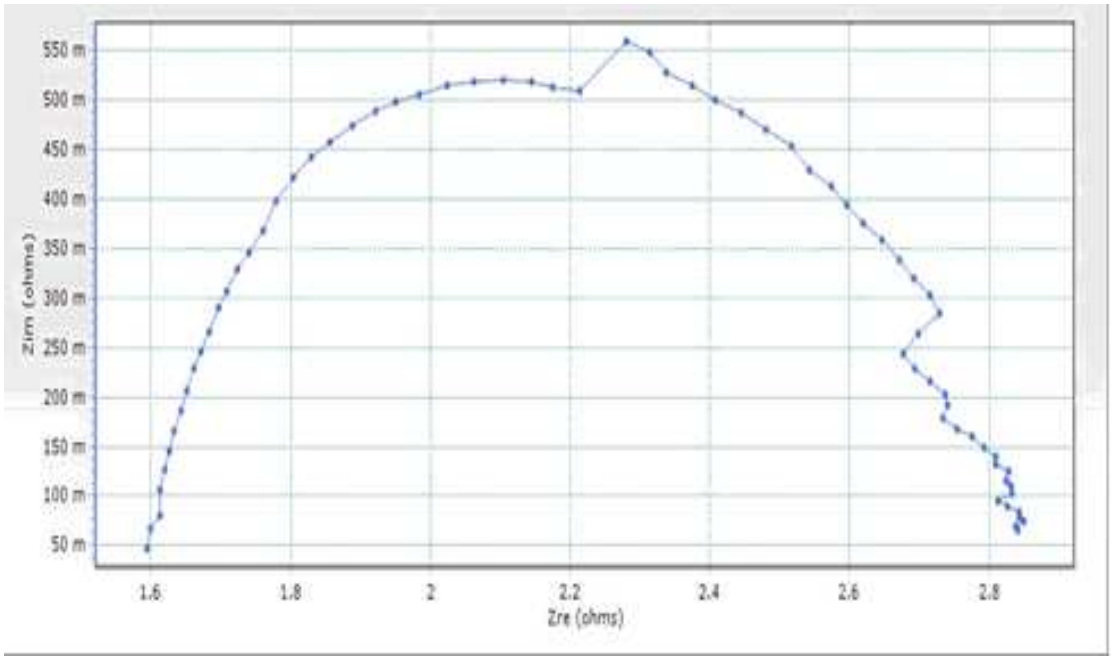


Figure-38: Impedance diagram for mild steel in 1.0 M H_2SO_4

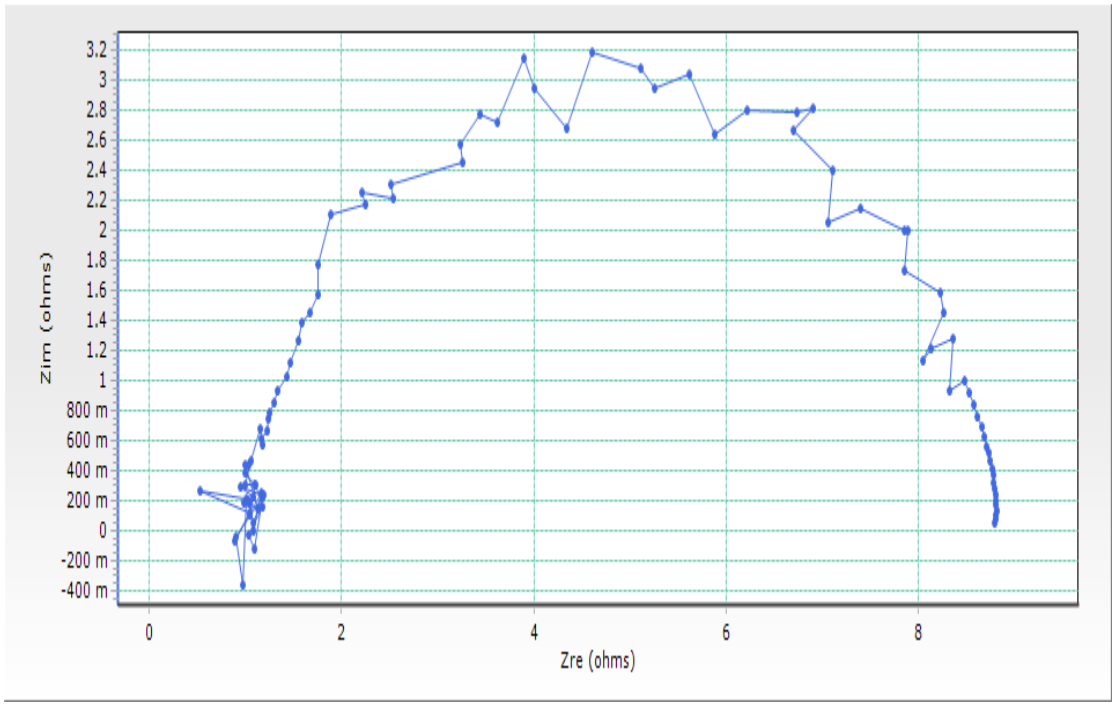


Figure -39: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 2% of *Cajanus cajan* leaves aqueous extract.

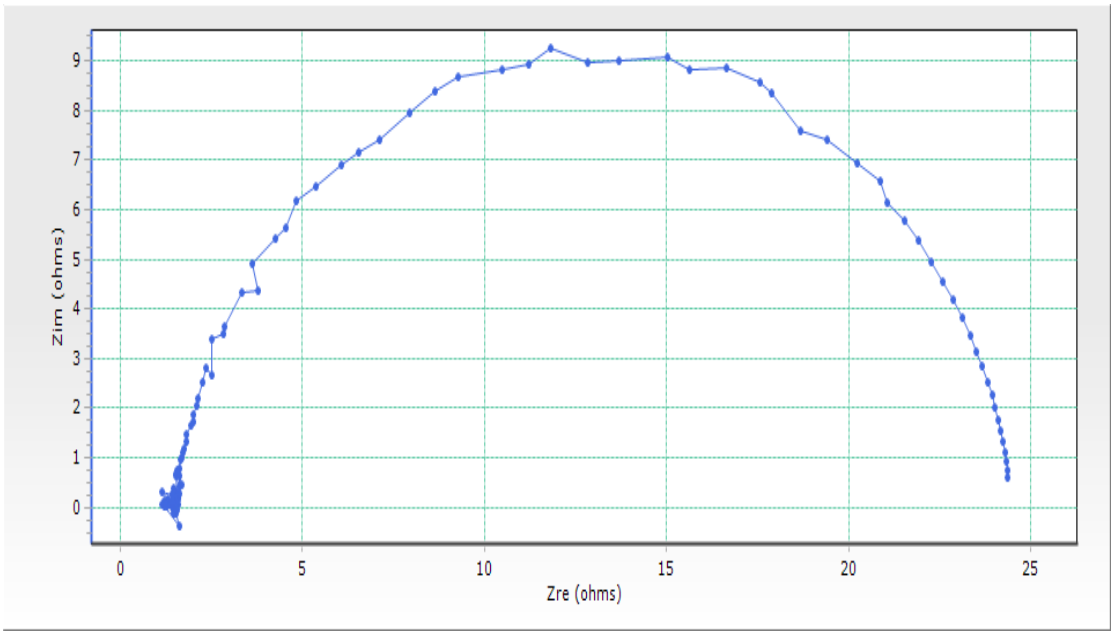


Figure 40-: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 6% of *Cajanus cajan* leaves aqueous extract.

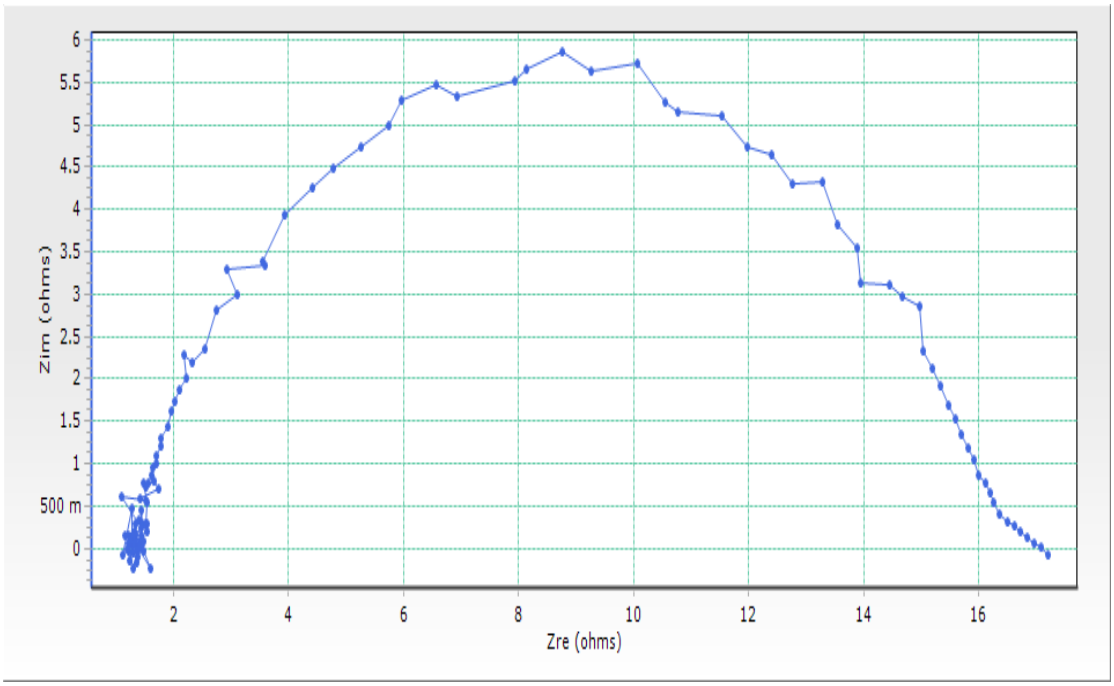


Figure -41: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the Presence of 10% of *Cajanus cajan* leaves aqueous extract.

TABLE-11

Comparison of inhibition efficiency measured by Weight loss, Polarization method and Impedance method

Inhibitor concentration, (%) v/v	Inhibitor efficiency (%)		
	Weight loss	Polarization studies	Impendence studies
2	41	41.94	46.75
6	69	64.67	65.51
10	97	99.69	99.37

CHAPTER-V

SUMMARY AND CONCLUSION

The inhibitive influence of leaves of *Cajanus cajan* on the corrosion of mild steel in 1.0 M H_2SO_4 medium was studied by weight loss method, polarization and impedance measurements. The corrosion is decreased with increase in the addition of *Cajanus cajan* leaves extract probably due to the progressive adsorption of the inhibitor on themetal surface. The maximum inhibition efficiency was found to be 97%

- The corrosion of mild steel in 1.0 M H_2SO_4 solution is inhibited by the addition of leaves extract of *Cajanus cajan.*
- The percentage of inhibition efficiency increases with increase of the inhibitor concentration.
- The corrosion of mild steel inhibited by leaves extract of *Cajanus cajan* is attributed to the adsorption of phytochemical components present in the inhibitor onto themild steel surface.
- The values obtained from the weight loss technique for the studied inhibitor fit well into the Langmuir, Florry-Huggins and Frumkin isotherm. The values of free energy for the adsorption process indicate that the adsorption of the inhibitor on the mild steel surface occurs spontaneously. It suggests that the inhibition is followed by physisorption of the inhibitor on the metal surface.
- The leaves of *Cajanus cajan* prevents the corrosion of mild steel due to the presence of phytochemical components shifting the corrosion into the noble.
- The polarization and impedance study also shows an agreement with inhibitor efficiency obtained from weight loss studies and also it indicates the corrosion inhibition by investigated inhibitor acts as mixed type of inhibitor.
- The results obtained suggest that the *Cajanus cajan* leaves extract is a good corrosion inhibitor for mild steel in 1.0 M H_2SO_4 medium and it can be preferentially usedto replace toxic and non-biodegradable inhibitor.

``

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Post Graduate Project 4

A Study on synthesis and spectroscopic characterization of cobalt complex with Isoniazid ligand

Name of the Guide: Dr. G. Hema Sindhuja
Name of the Candidate: S. Premalatha

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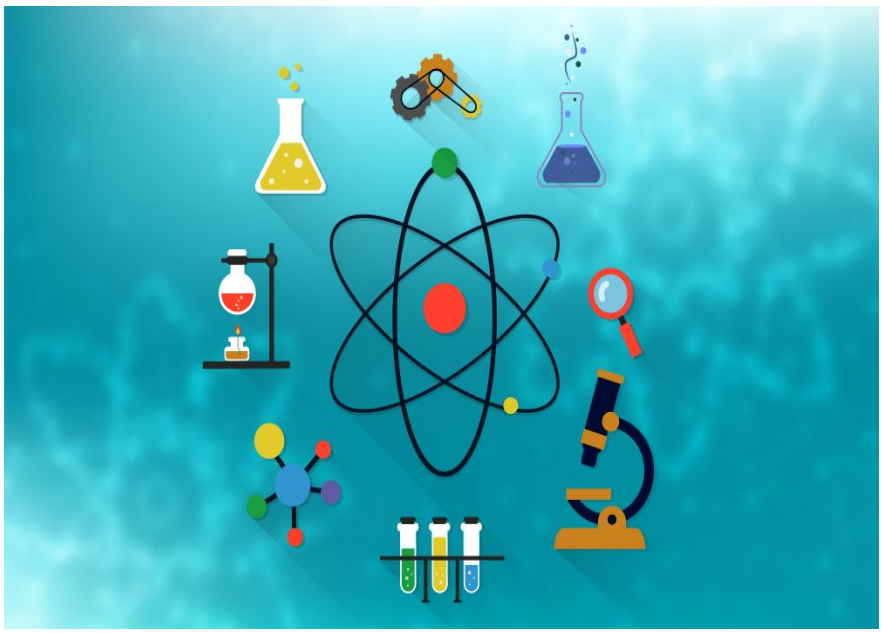
INTRODUCTION



Chapter – I

1 *Introduction*

Coordination chemistry plays a vital role and it is one of the most active research fields in inorganic chemistry. Coordination chemistry assumed a vital significance with the development of bioinorganic chemistry, which is mainly the chemistry of coordination compounds. Coordination chemistry, emerged from the work of Alfred Werner, a Swiss Chemist who examined different compounds composed of cobalt (III) chloride and ammonia. The coordination chemists have showed their major interest in the stereochemistry of the coordination compounds. Nowadays, the research on coordination complexes has been increased due to their magnetic, optical, electronic properties and also due to their complex structures.

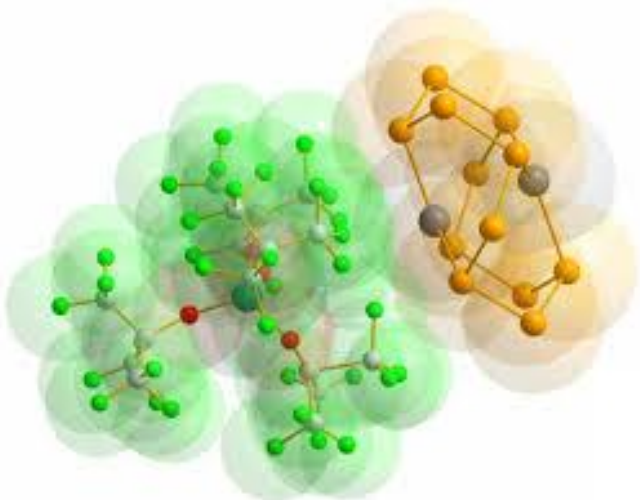


Fig 1 Coordination complex

1.1 Coordination complex

In chemistry, a coordination complex consists of a central atom or ion, which is usually metallic and is called the coordination centre, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents. Many metal-containing compounds, especially those of transition metals, are coordination complexes.

A coordination complex whose centre is a metal atom is called a metal complex. A coordination complex is the

product of a Lewis acid-base reaction in which neutral molecules or anions (called ligands) bond to a central metal atom (or ion) by coordinate covalent bonds. Ligands are Lewis bases - they contain at least one pair of electrons to donate to a metal atom/ion. Ligands are also called complexing agents. Metal atoms/ions are Lewis acids - they can accept pairs of electrons from Lewis bases. Within a ligand, the atom that is directly bonded to the metal atom/ion is called the donor atom. A coordinate covalent bond is a covalent bond in which one atom (i.e., the donor atom) supplies both electrons. This type of bonding is different from a normal covalent bond in which each atom supplies one electron. If the coordination complex carries a net charge, the complex is called a complex ion. Compounds that contain a coordination complex are called coordination compounds. Coordination compounds and complexes are distinct chemical species - their properties and behavior are different from the metal atom/ion and ligands from which they are composed.

For the last two decades, the synthesis of coordination compound with transition metals and their applications have become an attractive field because of the excellent properties such as catalysis, ion exchange, microelectronics, nonlinear optics, porous materials, etc. Due to the smaller size, and coordination numbers (4 or 6) of first row transition metal ions are easily coordinated with nitrogen and oxygen atoms and that's why their coordination geometric structures are simple. The mixed ligand complexes of transition metals are very important in different field of chemistry like photochemistry, analytical chemistry, magneto chemistry etc. The magnetic properties, diverse catalytic activity of such compounds is now being explored for its biological importance. Transition metal complexes are cationic, neutral or anionic species in which a transition metal is coordinated by ligands. Transition metal ions are known to play very important roles in biological processes in the human body. For example, Zn (II) and Cu (II) ions are the second and third most abundant transition metals in humans. They are found either at the active sites or as structural components of a good number of enzymes.

The fact that coordination compounds have been a great challenge to the Inorganic chemists because of their structure and wide range of application from materials to medicine was identified in the nineteenth century. More recent researches on coordination compounds have been concerned with nearly all the metals in the periodic table, with all coordination numbers from two to twelve and in many oxidation states. The growth of interest in coordination chemistry has been greatly stimulated by developments in catalysis, especially for hydrogenation, activation of carbon-hydrogen bonds and also by the effective role of metals in biochemistry. It has also attracted interest chiefly because of its role in biological processes. One can think, of course iron and magnesium, but there are many others (e.g. copper, zinc, cobalt, molybdenum and manganese). It is known that all metals in the periodic table from vanadium to zinc are essential to human life. Complexes of even the alkali and alkaline earth metals with crown ethers and other cyclic ligands play important biological roles. Other coordinated metals have found their use in the of treatment of disease, e.g. gold compounds for arthritis and platinum compounds for some cancers still others are injected inadvertently and cause disease, e.g. cadmium. Metal complexes of biologically important ligands such 4 – amino pyridine (4AP) are mostly known for their anti-inflammatory, anti-tumor and anti-bacterial activities.

1.2 MIXED LIGAND COMPLEX

Developments in the field of coordination chemistry, which is closely bound up with the study of mixed and mixed polynuclear complexes, have been very extensive in recent years. A study of mixed ligand complex formation is of extreme interest to analytical chemists for the following reasons.

- Mixed ligand complexes are the most general and probable form of existence of the elements in solution. Studies of mixed ligand complex formation make it possible to estimate the characteristics of the intermediate and final forms of the complexes, and therefore to comprehend the mechanism and kinetics of analytical reactions.
- Certain peculiarities of elements, which are most pronounced in mixed ligand complexes, as well as the physical phenomena accompanying the process of

mixed ligand complex formation, open new prospects for the development of selective and sensitive methods for the determination, separation and concentration of elements. The quantitative evaluation of these physical phenomena enables solution of the problems of the composition and stability of mixed ligand complexes.

- The processes of mixed ligand complex formation are closely bound up with one of the most challenging problems in modern analytical chemistry—the problem of extraction. Hence it becomes clear why the number of publications on the experimental study, theoretical generalization and practical use of mixed ligand complexes increases at such speed. At the present time there is a large number of physicochemical methods for the identification of mixed ligand complexes in solutions. These are spectroscopic methods, such as electron absorption spectra, Raman spectra, electron paramagnetic resonance spectra, Mössbauer spectra and fluorescence spectra.
- In addition, electrochemical methods, such as potentiometric, conductometric and high-frequency titrations, polarography and high-voltage ionic electrophoresis find general application refractometry and measurements of the solution viscosity are also used. The absorption spectroscopic and electron paramagnetic resonance methods should be considered as the most reliable. These methods are used not only for the qualitative detection of mixed ligand complexes in solution, but also for the quantitative study of their formation, composition and stability.
- Many of the factors that control the processes of mixed ligand complex formation, and determine the composition and stability of mixed ligand complexes, have already been established. Such factors as the electronic structure of the central atom and its coordination number, the donor nature of ligands and the mutual effect of ligands in a mixed ligand complex, the geometric structure of the complex and the coordination equilibria in solutions of mixed ligand complexes, have been studied for a large number of examples. The theoretical studies of these

factors and their generalization from the viewpoints of polarization theory 2, charge neutralization3 and asymmetry of the ligand field4, have made it possible to choose the most suitable ligands arid to predict the probability of formation and the properties of mixed ligand complexes.

- However, the complexity of this field of coordination chemistry still perplexes many chemists, and various theoretical problems, as well as practical problems closely connected with them, have not yet been solved. For example, investigations in the thermodynamics of mixed ligand complexes have been limited to data on the values of isobaric potential, which shows only the general direction of the mixed ligand complex formation.
- There are practically no data on the change of entropy and enthalpy values during the formation of mixed ligand complexes and these are the values that reflect changes in the nature of the metal—ligand bond when one turns from simple to mixed compounds (MI), as well as various structural changes in solutions and various configuration equilibria (1S). The reasons for the extreme stability of mixed ligand complexes as compared with simple complexes would be much more readily explained if every step of the mixed ligand complex formation could be characterized by the complete thermodynamic functions. Unfortunately, at present this question is being solved only by the ratio of stepwise stability constants. It is not yet possible to describe with sufficient certainty, the mechanism of extraction of metal chelates with neutral donors, or to elucidate fully their composition, because reliable data on the interaction of a chelating agent (HA) with neutral donors (B) (HAB, HAB2, H2A2B, etc.) or with the solvent molecules are not always available.
- The extraction of a metal with two chelating agents or with the participation of two neutral donors seems to be a very interesting but not sufficiently studied problem, as well as the problem of metal coextraction as mixed polynuclear complexes.

1.3 Isoniazid

Isoniazid, also known as isonicotinylhydrazide (INH), is an antibiotic used for the treating tuberculosis. For active tuberculosis it is often used together with rifampicin, pyrazinamide, and either streptomycin or ethambutol. For latent tuberculosis it is often used by itself. It may also be used for a typical types of mycobacteria, such as *M. avium*, *M. kansasii*, and *M. xenopi*. It is usually taken by mouth but may be used by injection into muscle. Isoniazid was first made in 1952. It is on the World Health Organization's List of Essential Medicines, the most effective and safe medicines needed in a health system. Isoniazid is available as a generic medication.

Isoniazid is often used to treat latent and active tuberculosis infections. In persons with isoniazid-sensitive Mycobacterium tuberculosis infection, drug regimens based on isoniazid are usually effective when persons adhere to the prescribed treatment. However, in persons with isoniazid-resistant Mycobacterium tuberculosis infection, drug regimens based on isoniazid have a high rate of failure.

Isoniazid has been approved as prophylactic therapy for the following populations. People with HIV infection and a PPD (purified protein derivative) reaction of at least 5 mm induration. Contacts of people with tuberculosis and who have a PPD reaction at least 5 mm induration. People whose PPD reactions convert from negative to positive in a two-year period – at least 10 mm induration for those up to 35 years of age, and at least 15 mm induration for those at least 35 years old. People with pulmonary damage on their chest X-ray that is likely to be due to healed tuberculosis and also have a PPD reaction at least 5 mm induration. Injection drug users whose HIV status is negative who have a PPD reaction at least 10 mm in duration. People with a PPD of greater than or equal to 10 mm induration who are foreign-born from high prevalence geographical regions, low-income populations, and patients residing in long-term facilities.

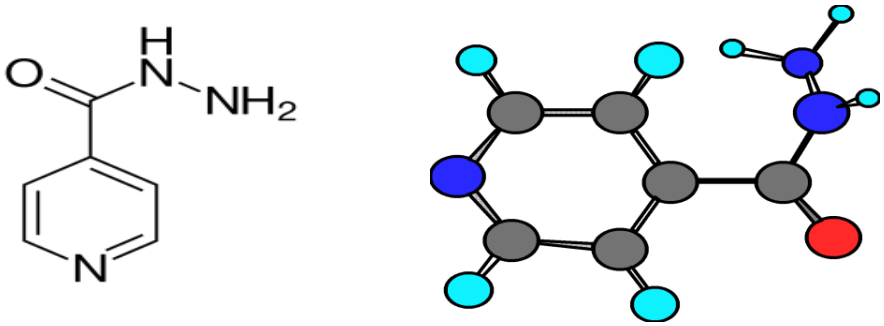


Fig 1.3 Structure of Isoniazid

4 Cadmium

Cadmium is a chemical element with symbol **Cd** and atomic number 48. This soft, bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and mercury. Like zinc, it demonstrates oxidation state +2 in most of its compounds, and like mercury, it has a lower melting point than the transition metals in groups 3 through 11. Cadmium and its congeners in group 12 are often not considered transition metals, in that they do not have partly filled *d* or *f* electron shells in the elemental or common oxidation states. The average concentration of cadmium in Earth's crust is between 0.1 and 0.5 parts per million (ppm). It was discovered in 1817 simultaneously by Stromeyer and Hermann, both in Germany, as an impurity in zinc carbonate.

Cadmium occurs as a minor component in most zinc ores and is a by product of zinc production. Cadmium was used for a long time as a corrosion-resistant plating on steel, and cadmium compounds are used as red, orange and yellow pigments, to color glass, and to stabilize plastic. Cadmium use is generally decreasing because it is toxic (it is specifically listed in the European Restriction of Hazardous Substances) and nickel-cadmium batteries have been replaced with nickel-metal hydride and lithium-ion batteries. One of its few new uses is cadmium telluride solar panels.

Although cadmium has no known biological function in higher organisms, a cadmium-dependent carbonic anhydrase has been found in marine diatoms. Cadmium has no known function in higher organisms, but a cadmium-dependent carbonic anhydrase has been found in some marine diatoms.

The diatoms live in environments with very low zinc concentrations and cadmium performs the function normally carried out by zinc in other anhydrases. This was discovered with X-ray absorption fluorescence spectroscopy (XAFS).

Fig 1.4 Image of Cadmium

The highest concentration of cadmium is absorbed in the kidneys of humans, and up to about 30 mg of cadmium is commonly inhaled throughout human childhood and adolescence. Cadmium is under preliminary research for its toxicity in humans, potentially affecting mechanisms and risks of cancer, cardiovascular disease, and osteoporosis. The biogeochemistry of cadmium and its release to the environment has been the subject of review, as has the speciation of cadmium in the environment.

1.5 Thiocyanate

Molecular formula: CNS^-

Molar mass: 58.0824

Thiocyanate (also known as sulphocyanate or thiocyanide or rhodanide) is the anion, $[SCN]^-$. Common compounds include the colourless salts potassium thiocyanate and sodium thiocyanate.

Organic compounds containing the functional group SCN are also called thiocyanates. Mercury(II) thiocyanate was formerly used in pyrotechnics.

Thiocyanate is analogous to the cyanate ion, $[OCN]^-$, where in oxygen is replaced by sulphur. $[SCN]^-$ is one of the pseudohalides, due to the similarity of its reactions to that of halide ions. Thiocyanate was formerly known as rhodanide (from a Greek word for rose) because of the red colour of its complexes with iron. Thiocyanate is produced by the reaction of elemental sulfur or thiosulfate with cyanide.

$$8\ CN^- + S_8 \rightarrow 8\ SCN^-$$

$$CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$$

The latter reaction is catalyzed by the enzyme sulfotransferase known as rhodanase and may be relevant to detoxification of cyanide in the body.

Structure, bonding and coordination chemistry

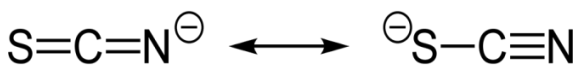


Fig 1.5 Resonance structures of the thiocyanate ion

Thiocyanate shares its negative charge approximately equally between sulphur and nitrogen. Consequently, thiocyanate can act as a nucleophile at either sulfur or nitrogen — it is an ambidentate ligand. $[SCN]^-$ can also bridge two (M−SCN−M) or even three metals (>SCN^- or $^-$SCN<). Experimental evidence leads to the general conclusion that class a metals (hard acids) tend to form N-bonded thiocyanate complexes, whereas class b metals (soft acids) tend to form S-bonded thiocyanate complexes. Other factors, e.g. kinetics and solubility, are sometimes involved, and linkage isomerism can occur, for example $[Co(NH_3)_5(NCS)]Cl_2$ and $[Co(NH3)_5(SCN)]Cl_2$.

1.6 ANTI MICROBIAL STUDIES

Antibacterial resistance is becoming an important and challenging problem with the rapid increase in number of the multidrug resistant microbial pathogens. Some previously treatable pathogens are now becoming untreatable, like methicillin-resistant staphylococcus aurous and vanomycin –resistant entercoccus, isoniazid resistant M.tuberculosis and klebsiell pneumonia. In spite of a large number of antibiotics and chemotherapeutics available for medical use, at the same time the emergence of old and new antibiotics resistance created in the last decades revealed a substantial medical need for new classes of antimicrobial agents. Due to the outbreak of infectious diseases caused by different pathogenic bacteria and the development of antibiotic resistance, researchers are searching for new antibacterial agents.

The treatment of infectious diseases still remains an important and challenging problem because of a combination of factors including emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens. In spite of a large number of antibiotics and chemotherapeutics available for medical use, at the same time emergence of old and new antibiotic resistance created in the last decades revealed a substantial medical need for new classes of antimicrobial agents. There is a real perceived need for the discovery of new compounds endowed with antimicrobial activity, possibly acting through mechanism of action, which is distinct from those of well-known classes of antimicrobial agents to which many clinically relevant pathogens are now resistant.

Due to outbreak of infectious diseases caused by different pathogenic bacteria and the development of antibiotic resistance, researchers are searching for new antibacterial agents. Therefore, new antimicrobial agents and nanotechnological materials have to be synthesized for the treatment of resistant bacterial diseases. The field of bioinorganic chemistry, which deals with the study of role of metal complexes in biological systems, has opened a new horizon for scientific research in coordination compounds. A large number of compounds are important from the biological point of view.

Biologically relevant metal complexes have several requirements in terms of their synthetic design.

First, a biologically active metal complex should have a sufficiently high thermodynamic stability to deliver the metal to the active site. The metal-ligand binding should be hydrolytically stable. The kinetics with which the metal ion undergoes ligation or deligation reactions is of great importance. The molecular weight of the metal complex is also critical. The compounds of low molecular weight with neutral charge and some water solubility are soluble in almost any medium and may slip through biological membranes by passive diffusion.

Generally, drug combinations have proven to be an essential feature of antimicrobial treatment due to a number of important considerations; (1) they increase activity through the use of compounds with synergistic or additive activity; (2) they thwart drug resistance; (3) they decrease required doses, reducing both cost and the chances of toxic side effects; (4) they increase the spectrum of activity.

Fig 1.6 Image of bacteria

AIM AND SCOPE

Aim and Scope

The present work aims at the preparation of the coordination complex of cadmium using Isoniazid and Ammonium thiocyanate as ligands.

To arrive at the composition and structure of the complexes, it is proposed to

1. **Measure the electrical conductivity of complex solution in acetonitrile, to find whether the complex is ionic or neutral.**
2. **Compare the infrared spectra of complexes with those of parent ligand, to determine the coordination position of the ligands.**
3. **Record the electronic spectra of the complexes, which will throw light on the probable geometry of the complexes.**
4. **To test the antimicrobial activity of the complex and pure ligand.**

REVIEW OF LITERATURE

1. Complexation of nicotinamide with Ag+ ions in water - organic solvents was published in the Journal of inorganic chemistry volume 51 on 30th march 2006 by M.A.Zevakin, K.v.Grazhdan, V.A.Sharnin and S.V.Dushina.

2. In 2006, thermal study of Zn(II) chlorosalicylate complex compounds with bioactive ligands such as Thiourea, nicotinamide and caffeine was published by Gyoryova Katarina, Chomic.J, Szunyogoba Eirka, Piknova Lenka,zelenak V and Vargova zuzana in the Journal of thermal analysis and calorimetry.

3. The enthalpies of complex formation between nicotinamide and copper(II) percolate in aqueous ethanol and DMSO were determined calorimetrically by A.S.Kursheva, S.F.Ledenkov and V.A.Sharnin and was published in the Journal of physical chemistry on July 25th 2006.

4. Synthesis and characterization of molecular structure and properties of the generated Cu(II) and Ni(II) complexes was reported by particia A.M.Williams, Natialia Bolza and published in Indian Journal of chemistry on 15th Jan 2005.

5. Synthesis and characterization of three 5-(4-pyridyl)tetrazolato complexes obtained by reaction of 4-cyanopyridine with metal azides from aqueous solutions was reported by Mauter Franz A., Gspan Chiristian, Gatterer Karl, Gohr Mohamed A.S.,Abuyoussey Morsy A.M., Bucher Edith and Sittle Werner in 2005 in the Journal of physical chemistry.

6. A study of copper (II) carboxylato complexes with the ligand nicotinamide was reported by Christina J.Williams, HarryMorris in 2003 was published in Journal of molecular structure.

7. In 2003, Balachandran Unni Nair and Thomas Eyhermuller was reported the preparation and structure of a dinuclear iron (II) complex with six terminally coordinated azides and published in the central research institute of America.

8. Molecular structure and properties of copper(II), Nickel(II) complexes was published on the online.

9. Spectroscopic and Lumimescence properties of an isonicotinic acid was reported by P.Starynowicz in the Journal of celal bayer university.

10. Analyses of co-operative transition in acyl carrier protein redutase upon cofactor and acyl carrier protein binding was published by N.Surolia in Jawaharlal Nehrua centre of advanced scientific research, on 17th Aug 2004.

11. A crystal structure and properties of Cu(II) complex containing azide ion was published in the Journal of coordination chemistry.

12. A Study of copper(II) carboxylato with the ligand nicotinamide was reported by Jan moncol, Milan melnik, Feder valach in the Journal of transistion metal chemistry on 24th July2003,p.53-60.

13. Michael G.Finnegan et al have reported the synthesis and UV-Visible, solution IR and EPR spectroscopy of (porphinato) iron (III) nitrite complexes.

14. Scarpellini marciele et al have reported the synthesis and characterization of the new copper (II) – nitrite complex.

15. Synthesis and structure of catena_poly[bis(nicotinamide-kN)copper(I)]-μ-thiocyanato-k^2 N:S] was reported by Christian nather and Inke Jeb in 2002 and published in acta crystallographic section c volume 58(3), P190-192-march 2002.

16. The mixed ligand complexes have been characterized on the basic of elemental analysis, electrical conductance, room temperature, magnetic susceptibility measurements, spectral and thermal studies. Probable structures have been suggested for the mixed ligand complexes on the basic of the results of elemental analysis and various physico-chemical studies.

17. Mixed ligand nickel (II), copper(II) and zinc(II) complexes of nicotinanilide and thiocyanate were prepared and their electrochemical and biological properties were discussed [48]. Balan et.al have studied the structure of nicotinanilide and thiocyanate metal complexes. He performed cyclic voltammetric studies for all the complexes and differentiated the oxidation and reduction processes and indicated that the CV studies exhibit one electron irreversible process.

18. Microwave-associated synthesis of mixed ligand complexes of Zn(II), Cd(II) and Hg(II) derived from 4- aminopyridine and nitrite ion were reported by Dhaveethu et.al [49]. Microwave assisted synthesis and structural characterization of nicotinic acid and nitrito-ko mixed ligand complexes were reported and their geometry was interpreted by various characterization techniques.

19. Foziah et.al have reported the thermal studies of the alkaline earth metal nicotinamide complexes. She proposed that the complexes are non electrolytic in nature and the anions are coordinated to the central metal ion.

20. Guang et.al have reported the synthesis and crystal structure of non-interpenetrating metal organic coordination networks constructed from Cd(II) with thiocyanate and nicotinic acid. By using bridging ligands instead of monodentate ligands, they are successfully extended the one dimensional chain structure into two dimensional networks through covalent or the hydrogen bonds.

21. Bio potential efficiency and DNA cleavage applications have been reported for mixed ligand complexes using nicotinamide and nitrite as primary and secondary ligands respectively.

22. Marijina et.al reported the thiocyanate complexes of group 12 metals with pyridine-2- carboxamide and the crystal structure of the complexes have been elucidated by X-ray diffractometer. Here the thiocyanate shows a number of bonding modes with group 12 metals as terminal and bridging ligand. In the structure investigation of Zn and Hg complexes with thiocyanate, the authors proposed that both the N-donor and S-donor thiocyanate ligands can act as a bridged and terminal which are coordinated to mercury in a nonlinear fashion whereas the coordination sphere along the zinc ions are distorted tetrahedral in structure.

23. It was proposed that the nicotinamide complexes are six coordinate with a metal ion through nitrogen atom. Chandrasekaran et.al have reported the synthesis and characterization of metal complexes with FCNH ligand. He proposed that the ligand coordinate to the metal as a neutral bidentate ligand and possess octahedral geometry.

24. Sabbir et.al have prepared the nicotinamide complexes in aqueous medium in the ratio 2:1. They conclude that the compounds do not contain any chemically coordinated water molecules.

25. Lawal et.al have confirmed that the nicotinamide co-ordinate to the metals ions through the pyridine ring nitrogen atom. Nicotinamide act as a chelating ligand and it possesses good antimicrobial and antifungal activity.

26. Khawla have proposed the structure of the mixed ligand complexes with isoniazid and aminoacids to be distorted octahedral. These complexes show positive activity against tuberculosis bacteria.

CHARACTERIZATION TECHNIQUES

Chapter- 4

4.1 Solubility method

The newly synthesized complexes were tested for solubility, in different solvents. Sometimes the complex formation increases the solubility of sparingly soluble salts. For example, silver cyanide is sparingly soluble in water but on the addition of KCN, its solubility increases due to complex formation.

$$AgCN + KCN \rightarrow K[Ag(CN)_2]$$

$$K[Ag(CN)_2] \rightarrow K^+ + [Ag(CN)_2]^-$$

4.2 Conductivity method

Complex ion formation can be conveniently identified by conductivity measurements. Usually central metal atom combines with ligands (ions or molecules) to give complexes. During this process, there will be an appreciable change in the conductivity of the solution .For example, if metal ion combines with ligands to form a complex, there will be an appreciable drop in the conductivity of the solution, as the number of ions decreases during the above process.

Measurements of molar conductance of complexes

The conductance is a measure of the ease with which the current is passed through the solution. Equivalent conductance is generally used in the case in the study of electrolytic solution. However, in the case of complex compounds, molar conductance rather than the equivalent conductance is of immense importance. Molar conductance of a substance depends on the number of ions present in the solution, degree of dissociation, mobility of ions and temperature. Measurements of molar conductance, M at large dilutions gives information with regard to the number of electrical charges i.e., the sum of the charges on positive and negative and the number of charges furnished by a molecule of complex compound.

In general, the molar concentration of the order 10^{-3} M was used for the study

Molar conductance, M = 1000 K/ Concentration

Where, K is the specific conductance of solution in ohm^{-1} cm^{-1}

Accordingly, to the molar conductance values, the formula of the complex whether it is associated or dissociated or polymeric might be assigned.

4.3 Infrared spectroscopy

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14000–4000 cm^{-1} (0.7–2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond or collection of bonds, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency (or wavelength). This measurement can be achieved by scanning the wavelength range using a monochromator. Alternatively, the entire wavelength range is measured using a Fourier transform instrument and then a transmittance or absorbance spectrum. This technique is commonly used for analyzing samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity.

More complex molecular structures lead to more absorption bands and more complex spectra.

4.4 Electronic Spectroscopy

This is also known as UV-vis spectroscopy and covers the region from 200 to 800 nm of the electromagnetic spectrum. The region from 200 to 400 nm is called the ultraviolet (UV) and that from 400 to 800 nm is known as the visible region. A substance appeared colored when the emitted light falls in this visible region. This spectroscopy is used to find out the geometry of complexes because the number of bands seen in the visible region due to d-d transitions depends on the geometry of the complex. The aqueous solutions of transition metal ions are differently colored. Some examples are given below: Complex color $[Co(H_2O)_6]^{2+}$ is pink $[CoCl_4]^{2-}$ is blue. The different colors are due to the transition of electrons from one d level to another d level. These are called d-d transitions and the energy falls in the visible region of the electromagnetic spectrum. The color of the solution seen is the complementary color of the light absorbed by the solution.

If the color of the aqueous solution is due to the transition of electrons from one d level to another d level, there should be only one color. But the fact that different colors are seen for different compounds shows that the d orbitals are at different energy levels and hence there is not only one transition but many. In order to understand this, the splitting of d orbitals in different environments is to be understood. The splitting depends up on the geometry of the complex, the nature of the ligands present, and the oxidation state of the central metal atom.

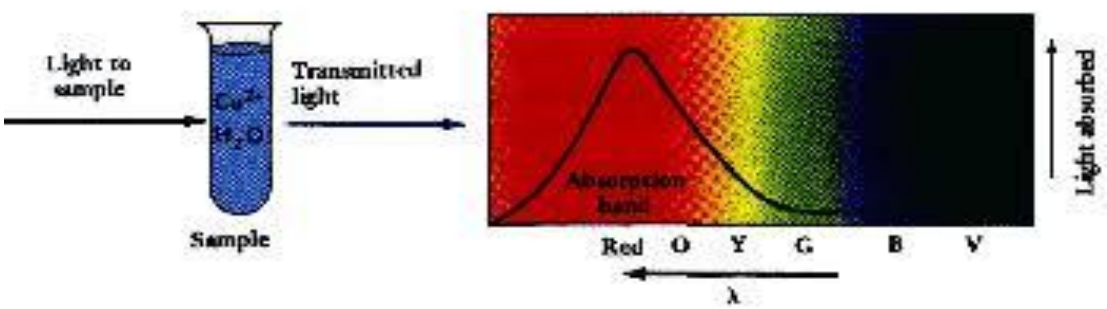


Fig 4.4 Electronic spectrum

The energy required for the promotion of an electron from one orbital to another or, more precisely, the excitation of a molecule from its electronic ground state to an electronic excited state, corresponds to absorption of light in the near-infrared, visible or ultraviolet regions of the spectrum. For transition metal complexes the absorption bands in the first two of these regions are relatively weak and are associated with transitions largely localized on the metal atom. The ultraviolet bands are intense. They are associated with the transfer of an electron from one atom to another and so are called *charge-transfer* bands. These bands are responsible for the colour changes associated with indicators for inorganic cations, such as the thiocyanate test for Fe^{III} or the indicators used in EDTA (Complexometric) titrations, but in these cases the charge-transfer bands fall in the visible region of the spectrum.

4.5 NMR Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is an information rich, non-destructive analytical technique. It provides detailed information about molecular structure, dynamic processes and allows the direct observation of chemical reactions. It is also a primary quantitative method allowing the determination of concentration of molecules even in complex mixtures. In addition to the well-known observation of hydrogen, carbon, fluorine and phosphorous it can be used on a large number of other elements.

NMR is an indispensable tool in chemistry. From structure elucidation and verification to monitoring of reactions, organic chemistry cannot be imagined without this powerful analytical method. In other areas of chemistry, NMR provides rare insight into such aspects as structure of catalysts, the state and reactions of electrolytes in batteries.

A significant proportion of biological research using NMR is thus focused on the structure of, and interaction between proteins. This is complemented with metabolic studies to determine the relative quantities of endogenous metabolites. Together, they have facilitated elucidation of numerous biological processes and their responses to external stimuli at a molecular level.

4.6 Biological studies

Antibacterial study

The treatment of infectious diseases still remains an important and challenging problem because of a combination of factors including emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens. In spite of a large number of antibiotics and chemotherapeutics available for medical use, at the same time the emergence of old and new antibiotic resistance created in the last decades revealed a substantial medical need for new classes of antimicrobial agents. mechanism of action, which is distinct from those of well-known classes of antimicrobial agents to which many clinically relevant pathogens are now resistant The field of bioinorganic chemistry, which deals with the study of role of metal complexes in biological systems, has opened a new horizon for scientific research in coordination compounds[51]. A large number of compounds are important from the biological point of view. The variation in the activity of different complexes against different organisms depends either on the impermeability of cells of the microbes or differences in the ribosomes of microbial cells.

Many researchers have studied characterization, antimicrobial and toxicological activity of mixed ligand complexes of transition metals. The role of mixed ligand complexes in biological process has been well recognized. Anti-tumor activity of some mixed ligand complexes has also been reported. The antibacterial and anti-fungal properties of a range of copper(II) complexes have been evaluated against several pathogenic bacteria and fungi. The metal complexes have been characterized by elemental analysis and various physico-chemical techniques such as molar conductance, magnetic susceptibility, electronic spectra, IR spectra and thermal studies.

4.6.1 Disc Diffusion method

The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of the test compounds is expressed by measuring the diameter of zone of inhibition.

Generally, the more susceptible the organisms, the bigger the zone of inhibition.

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibilition by test compound (diamter)}}{\text{Zone of inhibilition by standard (diamter)}} \times 100$$

The nutrient medium was prepared by following composition like Yeast extract- 5 g, Meat extract-10 g, Peptone-5 g, Sodium Chloride-5 g, Agar-20 g. The antibacterial activity of the compound was done by the disc diffusion method using DMSO as solvent. The test solutions were prepared by dissolving the compounds in DMSO.

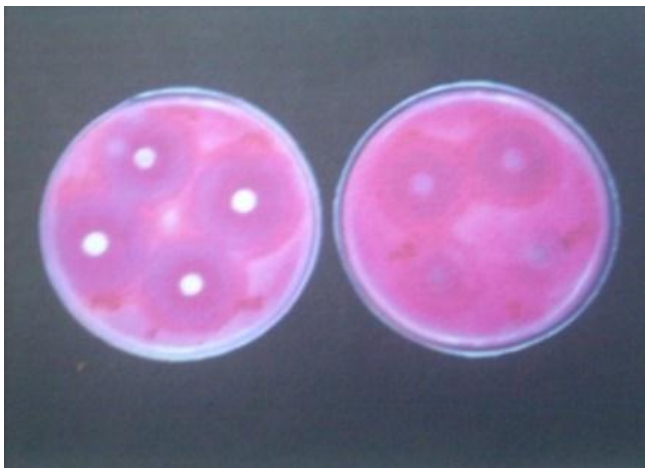
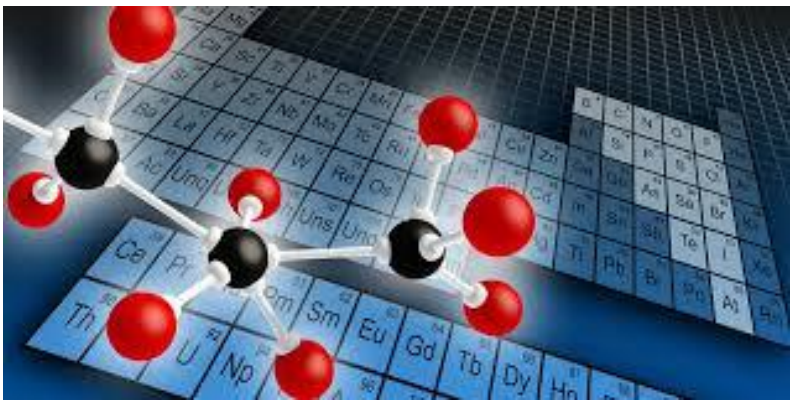


Figure 4.6.1 Disc diffusion method sample

In a typical procedure, agar medium was inoculated with microorganisms and it is filled with the test solution using micropipette and the plate is incubated at 35˚C for 24 to 48 hr. During this period, the test solution diffuses and the growth of the inoculated microorganism *E. Coli*, is found to be affected. The activity developed on the plate is measured by measuring the diameter of the inhibited zone in millimeters.

RESULTS AND DISCUSSION



Chapter- 5

Results and Discussion

5.1 PREPARATION OF MIXED LIGAND COMPLEXES

Chemicals required

Isoniazid (1.37g)

Cadmium Chloride (2.0g)

Thiocyanate (0.76g)

Procedure

About 2.0g of Cadmium chloride was dissolved in water and mixed with about 1.37g of Isoniazid in water. The mixture was heated and cooled. Then aqueous solution of Thiocyanate (0.76g) was added and shaken well.

The white precipitate was obtained and filtered through whatmann filter paper. It was dried and kept in air tight container.

Solubility

The solubility of the newly synthesized complex was found out by using different solvents.

5.2 Physicochemical properties

The physico chemical properties of the newly synthesized complex were analyzed and the conductance measurements were tabulated.

5.2.1 Electrical conductivity

The electrical conductivity of 10^{-3} M solution of the complex was found out. This observation reveals the neutral nature (non-electrolytic nature) of the complex.

S. No	Parameters	Observation
1.	Conductance (Ω^{-1} mol^{-1} cm^2)	18
2.	Colour	White
3.	Yield %	80
4.	Solubility	water
5.	Molecular formula	$C_{14}H_{14}CdN_8O_2S_2$
6.	Molecular Weight	502.9
7.	Elemental Analysis	
	C- 33.44, H- 2.81, Cd- 22.35, N- 22.28, O- 6.36, S- 12.75	

Table 5.2 Physicochemical parameters for the complex $[Cd(INH)_2(NCS)_2]$

5.3 IR Spectra

The structure of Isoniazid ligand and the metal complex has been confirmed by Infrared spectroscopy. The characteristic bands in infrared spectrum of the ligand and its metal complex are reported in table 5.3.

S.No	Complex	υNH_2		$\upsilon C=O$	$\upsilon C=N$	$\upsilon M-O$	$\upsilon M-N$	υCN of SCN	υCS of SCN
		Sym	Asy						
1	Isoniazid	3113	3304	1667	1556	-	-	-	-
2	$[Cd(INH)_2(NCS)_2]$	3198	3284	1663	1550	515	572	2090	860

Table 5.3 IR spectral data for the complex $[Cd(INH)_2(NCS)_2]$

The Isoniazid exhibits peaks at 3113 and 3304 cm^{-1} which corresponds to symmetric and asymmetric stretching of υUH_2 group. The nitrogen atom involves in the complexation and hence this peak seems to be broad in cadmium complex. Then NH_2 bond for Isoniazid is seen at 3198 cm^{-1} which possess positive shift in the complex the $\upsilon C=O$ for free isoniazid has been observed at 1667 cm^{-1} whereas for cadmium complex it was shifted to 1663 cm^{-1} predicting that the metal ion is coordinated through the C=O group. These observation indicates that the isoniazid ligand acts as a bidentate ligand coordinating through both the C=O and NH_2 group. The peaks at the range of 500 cm^{-1} were attributed to $\upsilon M-O$ and $\upsilon M-N$ vibrations . These frequencies were not seen in pure Isoniazid ligand. The pyridine ring vibration at 698 cm^{-1} for copper complex predicts that the pyridine ring nitrogen does not involve in coordination. In metal complex, the thiocyanate ion acts as an ambidentate ligand at the mode of the coordination either through N atom or S atom and it can be predicted by the characteristic IR peaks. The first transition series metals form M-N bonds whereas the second transition series metals form M-S bond. The mode of bonding in thiocyanate complexes can be determined by their vibrational modes of the thiocyanate ion.

The $\upsilon C-N$ of the N-bonded complexes lies in the range of 2050 cm^{-1} and at 2100 cm^{-1} for S-bonded complexes M-NCS-M bond shows the peaks >2100 cm^{-1}. $\upsilon C-S$ for N-bonded complexes exhibits frequencies in the range 860-780 cm^{-1}, whereas for S-bonded complexes 720-690 cm^{-1}. These bonds are weak .$\upsilon C-S$ values for $M(NCS)_2L_2$ tetrahedral complexes are high than the $M(NCS)_2L_4$ octahedral complexes.

The υC=N of bridging is higher than υC=N of terminal. The υC=N band appears at 2090 cm^{-1} indicating that the thiocyanate ligand N- bonded. The υC=S bands at 860 cm^{-1} provides evidence for N-bonded complex. The absence of peak at 2100 cm^{-1} predicts absence of bridging S-C-N bond. Hence the cadmium complex will be a N-bond terminal NCS complex.

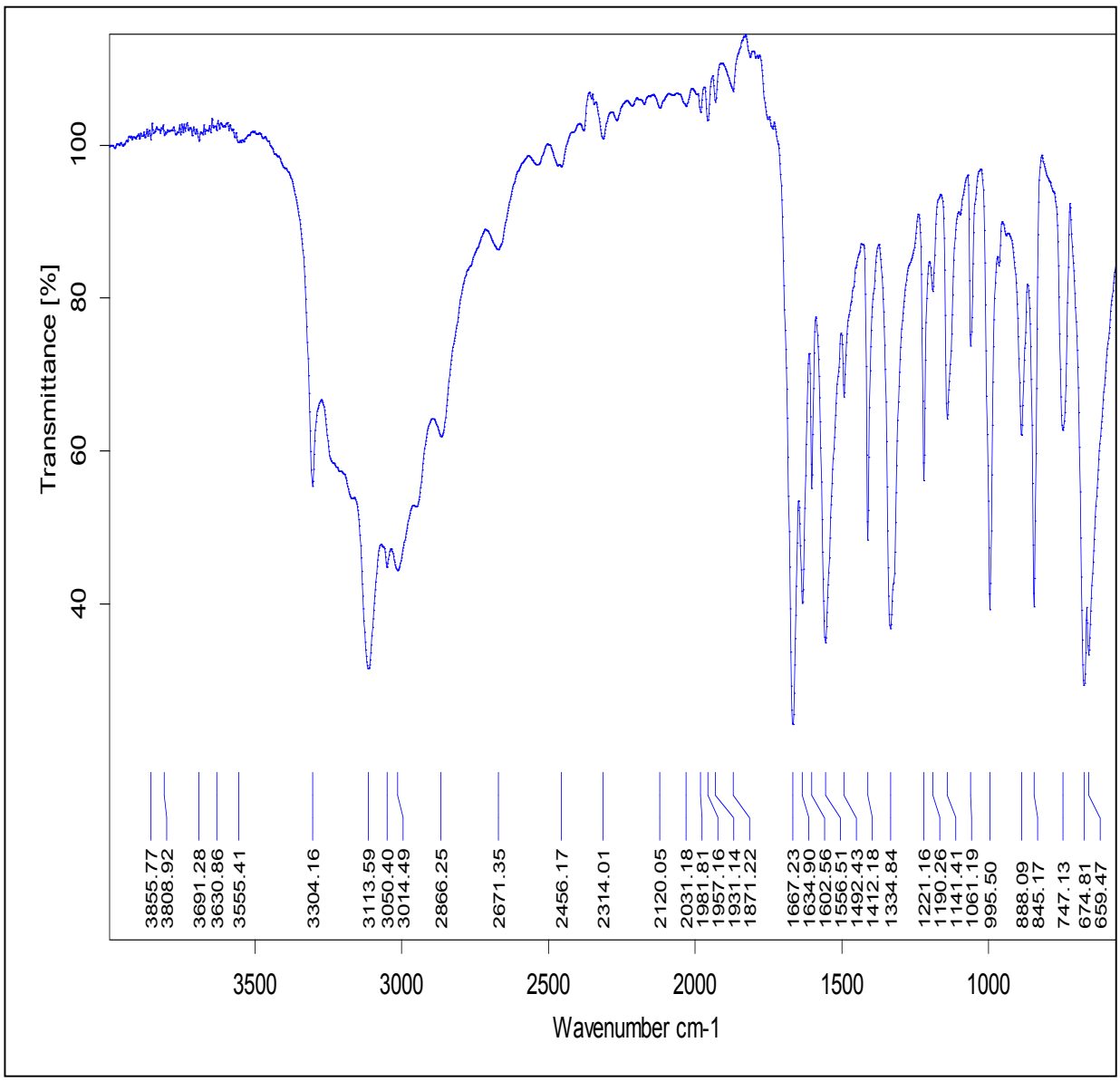


Fig 5.3 I R spectrum of pure Isoniazid

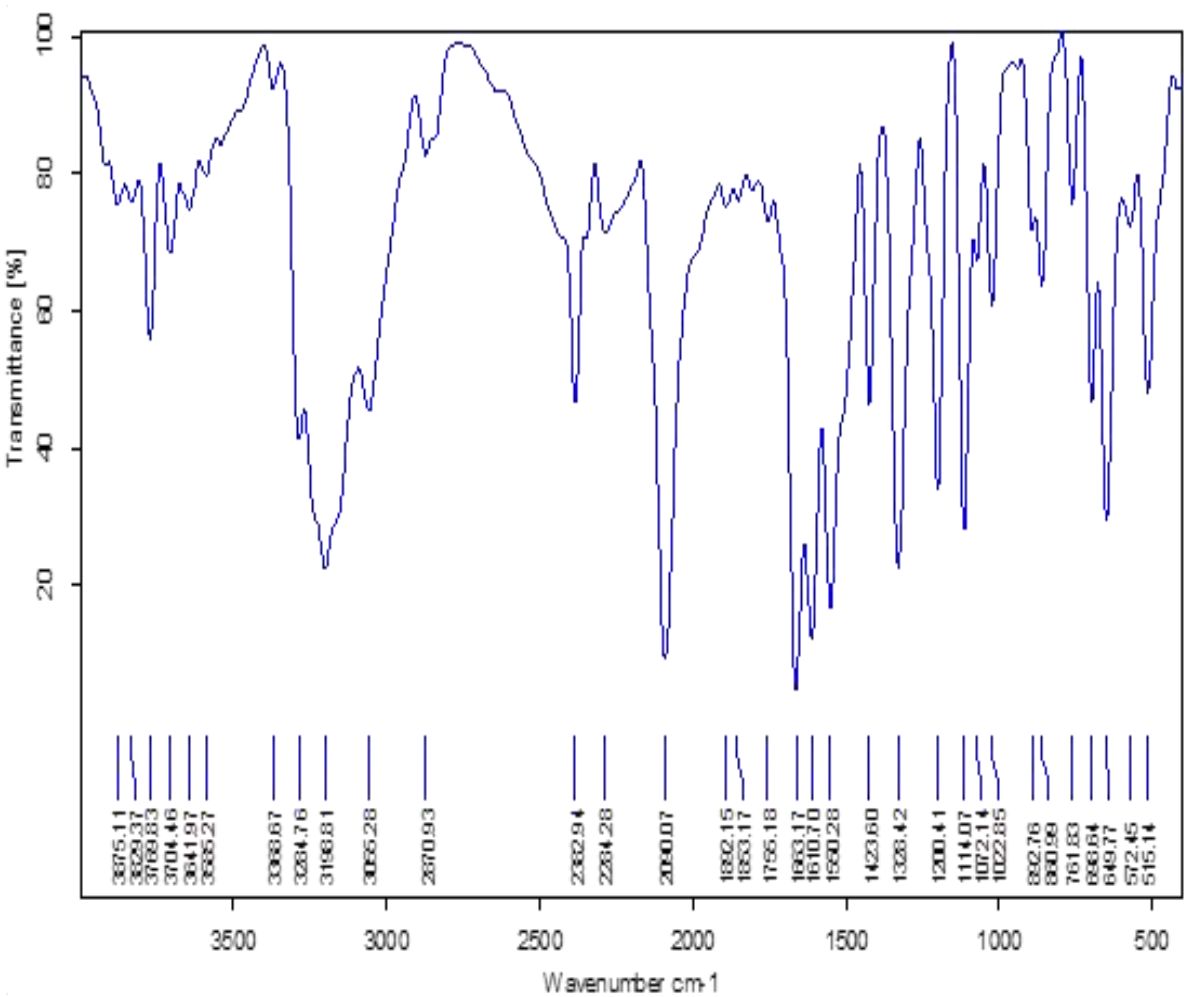


Fig 5.3.1 I R Spectrum of the complex $[Cd(INH)_2(NCS)_2]$

Sno	Complex	Absorption maxima		Transition Assignments	Probable geometry
		λ_{max} nm	cm^{-1}		
1	$Cd(INH)_2(NCS)_2$	207 264	48309.18 37878.79	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Distorted Octahedral

Table 5.4 Electronic spectral data for the complex $[Cd(INH)_2(NCS)_2]$

The UV-Visible spectra of the complexes were obtained in the range of 200-800 nm. The absorption arising from the transfer of an electron either, from a ligand orbital to the metal orbital (L → M) or from the metal orbital to a ligand orbital (M → L) in a complex is called the charge transfer spectrum. Charge transfer (CT) transitions do not violate the usual selection rules. Charge transfer transitions, unlike d-d transitions are normally neither multiplicity forbidden nor Laporte forbidden; therefore, they produce strong absorption bands. Such strong bands enable charge – transfer absorption to be distinguished from d-d transitions in a complex. The charge transfer bands have extinction coefficients in the 500- 2000 unit range (for d-d transitions, the coefficients are below 100 unit). These bands mostly occur in the near ultraviolet region. In the spectra of some complexes, an overlap between the end for the charge-transfer band and a d-d spectrum of the complex is impossible.

A CT transition is an intramolecular transition. Electronic transition from an orbital localized mainly on one atom to an orbital localized mainly on another atom occurs. This requires much higher energies than a d-d transition . The L→ M transfer is exhibited by complexes containing the ligands O^{2-}, Cl^{-}, Br^{-} and I^{-}. The M→L charge transfer occurs in complexes containing ligands which have stable but empty orbitals. Ligands such as NO, CO and CN which are the acceptor ligands, cause such M→L absorption bands. The organic ligands, such as pyridine, bipyridine and o-phenanthroline have empty antibonding orbitals which favour M→L transfer.

The synthesized cadmium complex exhibits two peaks at 207nm and 264nm which corresponds to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. These peaks denoted that the Cadmium complex may possess distorted octahedral geometry.

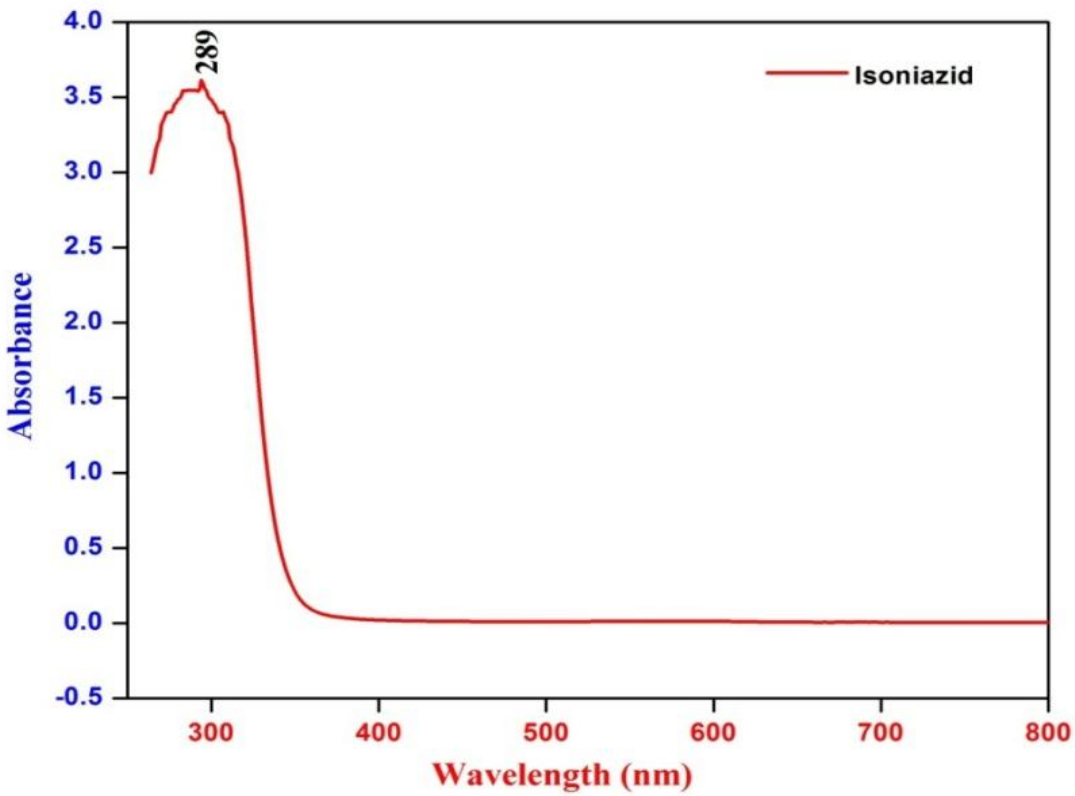


Figure.5.4 Electronic spectrum of Pure Isoniazid

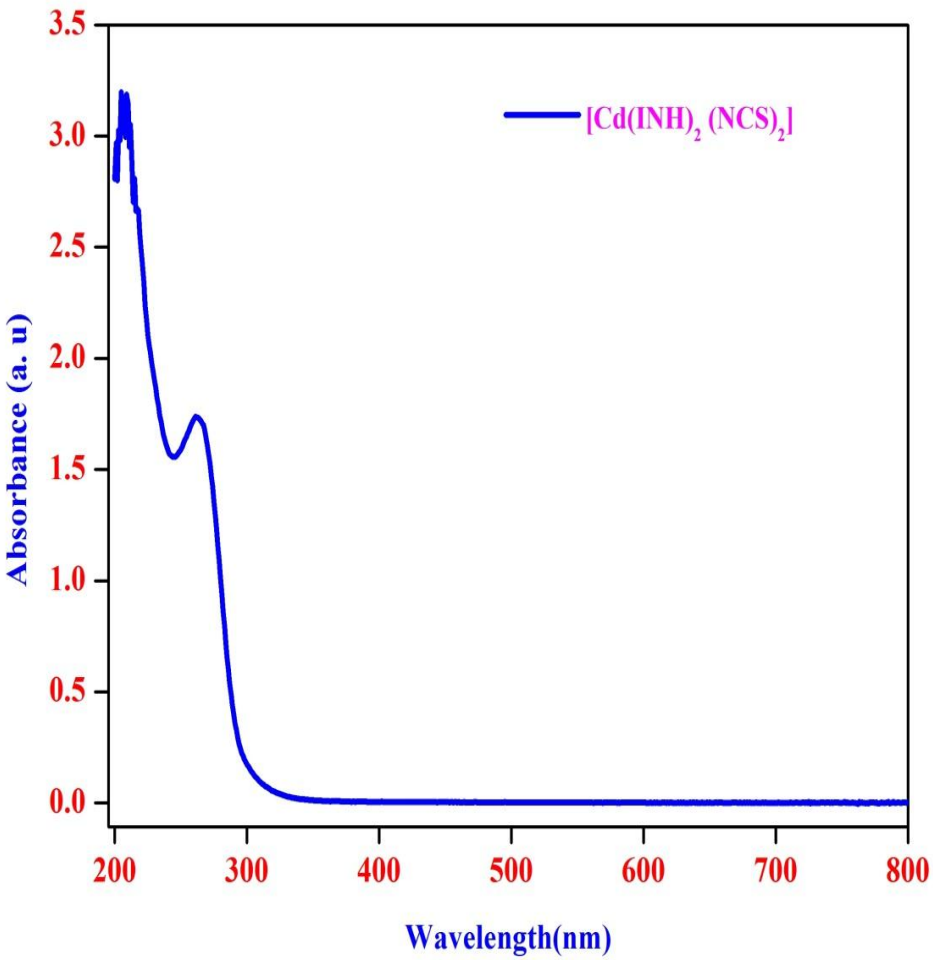


Figure.5.4. 1 Electronic spectrum of the complex $[Cd(INH)_2(NCS)_2]$

5.5 ^{1}H NMR Spectra

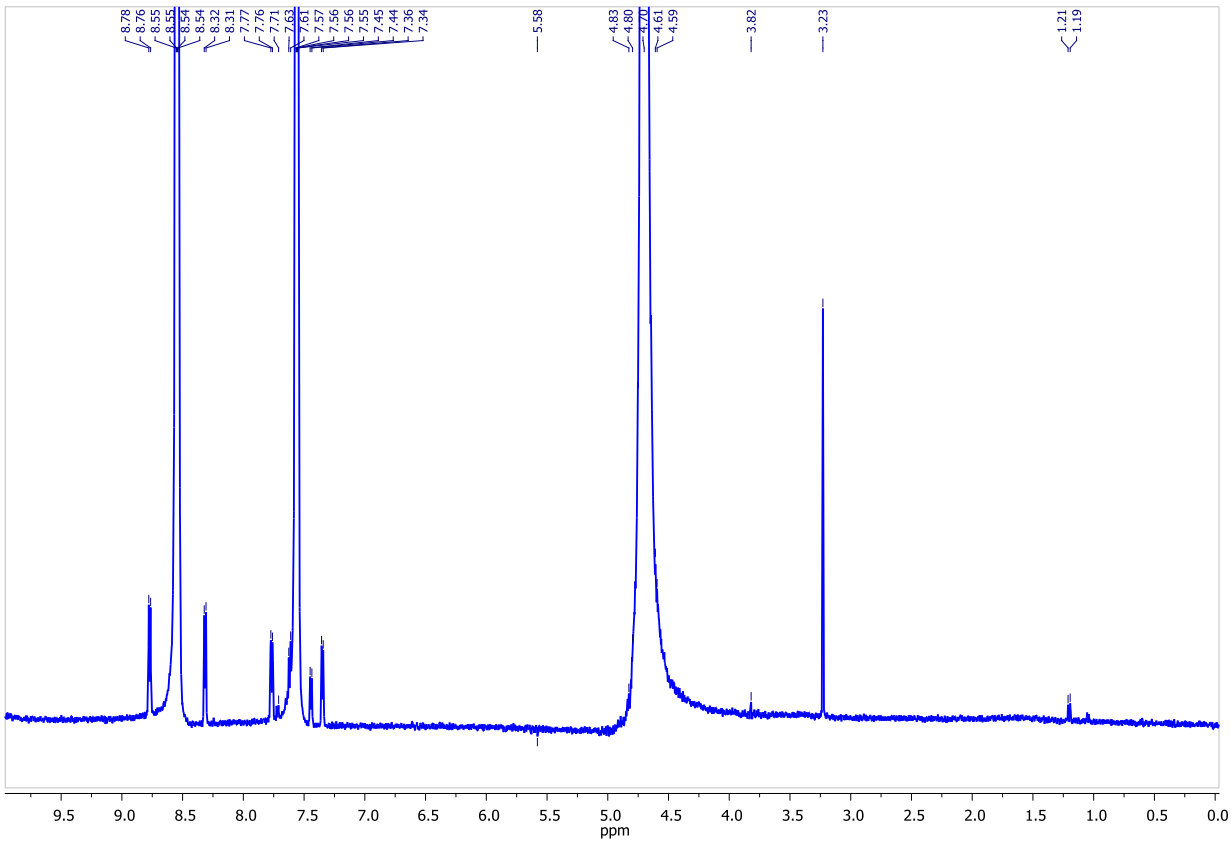


Figure. 5.5 NMR spectrum for Pure Isoniazid

A comparison of ^{1}H NMR spectra of the metal complex and their respective ligand were done. The proton peaks at δ 2.0 were assigned to NH protons of amine group. The peaks at δ 5.6 were assigned to CH protons of carbonyl group which were not seen in pure isoniazid ligand. Hence the presence of this peak shows the coordination occurs at Carbonyl oxygen. The peak around δ 8.7 and 7.5 was observed in both pure isoniazid and Cadmium complex which indicates that the pyridine ring protons provide the similar environment and do not involve in coordination with the Cadmium. The NMR peak values for Cadmium complex were given in the following table.

S. No	Peak value	Assignment
1.	2.0	N-H
2.	5.6	C-H protons of Carbonyl group
3.	7.7	Pyridine ring
4.	8.6	Pyridine ring

Table 5.5 Proton NMR values for the complex $[Cd(INH)_2(NCS)_2]$

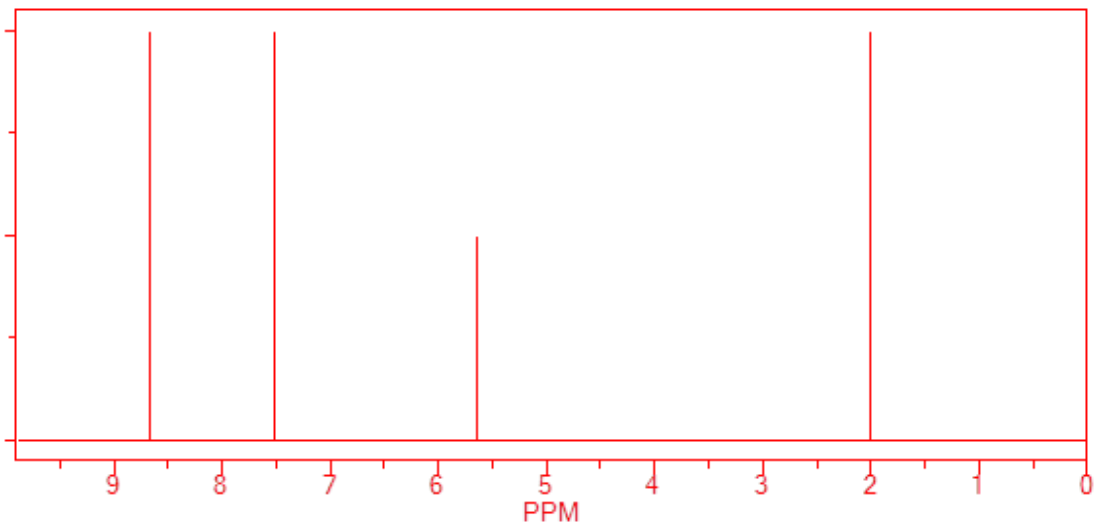


Table 5.5 ^{1}H NMR spectra of $[Cd(INH)_2(NCS)_2]$ complex

5.6 ANTIMICROBIAL ACTIVITY

The antibacterial screening of the free isoniazid and the Thiocyanate complexes against E.Coli are shown in Fig. The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of the test compounds is expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition. The antimicrobial studies showed that the ligands and their metal complex exhibit considerable activity against the pathogenic bacterial strains. The result show that the complex is more active than its parent ligand against the same microorganisms and as the concentration increases the activity also increases.

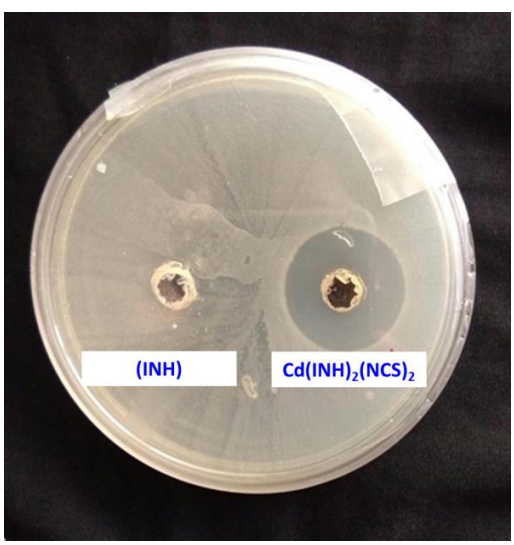


Figure. 5.6 Antibacterial activity of the $[Cd(INH)_2(NCS)_2]$ complex

5.7 Structure of the $[Cd(INH)_2(NCS)_2]$ complex

Based on above investigation the probable structure may be distorted octahedral in which the isoniazid acts as a bidentate ligand and Isothiocyanate co-ordinate with N-atom

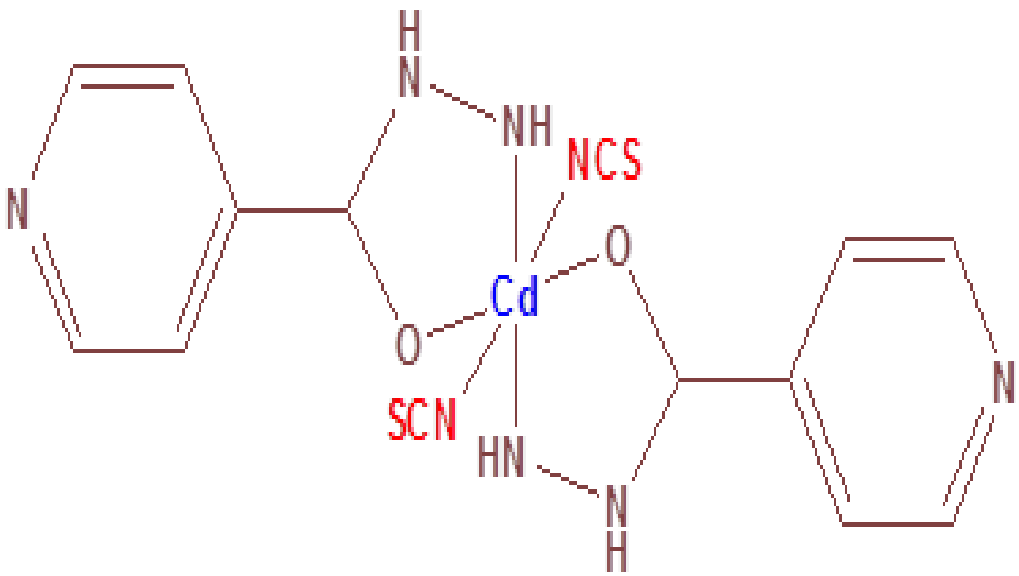


Figure. 5.7 Structure of the $[Cd(INH)_2(NCS)_2]$ complex

CONCLUSION

6. Conclusion

In the present study, the mixed ligand complex of cadmium has been prepared using Isoniazid and thiocyanate ligands. The analytical methods and physicochemical parameters have been found out and molar conductivity measurements predicted the non –electrolytic nature of the complex.

The electronic spectra of the complex was recorded and the corresponding transitions predict the probable geometry of the cadmium complex.

The IR spectra of the pure ligand and the complex was recorded and the metal ligand coordination peaks were observed. Isoniazid acts as a bidentate ligand where both oxygen and nitrogen atoms are coordinated with the metal atom. The pyridine nitrogen of isoniazid does not involve in the coordination which was confirmed by the IR peaks. Though thiocyanate is an ambidentate ligand, here the coordination takes place through the nitrogen atom and hence the coordination sphere contains isothiocyanate.

Based on the above results and discussions, the most probable formula and geometry is given as follows.

$[Cd(INH)_2(NCS)_2]$ **-** Distorted Octahedral

Chapter 6

6.1 Summary

The **first** chapter deals with introduction of co-ordination complexes, mixed ligand complexes and its applications

The **second** chapter proposed the aim and scope of the present investigation.

The **Third** chapter provides brief information about the review of literature

The **fourth** chapter describes about the various techniques employed

The **fifth** chapter deals with the the synthesis, spectral depiction and antibacterial screening of mixed ligand complexes.

The **sixth** chapter gives the overall summary and conclusion for the research work.

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Post Graduate Project – 5

Synthesis and Spectroscopic Characterization of Cu (II) complex with Isoniazid Complex

Name of the Guide: Dr. A. Mushira Banu
Name of the Candidate: R. Priya

CONTENTS

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1 Introduction

1.1. Coordination complexes

Coordination complexes are so pervasive that their structures and reactions are described in many ways. The atom within a ligand that is bonded to the central metal atom or ion is called the **donor atom**[1]. In a typical complex, a metal ion is bonded to several donor atoms, which can be the same or different. A polydentate (multiple bonded) ligand is a molecule or ion that bonds to the central atom through several of the ligand's atoms; ligands with 2, 3, 4 or even 6 bonds to the central atom are common. These complexes are called chelate complexes; the formation of such complexes is called chelation, complexation, and coordination. The central atom or ion, together with all ligands, comprise the coordination sphere. The central atoms or ion and the donor atoms comprise the first coordination sphere[2]. **Coordination** refers to the "coordinate covalent bonds" (dipolar bonds) between the ligands and the central atom. Originally, a complex implied a reversible association of molecules, atoms, or ions through such weak chemical bonds. Some metal complexes are formed virtually irreversibly and many are bound together by bonds that are quite strong. The number of donor atoms attached to the central atom or ion is called the coordination number. The most common coordination numbers are 2, 4, and especially 6. A hydrated ion is one kind of a complex ion (or simply a complex), a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electron[3]**.**

Coordination chemistry, the science concerned with the interaction of organic / inorganic ligands with metal centers has remained one of the most active research areas in inorganic chemistry. Coordination chemistry includes different types of coordination compounds

applicable in a wide diversity of fields such as dyes, colors, nuclear fuels, catalysis, photography, toxicology, bioinorganic chemistry, medicine, ceramics, materials science and toxicology. Inclusion of a variety of ligands in complexes has enabled their applications as biocides, catalysts, NMR shift reagents and DNA binders[4,5,6].

The development of sophisticated analytical instruments and synthesis of a wide variety of coordination compounds has encouraged many researchers to revisit the chemical reactions. This study has enabled the inorganic chemists to make significant progress in the modification of the concept of chemical bonding. In coordination chemistry, the different types of ligands, Schiff base ligands and chelates are well documented with synthesis, characterization and applications. The complexes of transition metals with its higher nuclearity have attracted the attention of many coordination chemists, where polytopic ligands are important for tailor made molecular structures of complexes[7,8,9]. The polytopic ligands are much better for the successful preparation of the homo polynuclear complexes whereas, the one-pot synthesis for the preparation of polynuclear complexes is very complicated. In order to facilitate the tailor making of heterometalic systems in a controlled manner and with expected properties the greatest concern is the development of synthetic routes. From amongst the variety of methodologies, the use of metal complexes as ligands has proven to be very successful. If the complexes formed by coordination with metal ions, have the tendency to coordinate further or react with other complexes, then they may act as 'metal organic ligands'. The different types of MOLs (metal organic ligands) which form various homo and hetero polynuclear complexes are reported here[10].

The polynuclear complexes are very useful in different fields, especially used as magnetic materials. Nowadays, magnetic materials are being used in biomedical applications

such as contrast agent in magnetic resonance imaging (MRI), targeted drug delivery and magnetic separation of cells, DNA, protein etc. Ligand is the species attached to a central metal atom / ion to form a coordination complex[11]. The ligand is the electron rich compound with extra electrons. The nature of metal – ligand bonding can be covalent or ionic. Ligands can be anions, cations or neutral molecules. According to the number of donating atoms, the ligands may be bidentate, tridentate or polydentate. The condensation of primary amines with aldehydes or ketones gives compounds with a functional group that contains a carbon-nitrogen double bond with the nitrogen connected to an alkyl group. These are called Schiff bases, since their synthesis was reported by Hugo Schiff (1864)[12,13,14]. The process in which polydentate ligand bonds to a metal ion, forming a ring structure or complex structure is called chelation. The polydentate ligand is referred to as a chelating agent and the complexes involving a ring in which metal ion is an integral part is called a chelate[15,16,17].

Ethylenediaminetetraacetic acid (EDTA) is a popular hexadentate ligand in coordination chemistry with four carboxylic acid groups along with two amine groups can form six bonds with a metal ion. EDTA forms chelates with a wide variety of metal ions under suitable conditions which contain five 5-membered rings in their structure. The hexacoordinated complexes from EDTA are octahedral in geometry. In recent years in coordination chemistry, much focus has been placed on the synthesis, characterization and applications of dinuclear and polynuclear transition metal complexes bridged by polyatomic ligands[18,19,20].

1.2. Homopolynuclear complexes

The homopolynuclear complexes synthesized by polytopic ligands allows the coordination of metal ions through the reactive groups having donor atoms such as nitrogen,

oxygen or sulfur. This self-assembly approach allows the rational preparation of linear double- and triple-stranded oligonuclear complexes from mono- to di- and trinuclear species. The preparation of complexes depends on the molecular symmetry, coordination mode of the polytopic ligands and the preferred coordination geometry of the metal ions[21,22]. The polynuclear complexes are prepared for the different purposes. The synthesis of molecular magnetic materials requires an intelligent design of the ligand which can organize the paramagnetic metal ions in a desired topology and efficiently transmit electron exchange interactions between the metal ions[23,24]. This basic principle is strongly supported by the work on the magnetic properties of oxamato – bridged multimetallic coordination compounds which was initiated by Kahn and coworkers in the late 1980's and then extended to the oxamidato – bridged analogues by Journaux and Lioret in the late 1990's[25,26]. In this work, as discussed earlier, aliphatic or aromatic group substituted bis(oxamato)- and related bis(oxamidato) – copper(II) complexes were used as ligands, referred to as metal-organic ligands (MOLs) for the preparation of multimetallic compounds. The study of polynuclear complexes was initiated using the ligands like oxalates which formed the homopolynuclear complexes. Since the1990's, a great number of oxalate-bridged homopolynuclear complexes have been synthesized and characterized to date. These compounds are normally obtained during the reaction between cationic complexes having potentially free coordination sites and the oxalate anion[27,28]. These types of homopolynuclear compounds can be formed using the polytopic ligands. But, as discussed earlier, one of the challenges in the field of polynuclear self – assembly of molecular organic, inorganic material is the controlled and on the spot generation of tailor made molecular structures and properties. The high degree of structural organization can be achieved through the multiple one to three binding of transition metals. Hence, it is important to design the organic ligand together with the proper choice of the metal ion[29,30,31]. The oxalate

type ligands can be modified to ligands having bis-chelating coordination ability, the bridging oxalate type units have produced different types of frameworks, which include 1D-chains, 2D-layer and 3D-networks bearing the same types of metal ions[32,33].

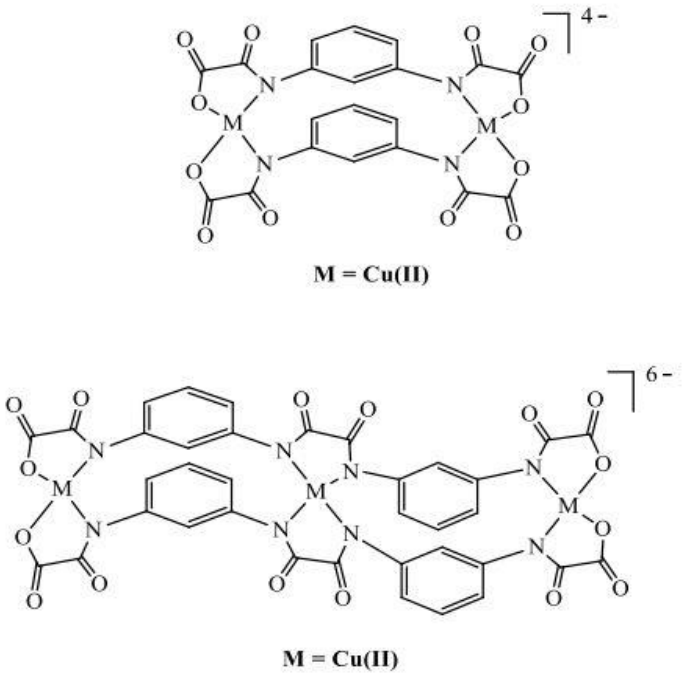
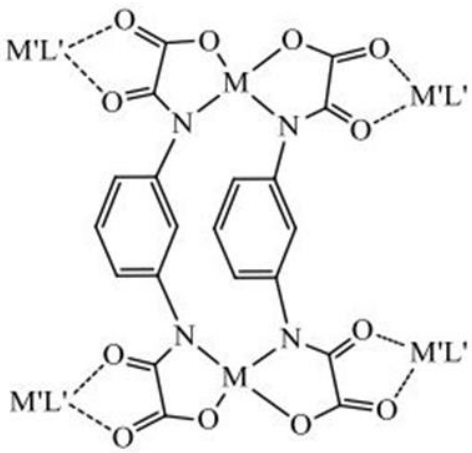


Fig 1.2 Homopolynuclear complexes

1.3. Heteropolynuclear complexes

The synthesis of heterometallic complexes is known to be difficult. A one-pot procedure involving the reaction of two different metal ions with the ligand anion produces a mixture of compounds. In order to overcome this difficulty, an alternative synthetic strategy (metal organic ligands) has been developed which consists the use of mononuclear complexes as ligands towards the second metal ion. Plenty of work on the well – recognized 'metal complex as ligands' approach has been done to date. The different researchers used different types of MOL for the preparation of homo and heteropolynuclear complexes. For the synthesis of tailor made

molecular structures of the polynuclear complexes, the preparation of the MOLs is very important. Whereas, the heterodinuclear complexes [M A M B (L)] $^{2+}$, where M A = Ni $^{2+}$, M B = Mn $^{2+}$, Fe $^{2+}$, Co $^{2+}$, Cu $^{2+}$, Zn $^{2+}$ were prepared by two step synthesis, based on the reaction of metal acetates with mononuclear nickel complex [34,35].



M = Cu(II), M' = Cu(II), Ni(II), Co(II), Mn(II)

Fig 1.3 Hetero polynuclear complexes

The first step of the reaction is the formation of mononuclear nickel complex; one of the coordination compartments was blocked by protonation of inner penalty groups. On other hand, in the second step acetate ions deprotonated the phenolate groups and made it available for the further coordination[36]. So, by the modification of the synthetic method the homodinuclear and heterodinuclear complexes from same Schiff base ligands can be formed.

Some other types of metal organic ligands have been designed using a ligand containing number of potential sites from which all cannot contribute in the coordination but, the monotopic complexes formed from these types of ligands can act as precursors and further coordination occurs. The mononuclear complexes of transition metals prepared from 6-amino-2-thiouracil containing the amine group as unutilized functionality.

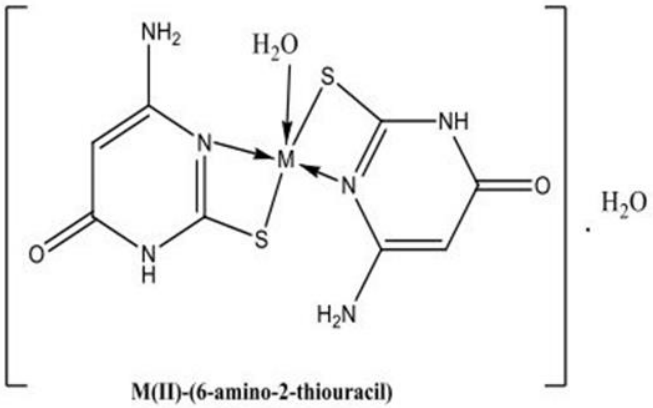


Fig 1.3.1 Mononuclear complexes with active sites

1.4 Application of polynuclear complexes

The transition metal complexes are widely used in catalysis but dinuclear Schiff base complexes of transition metal ions are more efficient catalysts than mononuclear complexes probably due to the synergistic effect of two metal ions[37]. The metal complexes exhibit a lot of bioactivity such as antimicrobial activity, antiviral activity, antifungal activity, analgesics, HIV protease and anticonvulsants. The polynuclear complexes generally exhibit interesting magnetic properties, moreover magnetic properties of materials have been utilized over years in mechanical applications such as electric motors, electric generators as well as in communication technologies such as television and telephones. More recently, magnetism has found extensive application in the area of data storage and processing, from magnetic tape to floppy discs and computer hard drives. Traditional magnetic materials consist of two- and three-dimensional structures of transition metal or lanthanide metal containing spin units[38,39,40]. In contrast to that, molecular magnets are organic or inorganic/organic hybrid materials consisting of either metal with spin units or organic radical containing spin units. Such molecular magnetic materials can possess better optical properties and the combination of magnetic properties with other properties like mechanical, electrical and / or optical properties

makes them easily processable. In the last two decades, an increasing interest in polynuclear complexes containing ligand structures capable of holding two or more metal centers in close proximity to act as single molecular magnets has been observed. The field of molecular magnetism exhibited a rapid development in the last two decades with a particular emphasis on heteropolymetallic complexes.

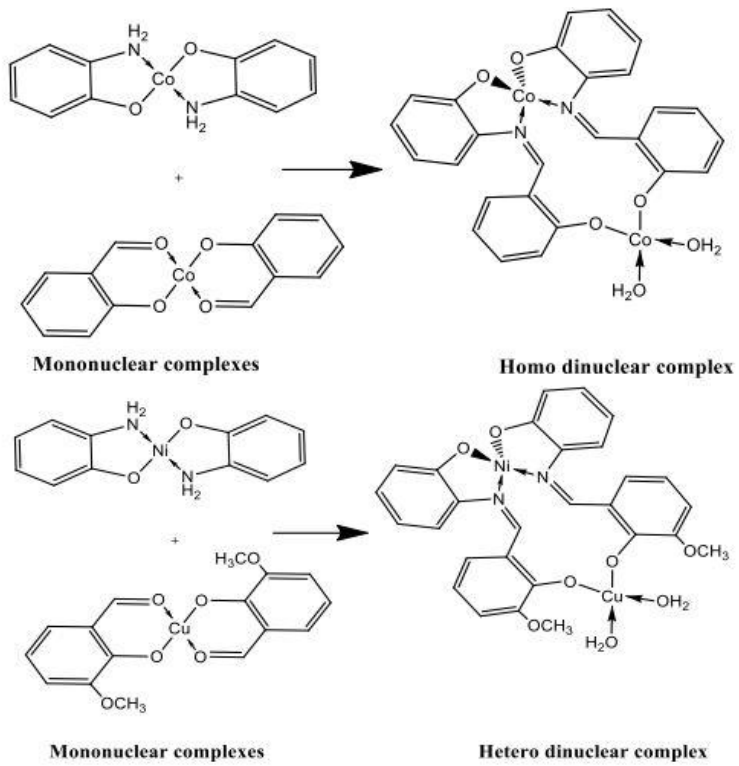


Figure 21 Homo and heterodinuclear complexes.

Fig 1.4 Homo and hetero dinuclear complexes

1.5 ISONIAZID

Isoniazid, also known as **isonicotinylhydrazide** (**INH**), is an antibiotic used for the treatment of tuberculosis. For active tuberculosis it is often used together with rifampicin, pyrazinamide, and either streptomycin or ethambutol[41]. For latent tuberculosis it is often used by itself.[1] It may also be used for atypical types of mycobacteria, such as *M. avium*, *M. kansasii*,

and *M. xenopi*. It is usually taken by mouth but may be used by injection into muscle. Common side effect include increased blood levels of liver enzymes and numbness in the hands and feet. Serious side effects may include liver inflammation.

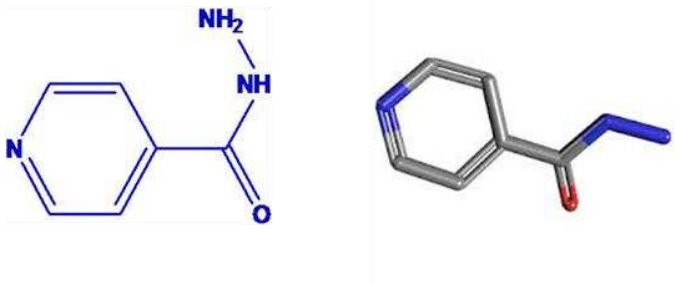


Figure 1.5 Structure of Isoniazid

Isoniazid is often used to treat latent and active tuberculosis infections. In persons with isoniazid-sensitive Mycobacterium tuberculosis infection, drug regimens based on isoniazid are usually effective when persons adhere to the prescribed treatment. However, in persons with isoniazid-resistant Mycobacterium tuberculosis infection, drug regimens based on isoniazid have a high rate of failure. Isoniazid has been approved as prophylactic therapy for the following populations: People with HIV infection and a PPD (purified protein derivative) reaction of at least 5 mm induration. Contacts of people with tuberculosis and who have a PPD reaction at least 5 mm induration. People whose PPD reactions convert from negative to positive in a two-year period – at least 10 mm induration for those up to 35 years of age, and at least 15 mm induration for those at least 35 years old. People with pulmonary damage on their chest X-ray that is likely to be due to healed tuberculosis and also have a PPD reaction at least 5 mm induration. Injection drug users whose HIV status is negative who have a PPD reaction at least 10 mm induration. People with a PPD of greater than or equal to 10 mm induration who are foreign-born from high prevalence geographical regions, low-income populations, and patients residing in long-term, facilities[42,43].

Tuberculosis (TB) is a public health disease that produces several millions deaths annually worldwide. In developing countries is a leading cause of mortality. Isoniazid, also known as isonicotinylhydrazide **(INH)**, is an antibiotic used for the treatment of tuberculosis[44]. For active tuberculosis it is often used together with rifampicin, pyrazinamide, and either streptomycin or ethambutol. The big problem in pharmaceutical chemistry is the alarming increase of drug resistant microbial strains (MDR-TB) that makes difficult the effective control of the disease. Due to this critical situation, innovation in TB drug discovery and evolving strategies to bring new agents with best performance is a current health priority. One strategy to obtain new antimycobacterial drugs is the decobacteria activity and to obtain better resistance profiles, bioavailability and tolerability, among others. In particular, the coordination of metal cations with organic drugs is a promising development of new molecules by reengineering old drugs with the aim to improve the antimycobacterial strategy that has been successful in many cases with different pharmacological activities.

1.6 Copper

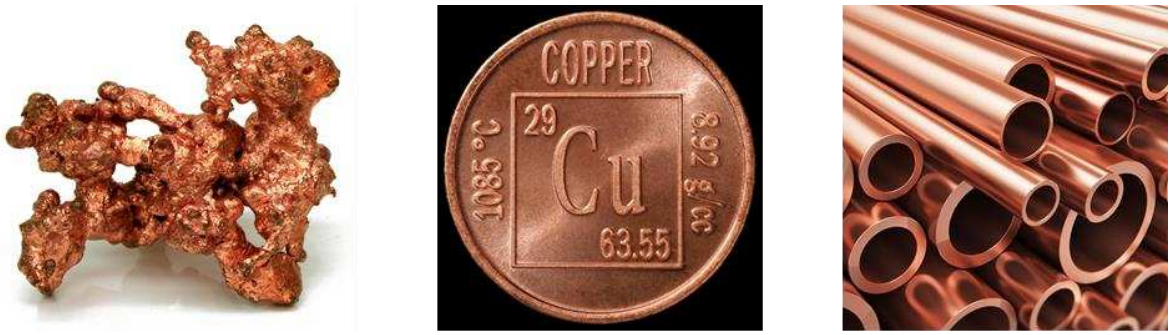


Fig 1.6 Images of Copper

Copper is a chemical element with symbol **Cu** (from Latin: *cuprum*) and atomic number 29. It is a soft, malleable, and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a pinkish-orange color[45]. Copper is used as a conductor of heat and electricity, as a building material, and as a constituent of various metal alloys, such as sterling silver used in jewelry, cupronickel used to make marine hardware and coins, and constantan used in strain gauges and thermocouples for temperature measurement. Copper is one of the few metals that can occur in nature in a directly usable metallic form (native metals). This led to very early human use in several regions, from c. 8000 BC. Thousands of years later, it was the first metal to be smelted from sulfide ores, c. 5000 BC, the first metal to be cast into a shape in a mold, c. 4000 BC and the first metal to be purposefully alloyed with another metal, tin, to create bronze, c. 3500 BC.

1.6.1 Biomedical applications of copper

1. As a biostatic surface in hospitals, and to line parts of ships to protect against barnacles and mussels, originally used pure, but superseded by Muntz metal. Bacteria will not grow on a copper surface because it is biostatic. Copper doorknobs are used by hospitals to reduce the transfer of disease, and Legionnaires' disease is suppressed by copper tubing in air-conditioning systems

2. Copper(II) sulfate is used as a fungicide and as algae control in domestic lakes and ponds. It is used in gardening powders and sprays to kill mildew.

3. Copper-62-PTSM, a complex containing radioactive copper-62, is used as a Positron emission tomography radiotracer for heart blood flow measurements.

4. Copper-64 can be used as a positron emission tomography radiotracer for medical imaging. When complexed with a chelate it can be used to treat cancer through radiation therapy.

1.7 UREA

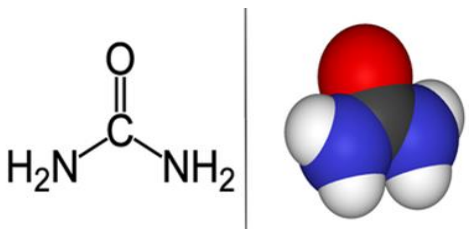


Fig 1.7 Images of Urea

Urea, also known as **carbamide**, is an organic compound with chemical formula $CO(NH_2)_2$. This amide has two $–NH_2$ groups joined by a carbonyl (C=O) functional group. Urea serves as an important role in the metabolism of nitrogen-containing compounds by animals and is the main nitrogen-containing substance in the urine of mammals[46]. It is a colorless, odorless solid, highly soluble in water, and practically non-toxic.

Uses

Urea-containing creams are used as topical dermatological products to promote rehydration of the skin. Urea 40% is indicated for psoriasis, xerosis, onychomycosis, ichthyosis, eczema, keratosis, keratoderma, corns, and calluses. If covered by an occlusive dressing, 40% urea preparations may also be used for nonsurgical debridement of nails. Urea 40% "dissolves the intercellular matrix" of the nail plate. Only diseased or dystrophic nails are removed, as there is no effect on healthy portions of the nail[47]. This drug is also used as an earwax removal aid.

Urea has also been studied as a diuretic. It was first used Dr. W. Friedrich in 1892. In a 2010 study of ICU patients, urea was used to treat euvolemic hyponatremia and was found safe, inexpensive, and simple. Like saline, urea injection has previously been used to perform abortion. The blood urea nitrogen (BUN) test is a measure of the amount of nitrogen in the blood that comes from urea. It is used as a marker of renal function, though it is inferior to other markers such as creatinine because blood urea levels are influenced by other factors such as diet and dehydration.

- A component of animal feed, providing a relatively cheap source of nitrogen to promote growth
- A non-corroding alternative to rock salt for road de-icing. It is often the main ingredient of pet friendly salt substitutes although it is less effective than traditional rock salt or calcium chloride.
- A main ingredient in hair removers such as Nair and Veet
- A browning agent in factory-produced pretzels
- An ingredient in some skin cream, moisturizers, hair conditioners, and shampoos

  As an optical parametric oscillator in nonlinear optics

1. Complexation of nicotinamide with Ag+ ions in water - organic solvents was published in the journal of inorganic chemistry volume 51 on 30th march 2006 by M.A.Zevakin, K.v.Grazhdan, V.A.Sharnin and S.V.Dushina.

2. In 2006, thermal study of Zn(II) chlorosalicylate complex compounds with bioactive ligands such as Thiourea, nicotinamide and caffeine was published by Gyoryova Katarina, Chomic.J, Szunyogoba Eirka, Piknova Lenka,zelenak V and Vargova zuzana in the journal of thermal analysis and calorimetry.

3. The enthalpies of complex formation between nicotinamide and copper(II) percolate in aqueous ethanol and DMSO were determined calorimetrically by A.S.Kursheva, S.F.Ledenkov and V.A.Sharnin and was published in the journal of physical chemistry on July 25th 2006.

4. Synthesis and characterization of molecular structure and properties of the generated Cu(II) and Ni(II) complexes was reported by particia A.M.Williams, Natialia Bolza and published in Indian journal of chemistry on 15th Jan 2005.

5. Synthesis and characterization of three 5-(4-pyridyl)tetrazolato complexes obtained by reaction of 4-cyanopyridine with metal azides from aqueous solutions was reported by Mauter Franz A., Gspan Chiristian, Gatterer Karl, Gohr Mohamed A.S.,Abuyoussey Morsy A.M., Bucher Edith and Sittle Werner in 2005 in the journal of physical chemistry.

6. A study of copper (II) carboxylato complexes with the ligand nicotinamide was reported by Christina J.Williams, HarryMorris in 2003 was published in journal of molecular structure.

7. In 2003, Balachandran Unni Nair and Thomas Eyhermuller was reported the preparation and structure of a dinuclear iron (II) complex with six terminally coordinated azides and published in the central research institute of America.

8. Molecular structure and properties of copper(II), Nickel(II) complexes was published on the E-resources.

9. Spectroscopic and Lumimescence properties of an isonicotinic acid was reported by P.Starynowicz in the journal of celal bayer university.

10. Analyses of co-operative transition in acyl carrier protein redutase upon cofactor and acyl carrier protein binding was published by N.Surolia in Jawaharlal Nehrua centre of advanced scientific research, on 17th Aug 2004.

11. A crystal structure and properties of Cu(II) complex containing azide ion was published in the journal of coordination chemistry.

12. A Study of copper(II) carboxylato with the ligand nicotinamide was reported by Jan moncol, Milan melnik, Feder valach in the journal of transistion metal chemistry on 24th July2003,p.53-60.

13. Michael G.Finnegan et al have reported the synthesis and UV-Visible, solution IR and EPR spectroscopy of (porphinato) iron (III) nitrite complexes.

14. Scarpellini marciele et al have reported the synthesis and characterization of the new copper (II) – nitrite complex.

15. Synthesis and structure of catena_poly[bis(nicotinamide-kN)copper(I)]-μ-thiocyanato-k^2 N:S] was reported by Christian nather and Inke Jeb in 2002 and published in acta crystallographic section c volume 58(3), P190-192-march 2002. The mixed ligand complexes have been characterized on the basic of elemental analysis, electrical conductance, room temperature, magnetic susceptibility measurements, spectral and thermal studies. Probable structures have been suggested for the mixed ligand complexes on the basic of the results of elemental analysis and various physico-chemical studies.

16. Mixed ligand nickel (II), copper(II) and zinc(II) complexes of nicotinanilide and thiocyanate were prepared and their electrochemical and biological properties were discussed [48]. Balan et.al have studied the structure of nicotinanilide and thiocyanate metal complexes. He performed cyclic voltammetric studies for all the complexes and

differentiated the oxidation and reduction processes and indicated that the CV studies exhibit one electron irreversible process.

17. Microwave-associated synthesis of mixed ligand complexes of Zn(II), Cd(II) and Hg(II) derived from 4- aminopyridine and nitrite ion were reported by Dhaveethu et.al [49]. Microwave assisted synthesis and structural characterization of nicotinic acid and nitrito-ko mixed ligand complexes were reported and their geometry was interpreted by various characterization techniques.

18. Foziah et.al have reported the thermal studies of the alkaline earth metal nicotinamide complexes. She proposed that the complexes are non electrolytic in nature and the anions are coordinated to the central metal ion [50].

19. Guang et.al have reported the synthesis and crystal structure of non-interpenetrating metal organic coordination networks constructed from Cd(II) with thiocyanate and nicotinic acid. By using bridging ligands instead of monodentate ligands, they are successfully extended the one dimensional chain structure into two dimensional networks through covalent or the hydrogen bonds.

20. Bio potential efficiency and DNA cleavage applications have been reported for mixed ligand complexes using nicotinamide and nitrite as primary and secondary ligands respectively. Dilip et.al have proposed the probable structure for metal complexes with metal ions such as Ni, Co, Cu, Zn, Hg and also stated that chromium complex alone have bridged ligands and confirmed by IR spectroscopy[51].

21. Marijina et.al reported the thiocyanate complexes of group 12 metals with pyridine-2- carboxamide and the crystal structure of the complexes have been elucidated by X-ray diffractometer. Here the thiocyanate shows a number of bonding modes with group 12 metals as terminal and bridging ligand. In the structure investigation of Zn and Hg complexes with thiocyanate, the authors proposed that both the N-donor and S-donor thiocyanate ligands can act as a bridged and terminal which are coordinated to mercury in a nonlinear fashion whereas the coordination sphere along the zinc ions are distorted tetrahedral in structure [52].

22. It was proposed that the nicotinamide complexes are six coordinate with a metal ion through nitrogen atom. Chandrasekaran et.al have reported the synthesis and characterization of metal complexes with FCNH ligand. He proposed that the ligand coordinate to the metal as a neutral bidentate ligand and possess octahedral geometry.

23. Sabbir et.al have prepared the nicotinamide complexes in aqueous medium in the ratio 2:1. They conclude that the compounds do not contain any chemically coordinated water molecules [58].

24. Lawal et.al have confirmed that the nicotinamide co-ordinate to the metals ions through the pyridine ring nitrogen atom. Nicotinamide act as a chelating ligand and it possesses good antimicrobial and antifungal activity [59].

25. Khawla have proposed the structure of the mixed ligand complexes with isoniazid and aminoacids to be distorted octahedral. These complexes show positive activity against tuberculosis bacteria.

Aim and Scope

The present work aims at the preparation of the coordination complex of copper using Isoniazid and Urea as ligands.

To arrive at the composition and structure of the complexes, it is proposed to

1. Measure the electrical conductivity of complex and to find whether the complex is ionic or neutral.
2. Compare the Infrared spectra of complex with those of parent ligand, to determine the coordination position of the ligands.
3. Record the electronic spectra of the complex, which will throw light on the probable geometry of the complex.
4. To test the antimicrobial activity of the complex and pure ligand.

4. CHARACTERIZATION TECHNIQUES

4.1. PREPARATION OF MIXED LIGAND COMPLEX

The following methods are commonly employed for the preparation of coordination compounds.

1. By mixing the metal ion solution and ligands in suitable concentration. By evaporating or cooling the concentrated solution in an ice-salt bath, we can induce crystallization. Adding seed crystals of desired compounds and scratching inside the liquid surface often helps to induce crystallization.

2. By the addition of a solvent which is miscible with the solvent of the mixture and the techniques of cooling, seeding and scratching may be necessary to cause the preparation from the solvent mixture.

3. If the desired complex is a cation, it may be isolated by the addition of an appropriate anion with which it forms an insoluble salt. Similarly, a suitable cation may be added to the reaction mixture to precipitate anionic complexes.

4.2. CHARACTERIZATION TECHNIQUES

Detection of complex ion in solution is related to the concentration of one of the species involved in the formation of the complex.

i. Solubility method

Sometimes the complex formation increases the solubility of sparingly soluble salts. For example, silver cyanide is sparingly soluble in water but on the addition of KCN, its solubility increases due to complex formation.

$$AgCN + KCN \rightarrow K[Ag(CN)_2]$$

$$K[Ag(CN)_2] \rightarrow K^+ + [Ag(CN)_2]^-$$

ii. Determination of molecular weight

Colligative properties (like depression in freezing point, elevation of boiling point and osmotic pressure) are the properties which depend upon the number of individual species present in a system. By using this property, molecular weight of the substance can be determined. During complex formation, as there is a change in the number of particles, measurement of the above properties gives information about complex formation.

iii. pH measurements

Generally ligands are either weak bases or acids. The formation of a complex is accompanied by the displacement of one or more usually weak, acidic protons of the concentration of H^+ in the complex formation and hence causes a drop in the value of pH. Thus the change in pH value can be used as an indication of the extent of complex formation.

iv. Measurements of molar conductance of complexes

The conductance is a measure of the ease with which the current is passed through the solution. Equivalent conductance is generally used in the case in the study of electrolytic solution. However, in the case of complex compounds, molar conductance rather than the

equivalent conductance is of immense importance. Molar conductance of a substance depends on the number of ions present in the solution, degree of dissociation, mobility of ions and temperature. Measurements of molar conductance, M at large dilutions gives information with regard to the number of electrical charges i.e., the sum of the charges on positive and negative and the number of charges furnished by a molecule of complex compound. In general, the molar concentration of the order 10-3 M was used for the study.

Molar conductance, M = 1000 K

Concentration

Where, K is the specific conductance of solution in ohm-1 cm-1

v. Conductivity method

Complex ion formation can be conveniently identified by conductivity measurements. Usually central metal atom combines with ligands (ions or molecules) to give complexes. During this process, there will be an appreciable change in the conductivity of the solution .For example, if metal ion combines with ligands to form a complex, there will be an appreciable drop in the conductivity of the solution, as the number of ions decreases during the above process.

4.3. SPECTRAL STUDIES

Besides the above mentioned methods, UV, IR, NMR, EPR and Raman spectral measurements give information about complex formation.

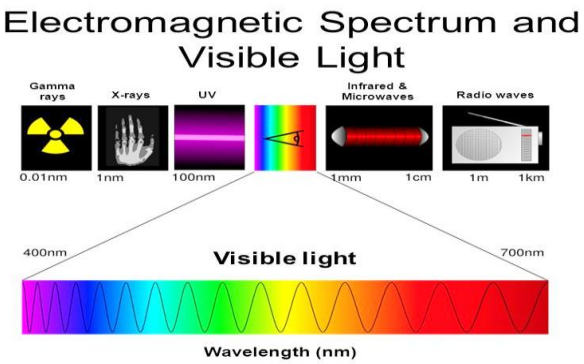


Figure 4.3. Electromagnetic spectrum

4.3.1 Electronic spectra

The absorption of light in the visible region (400-800 nm) by a metal ion depends on the electronic transitions within the ion and also on the type and strength of ligand → metal bonding[48]. Thus, the metal ions containing d-electrons (except those having 10 electrons in d-orbitals) give variable colors depending on the nature of the ligands attached with the metal ion. In many cases, the intensity of absorption is increased and the absorption shifts to higher energies (lower λ_{max}) when coordinated water molecules are replaced by ligands which are basic than water.

4.3.2 Infra-red spectra

Vibrational rotational spectra are found in the case of those molecules which posses permanent dipole moment only. In order to study such type of spectra, the energy supplied should be sufficient so as to result transition from one vibration level to another, keeping the

electronic level undisturbed. Since each vibrational change is accompanied by so many changes in the rotational energy also, absorption band consists of closely spaced line .

As the infra-red absorption bands of metal-donor atom provide information on the strength and character of the coordinate bond in a given complex, it is self evident that one should get reliable identification of the various absorption bands to arrive at the correct structure of a complex[49] .

When a ligand coordinates to a central metal atom, there will be changes in the bond lengths, bond angles and also interatomic forces. This means that the infra-red spectrum of a coordinated ligand differ from that of a free ligand .

The changes are outlined below:

- There may be a change in the band position.
- There may occur a change in relative band intensities. This results in the appearance of new, often weak bands.
- Single peaks in the free ligand may undergo splitting into several, closely spaced bands in the complex.

From the above changes in the infra-red spectrum of the coordinated ligands, one may conclude whether the ligand has entered into the coordination sphere or not. The shifts in the infrared vibrational bands of the ligands on complex formation may also provide useful information about the bonding characteristics of the complex.

4.3.3 NMR spectroscopy

Absorption of radio frequency v = 60- 600MHz brings about changes in the magnetic properties of certain atomic nuclei like $_1H$ and $_{13}C$. This is called Nuclear Magnetic Resonance. The hydrogen atoms of different environments of the molecules are detected and counted in the $_1H$ NMR spectrum. Similarly the different positions of carbon atoms in a molecule can be exactly known from the $_{13}C$ NMR spectrum of a compound.

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy or magnetic resonance spectroscopy (MRS), is a spectroscopic technique to observe local magnetic fields around atomic nuclei. The sample is placed in a magnetic field and the NMR signal is produced by excitation of the nuclei sample with radio waves into nuclear magnetic resonance, which is detected with sensitive radio receivers. As the fields are unique or highly characteristic to individual compounds, in modern organic chemistry practice, NMR spectroscopy is the definitive method to identify monomolecular organic compounds. NMR spectra are unique, well-resolved, analytically tractable and often highly predictable for small molecules. Correlation spectroscopy is a development of ordinary NMR. In two-dimensional NMR, the emission is centered around a single frequency, and correlated resonances are observed[50]. This allows identifying the neighboring substituents of the observed functional group, allowing unambiguous identification of the resonances. There are also more complex 3D and 4D methods and a variety of methods designed to suppress or amplify particular types of resonances. In nuclear Overhauser effect (NOE) spectroscopy, the relaxation of the resonances is observed. As NOE depends on the proximity of the nuclei, quantifying the NOE for each nucleus

allows for construction of a three-dimensional model of the molecule. The use of higher strength magnetic fields result in clear resolution of the peaks and is the standard in industry.

4.4 Antibacterial activities

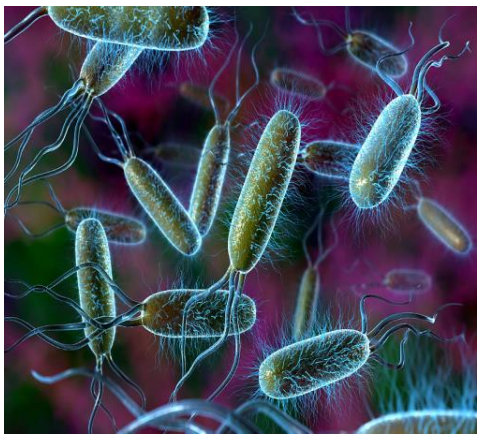


Fig 4.4 Structure of *Escherichia Coli*

The treatment of infectious diseases still remains an important and challenging problem because of a combination of factors including emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens. In spite of a large number of antibiotics and chemotherapeutics available for medical use, at the same time the emergence of old and new antibiotic resistance created in the last decades revealed a substantial medical need for new classes of antimicrobial agents. mechanism of action, which is distinct from those of well-known classes of antimicrobial agents to which many clinically relevant pathogens are now resistant The field of bioinorganic chemistry, which deals with the study of role of metal complexes in biological systems, has opened a new horizon for scientific research in coordination

compounds[51]. A large number of compounds are important from the biological point of view. The variation in the activity of different complexes against different organisms depends either on the impermeability of cells of the microbes or differences in the ribosomes of microbial cells.

Many researchers have studied characterization, antimicrobial and toxicological activity of mixed ligand complexes of transition metals. The role of mixed ligand complexes in biological process has been well recognized. Anti-tumor activity of some mixed ligand complexes has also been reported. The antibacterial and anti-fungal properties of a range of copper(II) complexes have been evaluated against several pathogenic bacteria and fungi. The metal complexes have been characterized by elemental analysis and various physico-chemical techniques such as molar conductance, magnetic susceptibility, electronic spectra, IR spectra and thermal studies.

4.4.1 Disc Diffusion method

The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of the test compounds is expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition.

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibilition by test compound (diamter)}}{\text{Zone of inhibilition by standard (diamter)}} \times 100$$

The nutrient medium was prepared by following composition like Yeast extract- 5 g, Meat extract-10 g, Peptone-5 g, Sodium Chloride-5 g, Agar-20 g. The antibacterial activity of the

compound was done by the disc diffusion method using DMSO as solvent. The test solutions were prepared by dissolving the compounds in DMSO.

Figure 4.4.1 Disc diffusion method sample

In a typical procedure, agar medium was inoculated with microorganisms and it is filled with the test solution using micropipette and the plate is incubated at 35˚C for 24 to 48 hr. During this period, the test solution diffuses and the growth of the inoculated microorganism *E. Coli*, is found to be affected. The activity developed on the plate is measured by measuring the diameter of the inhibited zone in millimeters.

5.1 Preparation of Copper complex

Chemicals required

- **Copper chloride (1.70g)**
- **Isoniazid (2.74g)**
- **Urea (1.36g)**

Procedure

About 1.70g of Copper chloride was dissolved in pure distilled water and mixed with about 2.74g of Isoniazid in water. The mixture was heated and cooled. Then Unhydrated solution of Urea (1.36g) was added in the ratio 1:2:2 and shaken well.

The light green colour precipitate was obtained and filtered through whatmann filter paper. It was dried and kept in air tight container.

5.2 Physicochemical properties

The physico chemical properties of the newly synthesized complex were analyzed conductance measurements were tabulated.

5.2.1 Electrical conductivity

The electrical conductivity of 10^{-3} M solution of each complex was found out. This observation reveals the neutral nature (non-electrolytic nature) of the complex.

S.No	Parameters	Observation
1.	Conductance (Ω^{-1} mol^{-1} cm^2)	86
2.	Colour	Light green
3.	Yield %	78
4.	Solubility	Toluene
5.	Molecular formula	$C_{14}H_{18}CuN_{10}O_4$
6.	Molecular Weight	453.9
7	Elemental Analysis	
	C, 37.05; H, 4.00; Cu, 14.00; N, 30.86; O, 14.10	

Table 5.2 Physicochemical parameters for the complex $[Cu(INH)_2(urea)_2]$

5.3 IR Spectra

The structure of Isoniazid ligand and the metal complex has been confirmed by Infrared spectroscopy. The characteristics bonds in infrared spectrum of the ligand and its metal complex are reported in table 5.3.

S. No	Complex	υNH_2	$\upsilon C=O$	$\upsilon C=N$	$\upsilon M-O$	$\upsilon M-N$	$\upsilon C=O$ of urea	$\upsilon C=N$ of urea	υNH_2 of urea
		Sym							
1	Isoniazid	3113	1667	1556	-	-	-	-	
2	**$[Cu(INH)_2(urea)_2]$**	3065	1618	1551	545	467	1707	1394	3401

Table 5.3 IR spectral data for the Complex $[Cu(INH)_2(urea)_2]$

The Isoniazid exhibits peaks at 3113 and 3304 cm^{-1} which corresponds to symmetric and asymmetric stretching of νNH_2 group. The nitrogen atom involves in the complexation and hence this peak seems to be broad in copper complex. Then NH_2 bond for Isoniazid is seen at 3065 cm^{-1} which possess positive shift in the complex. The $\nu C=O$ for free isoniazid has been observed at 1667 cm^{-1} whereas for copper complex it was shifted to 1618 cm^{-1} predicting that the metal ion is coordinated through the C=O group. These observations indicate that the isoniazid ligand acts as a bidentate ligand coordinating through both the C=O and NH_2 group. The peaks at the range of 545 cm^{-1} where attributed to $\nu M-O$ vibrations similarly M-N where seen at the range of 400 cm^{-1} in copper complex. These frequencies where not seen in pure Isoniazid ligand. The pyridine ring vibration at 694 cm^{-1} for copper complex predicts that the pyridine ring nitrogen does not involve in coordination.

The IR spectra of the urea complexes were interpreted having as reference the assignments of the observed frequencies of urea, on these bases, an earlier I R study divided the metal urea complexes into two groups, one with nitrogen, and other with oxygen as donor atom, particularly by the presence or absence of a carbonyl band near 1700cm^{-1} and by the presence or absence of shifted NH_2 peaks.[54,55]

If coordination occurs through nitrogen, there is an increase in the CO stretching frequency and decrease in the CN stretching frequency. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of the metal. Here the CO stretching frequency of the copper complex was observed at 1707 cm^{-1} whereas the pure urea exhibits CO peak at 1683 cm^{-1} . The CN frequency of pure urea was observed at 1471 cm^{-1} whereas it was shifted to 1394 in the copper complex. This increase in CO frequency and decrease in CN frequency predicts that the urea is nitrogen coordinated to the metal complex.

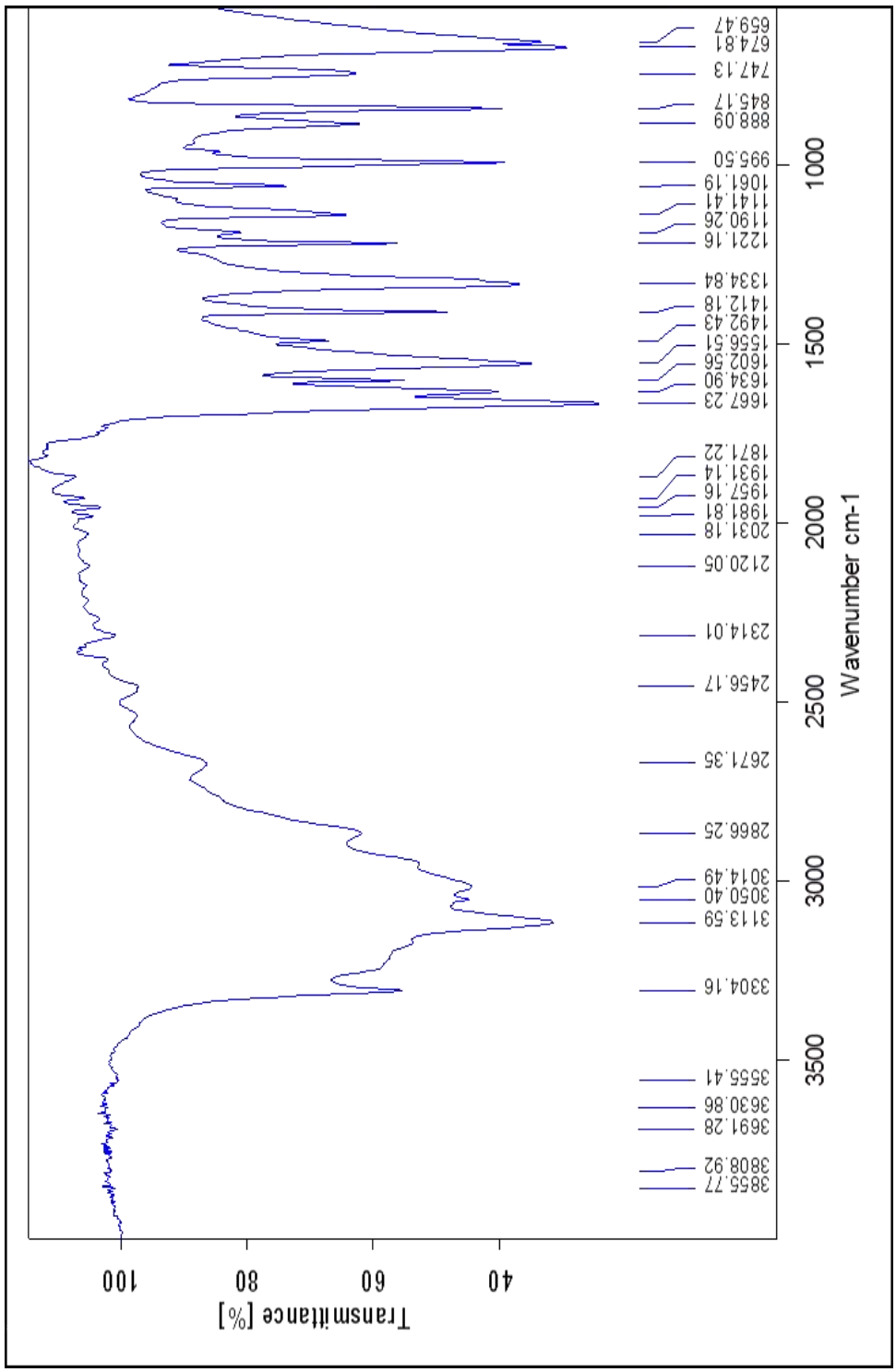


Figure. 5.3.I R spectrum of pure Isoniazid

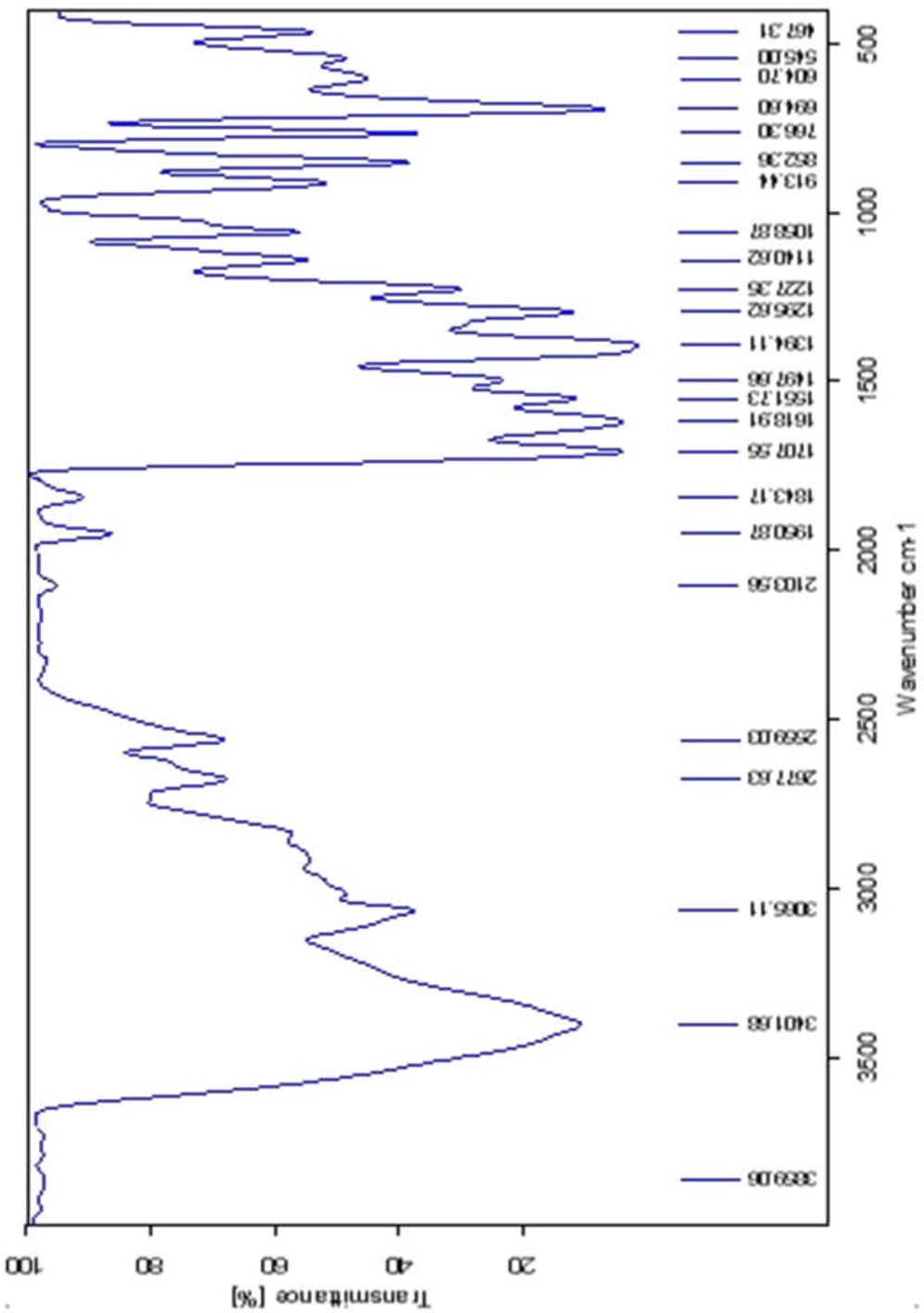


Fig 5.3.1 I. R Spectrum of the complex $[Cu(INH)_2(urea)_2]$

5.4 Electronic spectra

The UV-Visible spectra of the complexes in DMF medium were obtained in the range of 200-800 nm. The absorption arising from the transfer of an electron either, from a ligand orbital to the metal orbital (L → M) or from the metal orbital to a ligand orbital (M → L) in a complex is called the charge transfer spectrum. Charge transfer (CT) transitions do not violate the usual selection rules. Charge transfer transitions, unlike d-d transitions are normally neither multiplicity forbidden nor Laporte forbidden; therefore, they produce strong absorption bands. Such strong bands enable charge – transfer absorption to be distinguished from d-d transitions in a complex. The charge transfer bands have extinction coefficients in the 500-2000 unit range (for d-d transitions, the coefficients are below 100 unit). These bands mostly occur in the near

S.no	Complex	Absorption maxima		Transition Assignments	Probable Geomentry
		λ_{max} nm	cm^{-1}		
1	**$[Cu(INH)_2(urea)_2]$**	209 262 397	47846.89 cm^{-1} 38167.94 cm^{-1} 25188.92 cm^{-1}	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Distorted Octahedral

Table 5.4 Electronic spectral data for the complex $[Cu(INH)_2(urea)_2]$

ultraviolet region. In the spectra of some complexes, an overlap between the end for the charge-transfer band and a d-d spectrum of the complex is impossible.

A CT transition is an intramolecular transition. Electronic transition from an orbital localized mainly on one atom to an orbital localized mainly on another atom occurs. This requires much higher energies than a d-d transition. The L→ M transfer is exhibited by complexes containing the ligands O^{2-},Cl^{-},Br^{-} and I^{-}.The M→L charge transfer occurs in complexes containing ligands which have stable but empty orbitals. Ligands such as NO, CO and CN which are the acceptor ligands, cause such M→L absorption bands. The organic ligands, such as pyridine, bipyridine and o-phenanthroline have empty antibonding orbitals which favour M→L transfer.

Isoniazid

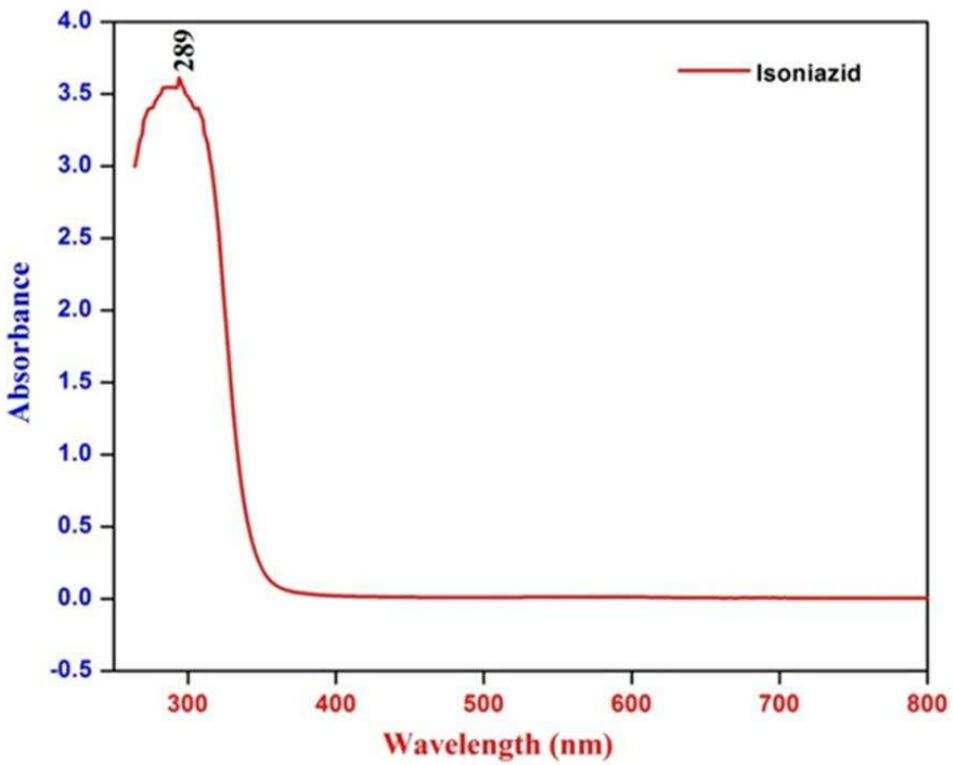


Fig.5.4. Electronic spectrum of Pure Isoniazid

The peaks at 209 and 262 nm corresponds the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively which depicts that the synthesised complex may possess distorted octahedral geometry . A small weak shoulder peak at 397nm may be attributed to the d-d transition of Cu(II).

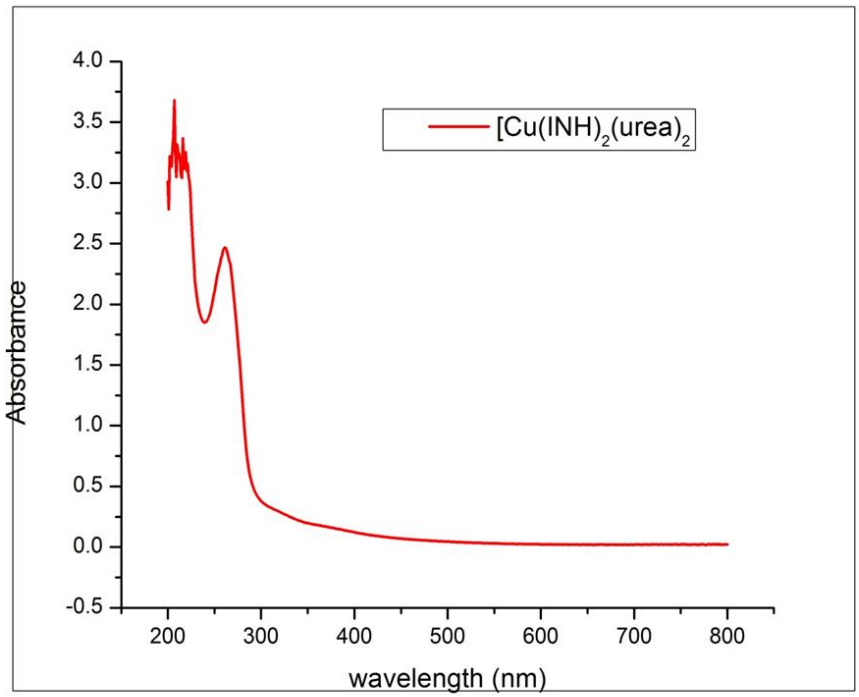


Fig 5.4.1 Electronic spectrum of the complex $[Cu(INH)_2(urea)_2]$

5.5 ^{1}H NMR Spectra

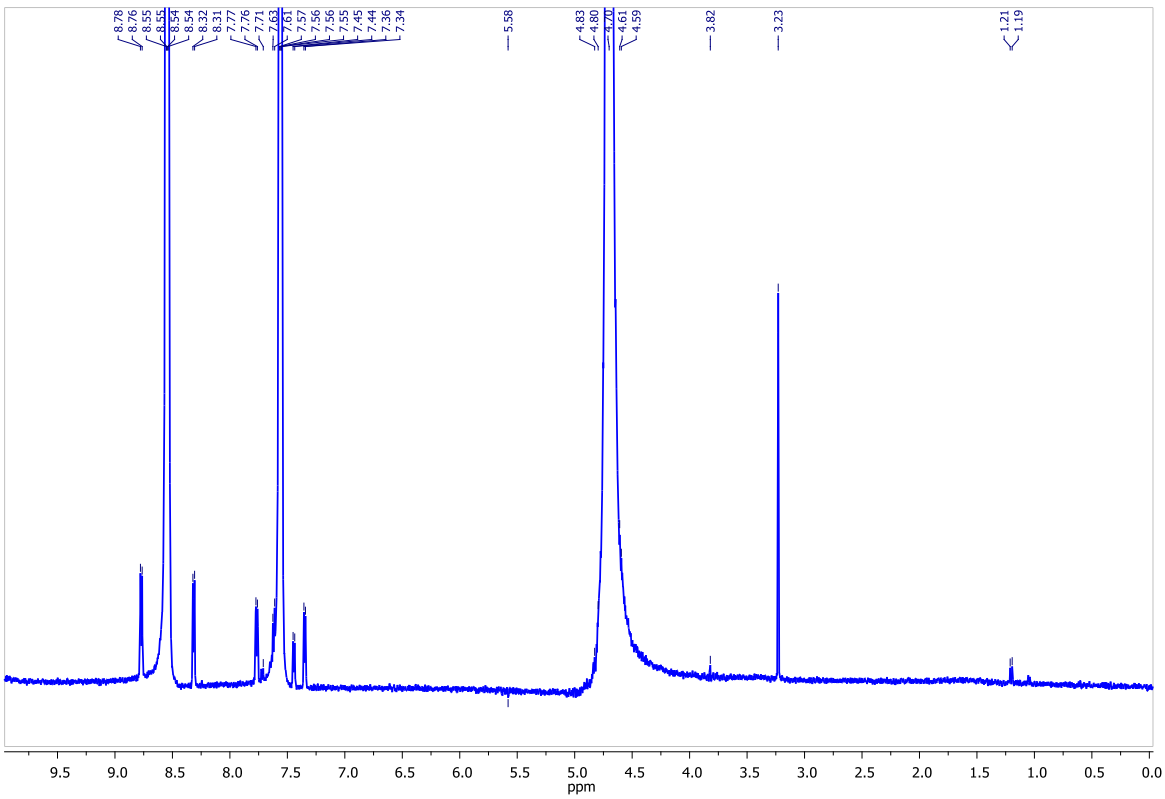


Figure. 5.5 NMR spectrum of Pure Isoniazid

A comparison of ^{1}H NMR spectra of the metal complex and their respective ligand were done. The proton peaks at δ 2.0 were assigned to NH protons of amine group. The peaks at δ 5.6 were assigned to CH protons of carbonyl group which were not seen in pure isoniazid ligand. Hence the presence of this peak shows the coordination occurs at Carbonyl oxygen. The peak around δ 8.6 and 7.4 was observed in both pure isoniazid and Copper complex which indicates that the pyridine ring protons provide the similar environment and do not involve in coordination with the Copper. The NMR peak values for Copper complex were given in the following table.

S.no	Peak value	Assignment
1.	2.0	N-H
2.	5.6	C-H protons of Carbonyl group
3.	7.4	Pyridine ring
4.	8.6	Pyridine ring

Table 5.5 NMR values for the complex $[Cu(INH)_2(urea)_2]$

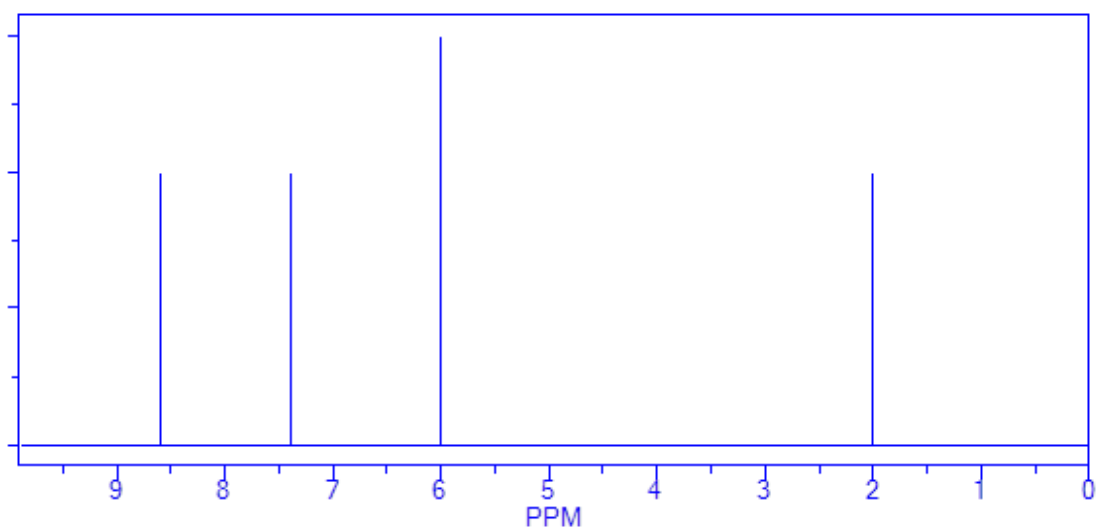


Figure 5.5.1 NMR spectrum for the complex $[Cu(INH)_2(urea)_2]$

5.6 ANTIMICROBIAL ACTIVITY

The antibacterial screening of the free isoniazid and the thiocyanate complex against E. Coli are shown in Fig.5.6. The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of

the test compounds is expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition. The antimicrobial studies showed that the ligands and their metal complexes exhibit considerable activity against the pathogenic bacterial strains[52,53]. The results show that the complexes are more active than their parent ligands against the same microorganisms and as the concentration increases the activity also increases.

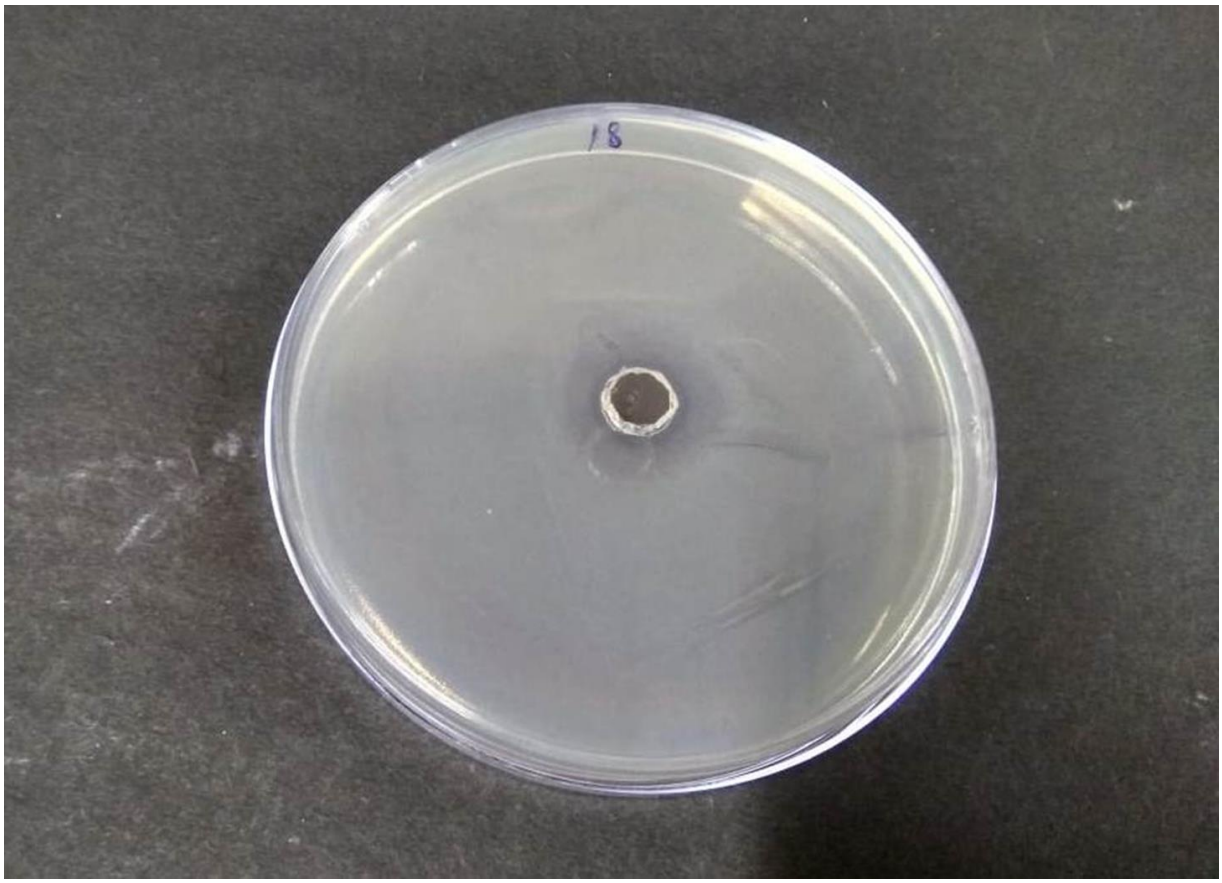


Fig 5.6 Antibacterial activity of the complex

5.7 Structure of the Complex

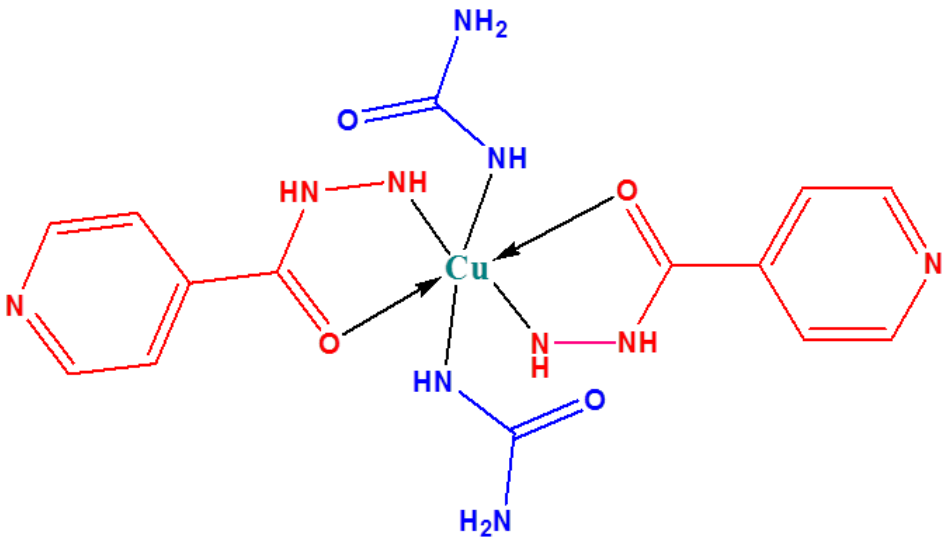


Fig 5.7 Structure of the complex $[Cu(INH)_2(urea)_2]$

Conclusion

In the present study, the mixed ligand complex of copper has been prepared using Isoniazid and urea ligands. The analytical methods and physicochemical parameters have been found out and molar conductivity measurements predicted the non –electrolytic nature of the complex.

The electronic spectra of the complex was recorded and the corresponding transitions predict the probable geometry of the copper complex as distorted octahedral.

The IR spectrum of the pure ligand and the complex was recorded and the metal ligand coordination peaks were observed. Isoniazid acts as a bidentate ligand where both oxygen and nitrogen atoms are coordinated with the metal atom. The pyridine nitrogen does not involve in the coordination which was confirmed by the IR peaks. Though Urea is an ambidentate ligand, here the coordination takes place through the nitrogen atom and hence the coordination sphere contains Urea.

Based on the above results and discussions, the most probable formula and geometry is given as follows.

$[Cu(INH)_2(Urea)_2]$ **-** Distorted Octahedral

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Post Graduate Project – 6

Synthesis, Characterization and Biological activity of N-[(4-hydroxy-3-methoxy-phenyl) -(4-methoxy-phenylamino) -methyl]-nicotinamide

Name of the Guide: Dr. G. Hema Sindhuja
Name of the Candidate: K. Rukshar

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Fig 5.6.1 Electronic spectra of the Mannich base

Fig 5.7 Anti microbial activity for newly synthesized Mannich base

INTRODUCTION

Chapter I

1. INTRODUCTION

1.1 COORDINATION CHEMISTRY

Coordination compoundshave been extensively used due to their attractive structures and topologies as well their potential applications as multifunctional materials in magnetism, conductivity, luminescence, gas adsorption, storage, catalysis and so on. The study of mixed ligand complexes is becoming increasingly more important in equilibrium chemistry. Using stability constants, the chemical behavior, coordination ability, coordination mode and the relation regarding the structure and the stability of the complexes can be obtained, and it is the basis of enzyme -mimicking investigations. If the complex formed by coordination with metal ions, have the tendency to coordinate further or react with other complexes, then they may act as metal ligand.The process in which polydentate ligand bond to a metal ion, forming a ring structure or complex structure is called chelation.

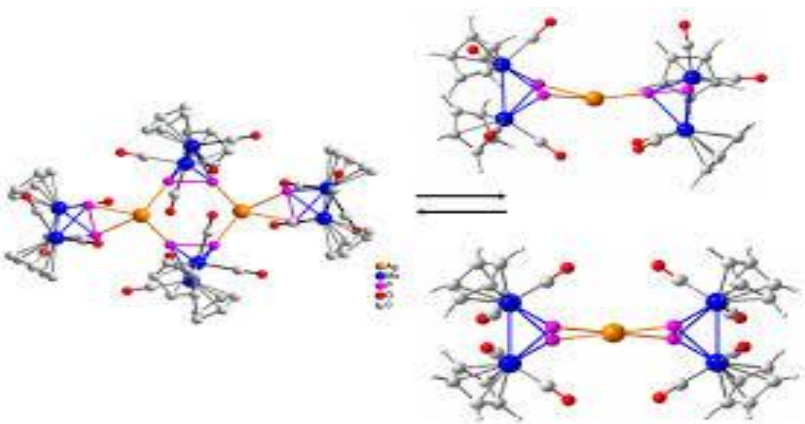

Fig 1.1 Coordination complexes

Heterocyclic nuclei have received a much attention due to their chemotherapeutic value in the development of novel anti tubercular, antifungal, antibacterial, anticancer, etc., The ligands containing N and O donor atom possess a number of biological activities.They are also useful as powerful pesticidesand insecticides apart from the biological applications.The presence

of heterocyclic atoms play an important role in the formation of a stable chelating ring and this situation facilitates the complexation process. Polytopic ligand range from ditopic and hexatopic displaying different geometry and length, can be designed in such a way that the synthesis becomes convenient. They may also contain a variety of functional groups; such rich libraries if ligand gives an opportunity to symmetrically study the relationship between the geometry of the ligand and the functionality of the product obtained. Example; Diketones, dicarboxylates, phenolic ligand, hetero cyclic ligand etc. The chemistry of coordination compounds with heterocyclic ligand containing oxygen and nitrogen as donor atoms has attracted the attention of chemists in recent years. It is well known that such ligand coordinate to metal atom in different ways in different media.

Transition metal ions are essential in many biological systems in nature. These metal complexes with bidentate and tetra dentate ligand containing both hard and soft donor groups have been used extensively in coordination and organometallic chemistry. The chelating properties of Schiff base and Mannich base display manifold applications in medicine, industry and agriculture. The indole moiety represents an important structural component associated with a variety of alkaloids and molecules having wide ranging biological activities, such as antiviral, antitumor, antimicrobial activities, anti-tuberculosis and antifungal activities. The discovery of new metal based drugs has been largely based on ability of metals to increase inhibitory potential of chemotherapy agents. Efficacy of some therapeutic agents has been reported to have increased upon coordination to transition metals .The development of more potent metal based drugs has been under investigations over the last three decades, and it has been discovered that inorganic compounds have enormous impart in medicine. Literally, thousands of compounds have been prepared based on well-conceived ideas of improving their efficacy and have been subsequently screened but few of them have successfully passed the clinical tests. Some metal-based antibiotics such as bleomycin, streptonigrin, and bactracin have gained recognition and are more effective than pure drugs. Ampicillin, a betalactam antibiotic, has been used extensively to treat bacterial infections. Coordination compounds of many of the metals are involved in life process. One can think, of course, iron and magnesium, but there are many others (e.g. copper, zinc, cobalt, molybdenum, and manganese). It is known that all metals in the periodic table from vanadium to zinc are essential to human life. Complexes of alkali and alkaline earth metals with crown ethers and other cyclic ligand play important biological roles. Other coordinated metals have found their

use in the treatment of diseases, e.g., gold compounds for arthritis and platinum compounds for some cancers still others are ingested inadvertently and cause disease.

Presently transition metal complexes have attracted the attention of inorganic, metallo organics as well as bioinorganic chemists because of their extensive applications in wide ranging areas from material to biological science[8].For example as vulcanization agents, protector for paintings, catalysts, antioxidants and in pharmaceuticals[9]. Metal ions are electron deficient, whereas most biological molecules (proteins and DNA) are electron rich. Consequently, there is a general tendency for metal ions to bind and interact with many biological molecules. The efficiency of various organic therapeutic agents can often be enhanced when they are in coordination with a suitable metal ion[10]. The pharmacological activity of metal complexes is highly dependent on the nature of the metal ion and the donor sequence of the ligand because different ligand exhibit different biological properties[11].The important application of coordination compounds find use in qualitative and quantitative chemical analysis. Many familiar color reactions are given by metal ions with a number of ligand. The importance of metal complexes in coordination chemistry gives various applications in biological process such as photosynthesis and dioxygen transport. The pigment responsible for photosynthesis, chlorophyll is a coordinated compound of magnesium. Hemoglobin, the red pigment of blood which acts as an oxygen carrier is a coordinated compound of iron. The coordinated compounds were used as dyes and pigments[12].

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1.2 MULTICOMPONENT REACTIONS

The design of novel reactions that proceed with high atom economy and enable multiple transformations through a shorter reaction sequence is an integral part of modern day organic synthesis. Multicomponent reactions (MCRs) constitute a major part in the present day organic synthesis with advantages ranging from lower reaction times, increased reaction rates to higher yields and reproducibility. The diversity, efficiency and rapid access to small and highly functionalized organic molecules make this approach of central current interest in the construction of combinatorial libraries and optimization in drug discovery process.

Multicomponent Reactions (MCRs) are convergent reactions, in which three or more starting materials react to form a product, where basically all or most of the atoms contribute to the newly formed product. The result is clearly dependent on the reaction conditions: solvent,

temperature, catalyst, concentration, the kind of starting materials and functional groups. Such considerations are of particular importance in connection with the design and discovery of novel MCRs.

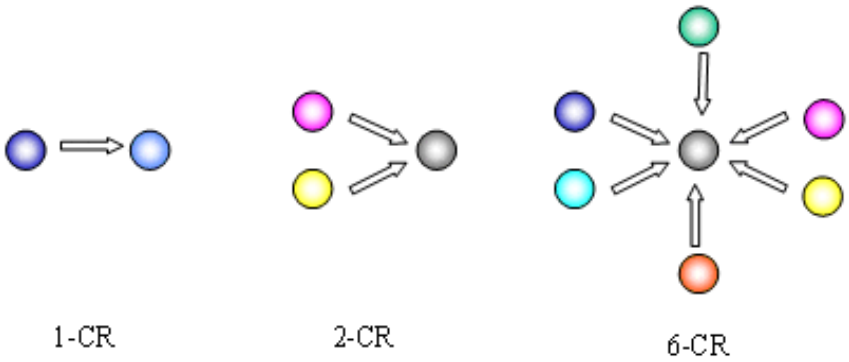


Fig 1.2 Multicomponent reactions

1.2.1 MULTICOMPONENT REACTIONS WITH CARBONYL COMPOUNDS

Some of the first multicomponent reactions to be reported function through derivatization of carbonyl compounds into more reactive intermediates, which can react further with a nucleophile. The best example is the Mannich Reaction:

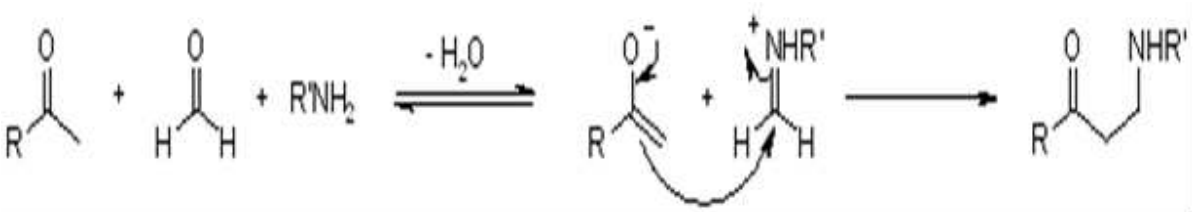


Fig 1.2.1 Scheme for Mannich reaction

1.3 MANNICH BASE

The Mannich reaction is an organic reaction which consists of an amino alkylation of an acidic proton placed next to a carbonyl functional group by formaldehyde and a primary or secondary amine or ammonia. The final product is a β amino-carbonyl compound also known as a Mannich base. Reactions between aldimines and α-methylene carbonyls are also considered Mannich reactions, because these imines are formed between amines and aldehyde. The reaction is named after chemist Carl Mannich[13].

The Mannich reaction is an example of nucleophilic addition of an amine to a carbonyl group followed by dehydration to the Schiff base.The Mannich reaction is also considered a condensation reaction. In this reaction, primary or secondary amines or ammonia, are employed for the activation of formaldehyde. Tertiary amines lack an N–H proton to form the intermediate enamine. Mannich bases are known to possess potent activities like anti-inflammatory, anticancer, anti filarial, antibacterial, antifungal, anticonvulsant, anthelmintic, anti tubercular, analgesic, anti-HIV, anti malarial, antipsychotic, antiviral activities and so forth. Along with biological activities Mannich bases are also known for their uses in detergent additives, resins, polymers, surface active agents, and so forth. Pro drugs of Mannich bases of various active compounds have been prepared to overcome the limitations .Mannich bases (optically pure chiral) of 2-naphthol are employed for catalysis (ligand accelerated and metal mediated) of the enantioselective carbon-carbon bond formation. Mannich bases and their derivatives are intermediates for the synthesis of bioactive molecules. Mannich reaction is widely used for the construction of nitrogen containing compounds. Mannich bases have gained importance due to their application in antibacterial activity and other applications are in agrochemicals such as plant growth regulators.

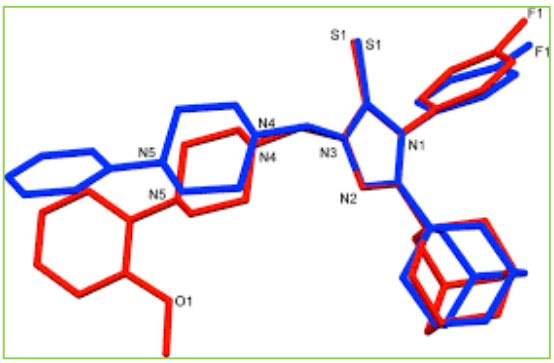


Fig1.3 Mannich base

1.4 P-ANISIDINE

Para-Anisidine (P-Anisidine) (**4-Methoxy aniline**)is an organic compound with the formula $CH_3OC_6H_4NH_2$. It is a white solid, and it commercial samples can appear grey-brown owing to air oxidation. It is one of the three isomers of Anisidine, methoxy-containing anilines. It is prepared by reduction of 4-nitroanisole. P-Anisidine may be sensitive to heat, light and moisture. It reacts with acids, acid chlorides, acid anhydrides, chloro formats and strong oxidizing agents. It is incompatible with alkaline materials. It is incompatible with aldehyde, ketones and nitrates. It is a strong irritant. Toxic when absorbed through the skin. It is a questionable carcinogen.

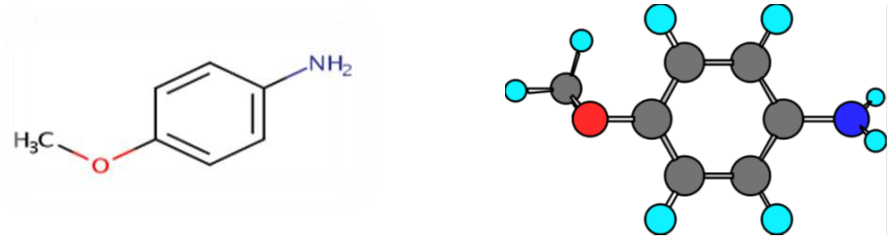


Fig 1.4 Structure of 4-Methoxy aniline

P-Anisidine are used in the manufacture of azo dyes; pharmaceuticals; textile-processing chemicals. It is particularly good at detecting unsaturated aldehydes, which are the ones that are most likely to generate unacceptable flavors, making it particularly useful in food quality testing.

1.5 NICOTINAMIDE

Nicotinamide was discovered between 1935 and 1937. Commercially nicotinamide is made from either nicotinic acid or 3-cyanopyridine. Nicotinamide occurs as a component of a variety of biological systems, including within the vitamin B family and specifically the vitamin B3 complex. It is also a critically important part of the structures of NADH and NAD+, where the N-substituted aromatic ring in the oxidised NAD+ form undergoes reduction with hydride attack to form NADH. The NADPH/NADP+ structures have the same ring, and are involved in similar biochemical reactions. Foods that contain nicotinamide include yeast, meat, milk, and green vegetables.

It is a form of niacin (vitamin B3) that the body needs in small amounts to function and stay healthy. Nicotinamide is found in many plant and animal products and in dietary supplements. It is water-soluble (can dissolve in water) and must be taken every day. Nicotinamide is a type of radio sensitizing agent and a type of chemo sensitizing agent. .

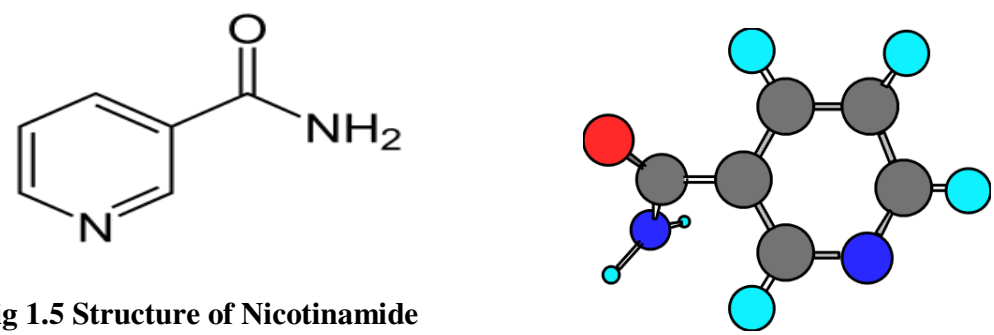


Fig 1.5 Structure of Nicotinamide

1.5.1 USES

- Lack of nicotinic acid and nicotinamide, results in pellagra. So they can prevent pellagra.
- They also play a role in the metabolism of protein and sugar, which can improve human and animal nutrition.
- In addition to be used as a medicine, it can also be applied in food and feed additives.
- The production capacity is more than 30000 tons in the world. In Japan, niacinamide used in medicine (40%), feed additives (50%) and food additives (10%). Nicotinic acid and nicotinamide are non-toxic, naturally contains in liver, kidney, yeast and honey.
- Can be used in skin care products, to prevent coarse skin, maintain healthy skin cells, and promote skin whitening.
- It can also be used in hair care products, to promote scalp blood circulation, healthy hair follicles, promotes hair growth and prevent alopecia.
- Used in biochemical researchto prepare tissue culture medium

1.6 VANILLIN

Vanillin is a phenolic aldehyde, which is an organic compound with the molecular formula $C_8H_8O_3$. Its functional groups include aldehyde, hydroxyl, and ether. It is the primary component of the extract of the vanilla bean. The purity is generally above 99.0% w/w on dried basis. In vanillin obtained from guaiacol, ethyl vanillin can be an impurity comprising up to 250 ppm. Calcium stearate is occasionally added (0.5%) to improve flow-ability. Vanillin has a characteristic pleasant smell and taste of vanilla which is reason for its widespread use. Vanillin has a vapourpresssure of 0.33 Pa and saturated air has a concentration of 0.00029 % at 25^{o} C, corresponding to 18.0 mg/m3. Vanillin is soluble in water and solubility increases with increasing temperature. The phenol group of vanillin has a pKa value of 7.38. With increasing pH, the molecule will lose a proton, become negatively charged and more soluble in water.

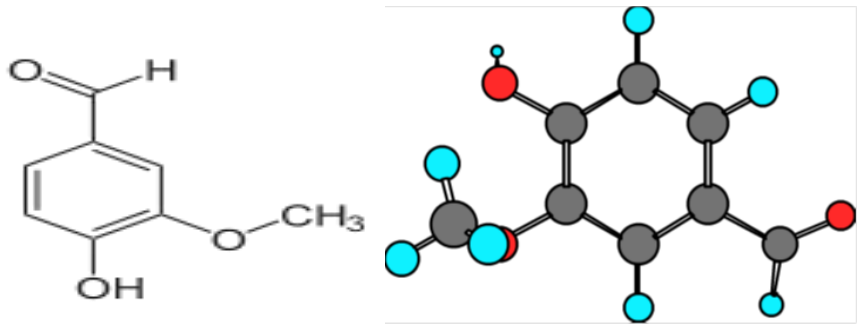
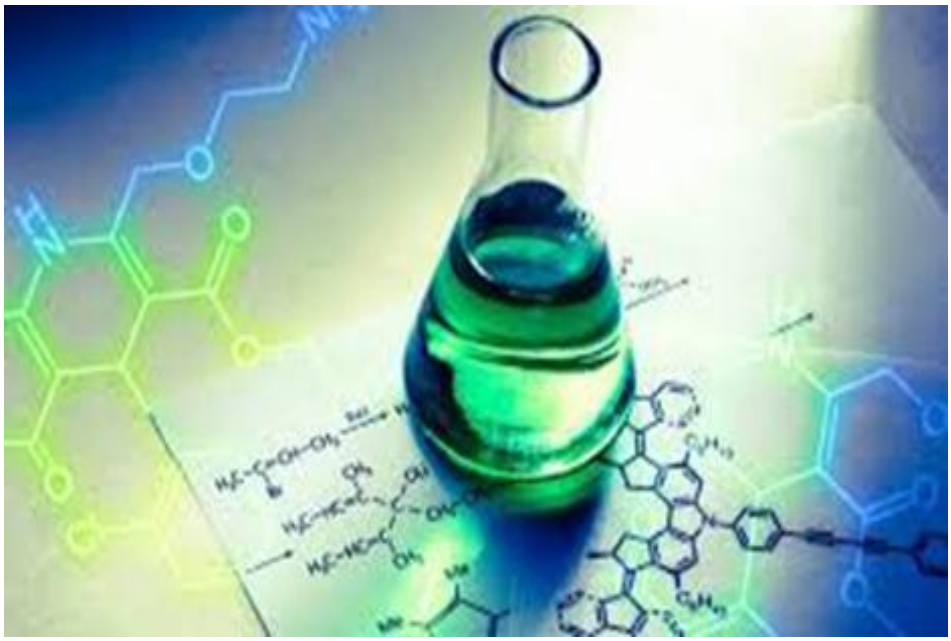


Fig 1.6 Structure of 3-Methoxy-4-hydroxy benzaldehyde (Vanillin)

1.6.1 USES

- Synthetic vanillin is now used more often than natural vanilla extract as a flavoring agent in foods, beverages, and pharmaceuticals
- Vanillin and ethyl vanillin are used by the food industry; ethyl vanillin is more expensive, but has a stronger note. It differs from vanillin by having an ethoxy group ($–O–CH_2CH_3$) instead of a methoxy group ($–O–CH_3$).
- It is also used in the flavor industry, as a very important key note for many different flavors, especially creamy profiles like cream soda.
- Vanillin has been used as a chemical intermediate in the production of pharmaceuticals and other fine chemicals. Vanillin can trigger allergic reactions.
- Vanillin can be used as a general-purpose stain for developing thin layer chromatography plates to aid in visualizing components of a reaction mixture. This stain yields a range of colors for these different components.
- Vanillin–HCl staining can be used to visualize the localisation of tannins in cells.

SCOPE OF TH E WORK



Chapter – II

Aim and scope

Compounds containing active hydrogen atoms yielded amino benzylated Mannich bases with secondary amines and aromatic aldehydes. Mannich bases are important compounds owing to their wide range of biological and industrial applications. Mannich bases have been reported as potential biological agents.

A search through the literature reveals that no work has been done on the condensation of p-anisidine, nicotinamide and vanillin.

Motivated by the above studies, we have aimed at synthesizing the new Mannich base Ligand using p-Anisidine.

The aim of this project is to synthesize, and characterize the Mannich base using the IR, Electronic spectra and ^{1}H NMR spectral studies. The compounds containing oxygen, nitrogen in the ring are found to be biologically important and also behave as potential donor

LITERATURE SURVEY

Chapter – III

3 LITERATURE SURVEY

3.1 Anti fungal activity

John Wiley et. el has explained a novel series of Mannich bases of 3-substituted-4-(5-nitro-2-furfurylidene) amino-5-mercapto-1,2,4-triazoles and screened for the antifungal activity against C. albicans by employing disc diffusion method using nitrofurazone and fluconazole as standard drugs for comparison. The results revealed that the compound substituted with methyl and chloro group has shown highest antifungal activity with 17 mm zone of inhibition which is higher than zone of inhibition of fluconazole. These results enlighten the key role of chloro group towards antifungal activity.

V. J. Belinelo, et al has synthesized mannich bases of 2-(phenyl)-2-(morpholine-4-yl)-N-phenylacetamide and screened for antimicrobial activity against various bacterial and fungal strains. Ciprofloxacin and clotrimazole were used as standard drugs for antibacterial and antifungal activities, respectively. From the synthesized compounds, 3-(4-chlorophenyl)-3-(morpholin-4-yl)-N-phenylpropanamide, has shown highest antibacterial activity against S.epidermidis with 20 mm of zone of inhibition as compared to ciprofloxacin with 15 mm.

S. Joshi, N. Khosla et al., has synthesized a series of novel mannich bases of 3-(4,6-disubstituted-2-thiomethylpyrimidyl)-4-amino-5-mercapto-1,2-4-triazoles and subjected to antibacterial activity. These were found to have equipotent antibacterial activity against P. aeruginosa, S. marcescens, S. aureus, and E. coli .

L. Racane, V. T. Kulenovic, L. F. Jakic, et al., synthesized a new series of benzamide substituted mannich bases and evaluated for antibacterial activity against E. coli, P. aeruginosa, E. faecalis, and S. aureus. Test tube dilution method was employed for evaluation by using amoxicillin and cefixime as standard drugs for comparison These results ensured that substitutions with sulphonamido, p-nitro, and dinitro groups enhance the antibacterial activity.

E. Kashiyama, I. Hutchinson, M.-S. Chua et.al have been synthesized a novel series of mannich bases of quinoline derivative (cinchophen) and screened for the antimicrobial activity against various bacterial and fungal strains. Norfloxacin and fluconazole were used as standard drugs for antibacterial and antifungal activities, respectively. The compounds substituted with morpholine, piperidine, and dicyclohexylamine, respectively, have emerged out as more potent antimicrobial agents than cinchophen and both of the standard drugs.

S. R. Bhusare, R. P. Pawar, and Y. B. Vibhute et al, have been synthesized a series of various substituted N-[(1-piperidinobenzyl) benzamide] (PBB) . The antimicrobial activity of synthesized PBB was carried out on the microorganisms S. aureus, B. subtilis, E. coli, and P. aeruginosa by well diffusion method using Ampicillin as standard drug. It has been found that all the compounds were found to be more active against all bacterial strains than Ampicillin whereas compounds substituted with chloro and cyano group were found to most potent. These results revealed that introduction of electron withdrawing groups on the phenyl ring enhance the activity whereas electron releasing groups are less active compared to un substituted phenyl ring.

B. Kalluraya, R. M. Chimbalkar, and J. C. Hegde et.al have been synthesized a series of novel mannich bases 2-(5-(3-chloro-2-oxo-4-p-tolylazetidin-1-yl)quinolin-8-yloxy)-N′-(2-oxo-1-(piperidin-1-ylmethyl)indolin-3-ylidine)acetohydrazides and screened for antibacterial activity against S. aureus, B. cereus, E. coli, and P. aeruginosa. Amoxicillin and cefaclor were used as reference drugs. These results suggested that substitution with the nitro, chloro, and bromo group has led to enhanced antibacterial activity.

Y. Ivanovo, G. Momekov, O. Petrov et.al have been synthesized a series of 4-[1H-benzimidazole-yl(substituted benzal)methyl-amino] benzoic acids and screened for the antibacterial and antifungal activities against S. aureus, B. subtilis, S. typhi, E. coli, A. Niger,

and C. albicans, respectively. Ciprofloxacin and ketoconazole were used as standard drugs for antibacterial and antifungal activities, respectively. The results were obtained in terms of MIC values. The compounds substituted with hydroxyl and methoxy group on aromatic ring have shown the highest antibacterial activity whereas compound with dimethyl amine has shown highest antifungal activity.

H. I. Gul, J. Vepsalainen et.al have been synthesized Mannich bases of thiosemicarbazide and evaluated for the antifungal activity against C. albicans and A. Niger by using brain heart infusion (BHI) method to estimate the MIC. Fluconazole was employed as standard drug for comparison. From the results it was concluded that analogs with only alkyl groups have shown comparable activity for both strains as compared to fluconazole whereas acyl derivatives were found to be partly active. Analogs with aromatic and substituted aromatic aldehydes showed least activity, while analogs with aliphatic aldehyde, ketones, and amines showed greater activity in C. albicans compared to A. Niger. The analogs substituted with morpholine and aromatic ketones were found to be highly active. Compounds have shown comparable highest activity.

M Ashok, B. S. Holla, and B. Poojary et.al have been synthesized a series of Mannich bases of isatin and its derivatives with 2-[2,6-dichlorophenyl)amino] phenyl acetic acid was synthesized. All the derivatives were evaluated for antibacterial and antifungal activities.. The reason for moderate activity may be due to steric hindrance in binding of bacteria caused by bulky phenyl acetic acid group present at nitrogen atom of isatin nucleus.. All the compounds have shown significant antifungal activity. It is indicating that unsubstituted phenyl ring at 3-position of isatin is desired for antifungal activity compared to substituted phenyl ring.

S. N. Pandeya, D. Sriram, G. Nath et.al have been synthesized a series of novel Mannich bases of 4-amino-3-(N-phthalimido-methyl)-1,2,4-triazole-5-thione and was evaluated for the antimicrobial activity against a variety of gram positive, gram negative, and fungal strains. Levofloxacin was used as standard drug. The results revealed that Mannich bases with electron donating substituents on phenyl ring showed comparable activity to Levofloxacin against E. coli and K. pneumonia. Mannich bases with halogens on phenyl ring have shown activity very close to Levofloxacin against P. aeruginosa. Mannich base with 2-hydroxy group has shown

highest antifungal activity against C. albicans. The results also enlightened the fact that the presence of morpholine ring in heterocyclic molecules increases the antimicrobial activity.

3.2. Anti-Inflammatory Activity

B. N. Singh, S. K. Shukla, and M. Singh et.al have been synthesized Mannich bases of nicotinamide with secondary amines like mefenamic acid, and Diclofenac, in the presence of formaldehyde and hydrochloric acid. Anti-inflammatory activity was studied by hind paw oedema method using carrageenan as a phlogistic agent on Wistar rats. Nicotinamide, Diclofenac, and mefenamic acid were used as standard drugs. Both the Mannich bases showed greater anti-inflammatory activity than the corresponding parent drugs.

Mannich bases of indole derivatives were synthesized by P. Lohitha, D. Giles, C. Sreedhar et al., by reacting different derivatives of indole with various aromatic and heterocyclic amines in the presence of formaldehyde and dimethylformamide. Anti-inflammatory activity was screened on albino rats of Wistar strains by carrageenan paw induced method. Diclofenac sodium was used as standard drug. Carrageenan suspension 0.9% in sodium chloride was injected in plantar region of hind paw and paw volume was measured with the aid of plethysmometer.

K. V. Sujith, J. N. Rao, P. Shetty, and B. Kallurayaet. al., have been synthesized a series of 4-[(4-aryl) methylidene] amino-2-(substituted-4-ylmethyl)-5-{1-[4-(2-methylpropyl)phenyl]ethyl}-2,4-dihydro-3H-1,2,4-triazole-3-thiones from ibuprofen by a three-component Mannich reaction. The synthesized Mannich bases were screened for their anti-inflammatory activity by using carrageenan induced rat paw oedema model. Diclofenac and ibuprofen were used as standard drug substances. The Mannich bases carrying morpholino and N-methylpiperazino residues were found to be most promising anti-inflammatory agents.

A series of Mannich bases of 5-methyl-2-[(2-oxo-2H-chromen-3-yl)carbonyl]-2,4-dihydro-3H-pyrazol-3-one17 was synthesized by K. Sivakumar, A. Rajasekaran, P. Senthilkumar, and P. P. Wattamwar et al., by using conventional and nonconventional (microwave) techniques. The newly synthesized Mannich bases were screened for their anti-inflammatory activity by means of

carrageenan induced rat paw oedema model. Indomethacin was used as standard drug substance for comparison of results. Among all the compounds, the compounds containing sulfonic group at Para and Meta positions, respectively, have shown potent anti-inflammatory activity along with minimum ulcerogenic index.

3.3. Anthelmintic Activity

R. Rita and P. Shrivastvaet. al., have synthesized N-Mannich bases of benzimidazole substituted 1H-isoindole-1,3(2H)-dione . All the synthesized compounds were screened for anthelmintic activity by Watkins technique, against common Indian earthworm P. posthuma. Piperazine hydrochloride was used as standard drug. All the synthesized derivatives have shown significant anthelmintic activity whereas the derivatives substituted with different groups, that is, piperazino-, morpholine, diphenylamino-, chloro, and nitro and dinitro groups, showed better activity than other derivatives.

A novel series of eight Mannich bases, 2-(3-chloro-2,5-dioxo-1-(4-substituted phenylamino)-8-(trichloromethyl)-1,6,7-triazaspirooct-7-en-6-yl)-N′-((3-methyl-5-oxo-1-(morpholine/piperidin/N-methylpiperazine-1-ylmethyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)acetohydazides were synthesized by K. R. Raju, A. Guru Prasad, B. Kumar et al., All the synthesized Mannich bases were evaluated for their anthelmintic activity against P. posthuma. Piperazine citrate was used as standard drug. The compound containing N-methylpiperazino moiety was found to have significant anthelmintic activity.

3.4. Anticonvulsant Activity

Synthesis of Mannich bases of 1, 5-benzodiazepines was carried out and evaluated for the anticonvulsant activity by isoniazid and thiosemicarbazide induced convulsion model. N. S. Pandeya and N. Rajput, et al., have explained that among all the synthesized compounds with methyl group at positions 2 and 4 were found to most active among all the synthesized compounds.

A series of various Mannich base derivatives of lamotrigine, were synthesized by A. Kulkarni, S. B. Wankhede et.al., Here all the synthesized compounds were screened for

anticonvulsant activity by maximal electroshock (MES) convulsion method. Phenobarbitonesodium and lamotrigine were used as reference drugs and % reduction of time spent by animals in extension, flexion, clonus, and stupor phase were noted

3.5. Anticancer Activity

A series of novel Mannich bases of 2-propoxybenzylideneisonicotinohydrazide, were synthesized by M. Malhotra, M. Arora et.al., were screened for the cytotoxicity studies against the A549 human lung adenocarcinoma. Dulbecco's modified eagle medium was used for the growth of cells and supplemented with glutamine, fetal bovine serum, penicillin, and streptomycin. Gemcitabine was used as a standard drug. The viability of the cells was assessed by MTT assay. Here all the compounds synthesized, are exhibited potential cytotoxic activity superior to that of the standard drug, gemcitabine.

Schiff-Mannich bases of fluoroquinolones, from antibacterial analogs were synthesized by G. Hua, T. Caoa, H. Wenlong et al., and screened for antitumor activity against L1210, CHO, and HL60 cell lines. The cell lines were maintained in RPMI 1640 medium supplemented with fetal bovine serum.

Y. Ivanovo, G. Momekov, O. Petrov et al., have been synthesized a new Mannich bases of 6-(3-aryl-2-propenoyl)-2(3H)-benzoxazolones and evaluated for cytotoxicity in human pre-B-cell leukemia cell line BV-173 using MTT-dye reduction assay. The selected compounds were further evaluated on chronic myeloid leukemia K-562 cells. The cytotoxic studies revealed that the compound bearing 4-methoxy function at R^1 in B-ring causes significant decrease in potency while non methoxy substituted analogues bearing bulky basic substituent at nitrogen were found to be more potent.

Novel Mannich bases of 2-arylimidazo benzothiazoles were synthesized by R. M. Kumbhare, K. Vijay Kumar et al., and evaluated for their anticancer activity. The anticancer activity was studied on HepG2 (hepatocarcinoma cell line), MCF-7 (breast carcinoma cell line), and HeLa 9 (human cervical carcinoma cell line) cell lines using MTT assay. All the synthesized compounds have shown cytotoxic activity against the used cell lines. The compounds substituted

with 4-(2-pyridinyl)piperazino and pyrrolidino, respectively, were found to induce G2/M cell cycle arrest with down regulation of cyclin B and up regulation of Chk2 protein. Both compounds have shown characteristic features of apoptosis. The compound 26f could be considered the potential lead for its development as a novel anticancer agent.

3.6. Antioxidant Activity

Ten new Mannich bases were synthesized by M. Malhotra, R. Sharma, M. Sanduja using (E)-2-{[-2-(2,4-dinitrophenyl)hydrazono]methyl}phenol, as a key intermediate and screened for antioxidant activity. From all the synthesized derivatives the compound containing morpholine moiety was found to be most active followed by the compound with Piperazine moiety and compound with diphenylamine moiety.

A novel series of Mannich bases of pyrazolines were synthesized and evaluated by P. C. Jagadish, N. Soni, and A. Verma et al., for the antioxidant activity using DPPH radical and NO radical scavenging methods. Ascorbic acid and rutin were employed as standard drugs for comparison. These results confirmed that phenolic compounds possess high antioxidant ability as compared to non phenolic compound.

Two Mannich bases of benzamide, that is, 1-((1H-benzod]imidazole-1-yl)methyl)urea (BIUF) and 1-((3-hydroxynaphthalen-2-yl)methyl)thiourea (TNTUF) were synthesized by, D K. Chakkaravarthi, K. Gokulakrishnan et al., and evaluated for the antioxidant activity. Both of the Mannich bases were found to be active antioxidant agents due to presence of electron releasing amide group in them. BIUF was found to more active than TNTUF due to the presence of two N atoms in the benzimidazole adjoined with amide group.

CHARACTERIZATION TECHNIQUES

4.1 SPECTRAL STUDIES

All organic compounds interact with electromagnetic radiation that is they absorb energy. When a molecule absorbs energy, a transform occurs that may be either temporary or permanent. Lower energy radiations may cause the promotion of electrons to higher energy levels or bond cleavage. Whether the transformation involves molecular rotation, bond vibration or electronic transition, the molecules absorb only the wavelength of radiation with exactly the energy necessary for the transition.

By measuring the absorption spectra of known compounds, we can correlate the wavelengths of energy absorbed with characteristic structural features. This information is then used to determine the structure of unknown compounds.

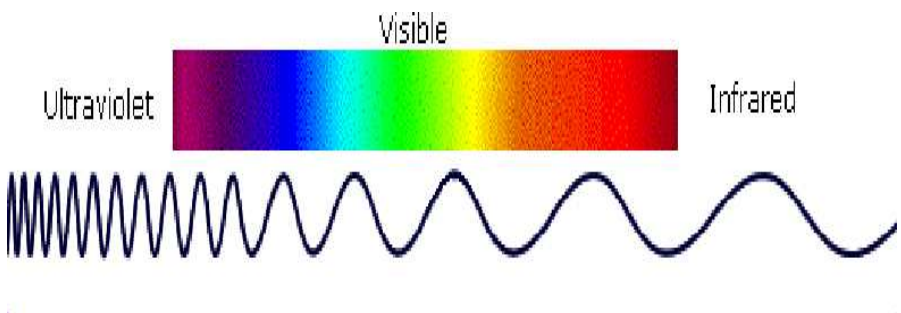


Fig 4.1 Electromagnetic spectrum

4.2 INFRA-RED SPECTRA

Vibrational rotational spectra are found in the case of those molecules which posses permanent dipole moment only. In order to study such type of spectra, the energy supplied should be sufficient so as to result transition from one vibration level to another, keeping the electronic level undisturbed. Since each vibrational change is accompanied by so many changes in the rotational energy also, absorption band consists of closely spaced line .

As the infra-red absorption bands of metal-donor atom provide information on the strength and character of the coordinate bond in a given complex, it is evident to get reliable identification of the various absorption bands to arrive at the correct structure of a complex .

Infrared spectroscopy is an absorption method in the wavelength region of 1 to 100 μminthat extendsthe region of visible light to longer wavelengths and smaller frequencies/energies. Instead, Infrared radiation excites vibrational and rotational motions in molecules. Because each inter atomic bond may vibrate in several different motions (stretching or bending), individual bonds may absorb at more than one IR frequency. Stretching absorption usually produce stronger peak than bending, however the weaker bending absorption can be useful in differentiating similar types of bonds (e.g. Aromatic substitution). It is also important to note that symmetrical vibrations do not cause absorption of IR radiation. For example, neither of the carbon-carbon bonds in ethane or ethyne absorbs IR radiation.

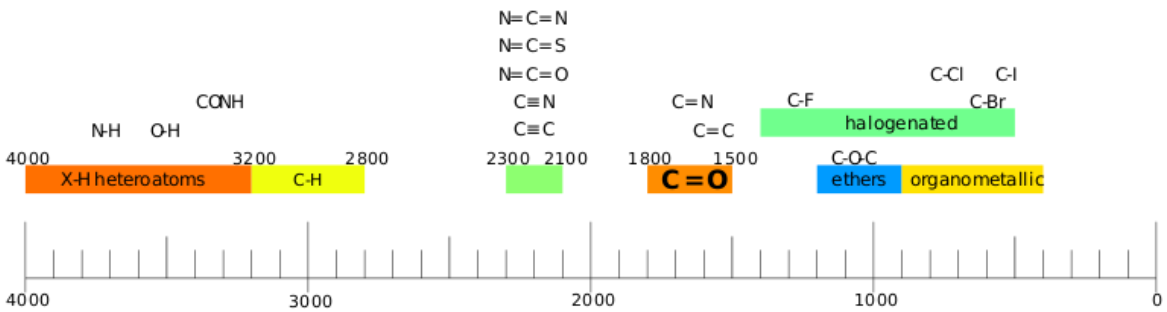


Fig 4.2 I R functional group values

4.3 NUCLEAR MAGNETIC RESONANCE (NMR)

Excitation of a nucleus of atoms occures through radio frequency irradiation. It provides extensive information about molecular structure and atom connectivity.

This important and well established application of NMR spectroscopy will serve to illustrate some of the novel aspects of this method. To begin with, the NMR spectrometer must be turning to a specific nucleus, in this case the proton. The nucleus of hydrogen atom (proton) behave as a spinning bar magnet, because it posses both electric and magnetic spin. Like any other charged

body, the nucleus of a hydrogen atom also generates a magnetic field. The actual procedure for obtaining the spectrum varied but the simplest is referred to as the continuous wave (CW) method.

The number of signals in an NMR spectrum tells the number of sets of equivalent protons in a molecule. The position of signals in the spectrum help us to know the nature of protons via., aromatic, aliphatic, acetylinic, vinyl, adjacent to some electron attracting or electron releasing group etc. Shift in the position of NMR absorption which arises due to the shielding (or deshielding) of protons by the electrons are called chemical shifts.

For measuring the chemical shift of various protons in a molecule, the signal of tetra methyl silane (TMS) is taken as a reference. This difference in the absorption position of the proton with respect to TMS signal is called chemical shift (δ- value).

4.4 ELECTRONIC SPECTROSCOPY

Electronic Spectroscopy relies on the quantized nature of energy states. Given enough energy, an electron can be excited from its initial ground state or initial excited state (hot band) and briefly exist in a higher energy excited state. Electronic transitions involve exciting an electron from one principle quantum state to another. Without incentive, an electron will not undergo transition to a higher level. Only by absorbing energy, can an electron be excited. Once it is in the excited state, it will relax back to it's original more energetically stable state, and in the process, release energy as photons.

Electronic spectra of transitions metal complexes

Electronic absorption spectroscopy requires consideration of the following principles:

a. Franck-Condon Principle

Electronic transitions occur in a very short time and hence the atoms in a molecule do not have time to change position appreciably during electronic transition ,So the molecule will find itself with the same molecular configuration and hence the vibrational kinetic energy in the excited state remains the same as it had in the ground state at the moment of absorption.

b. Electronic transitions between vibrational states

Frequently, transitions occur from the ground vibrational level of the ground electronic state to many different vibrational levels of particular excited electronic states. Such transitions may give rise to vibrational fine structure in the main peak of the electronic transition. Since all the molecules are present in the ground vibrational level, nearly all transitions that give rise to a peak in the absorption spectrum will arise from the ground electronic state. If the different excited vibrational levels are represented as υ1, υ2, etc., and the ground state as υ0, the fine structure in the main peak of the spectrum is assigned to υ0 → υ0 , υ0 → υ1, υ0 → υ2 etc., vibrational states. The υ0 → υ0 transition is the lowest energy (longest wave length) transition.

The changes are outlined below:

There may be a change in the band position.There may occur a change in relative band intensities. This results in the appearance of new, often weak bands.Single peaks in the free ligand may undergo splitting into several, closely spaced bands in the complex.

From the above changes in the infra-red spectrum of the coordinated ligands, one may conclude whether the ligand has entered into the coordination sphere or not. The shifts in the infrared vibrational bands of the ligands on complex formation may also provide useful information about the bonding characteristics of the complex.

4.5 Disc Diffusion method

The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent.In thismethod, the activity of the test compounds is expressed by measuring the diameter ofzone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition.

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibilition by test compound (diamter)}}{\text{Zone of inhibilition by standard (diamter)}} \times 100$$

The nutrient medium was prepared by following composition like Yeast extract- 5 g, Meat extract-10 g, Peptone-5 g, Sodium Chloride-5 g, Agar-20 g. The antibacterial activity of the compound was done by the disc diffusion method using DMSO as solvent. The test solutions

Figure 4.5 Disc diffusion method sample

were prepared by dissolving the compounds in DMSO. In a typical procedure, agar medium was inoculated with microorganisms and it is filled with the test solution using micropipette and the plate is incubated at 35˚C for 24 to 48 hr. During this period, the test solution diffuses and the growth of the inoculated microorganism *E. Coli*, is found to be affected. The activity developed on the plate is measured by measuring the diameter of the inhibited zone in millimeters.

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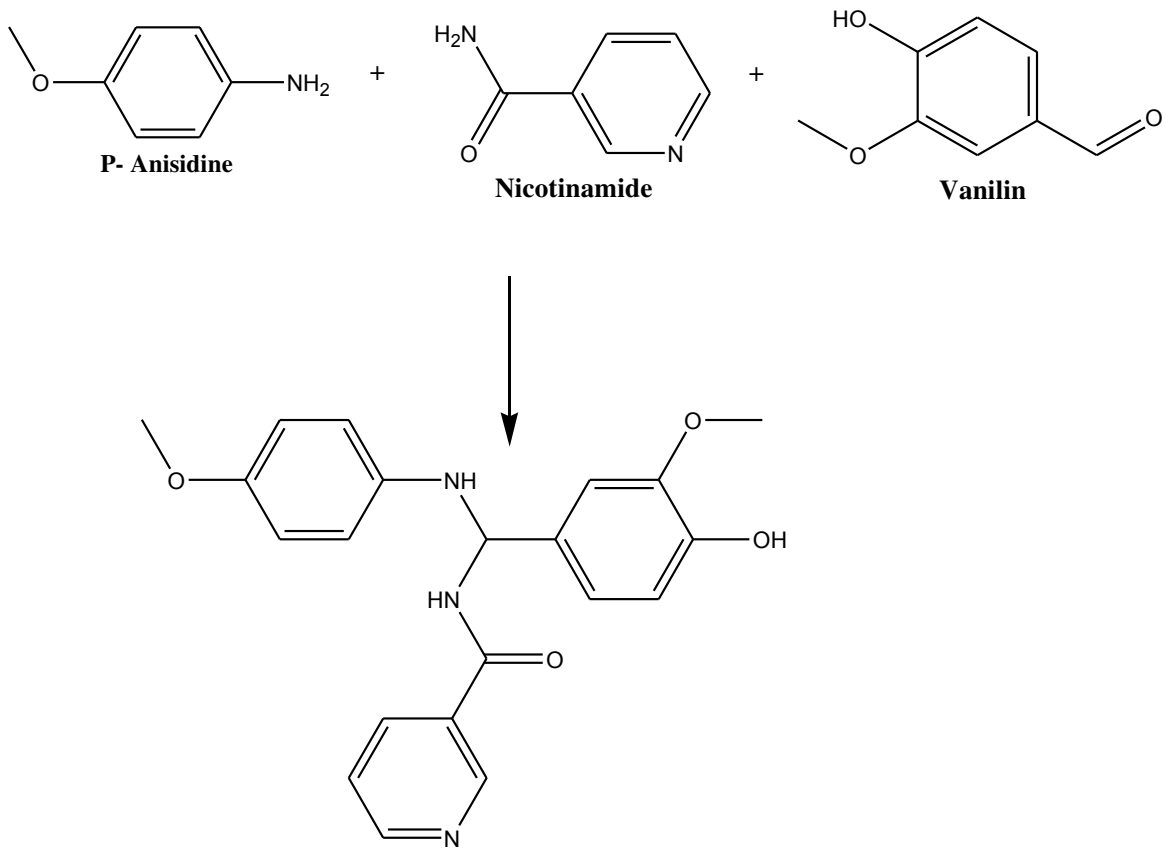
RESULTS AND DISCUSSION

5 RESULTS AND DISCUSSIONS

5.1 SYNTHESIS OF NOVEL MANNICH BASE

N-[(4-Hydroxy-3-methoxy-phenyl)-(4-methoxy-phenyl amino)-methyl]-nicotinamide

To the ethanoic solution of Nicotinamide (0.01 mol, 1.22 g), P-Anisidine (0.01 mol, 1.23g) was dissolved in ethanol added and the contents were stirred for 10 minutes in a magnetic stirrer. Vanillin (0.01 mol, 1.52g) dissolved in ethanol was added to the above mixture and the stirring was continued till six hours, A dirty white solid precipitate is obtained, washed, filtered, and recrystallized with toluene.



P- Anisidine **Nicotinamide** **Vanilin**

***N*-[(4-Hydroxy-3-methoxy-phenyl)-(4-methoxy-phenylamino)-methyl]-nicotinamide**

Fig 5.1 Schematic diagram for the synthesis of Mannich base

5.2 Analytical data

The synthesized Mannich base were analyzed for various physicochemical parameters and tabulated as follows.

S.NO	Parameters	Values
1.	Colour	**White**
2.	Yield	**80 %**
3.	Molecular weight	**379.2**
4.	Molecular formula	**$C_{21}H_{21}N_3O_4$**
5.	Melting point	**861 K**
6.	Boiling point	**1123 K**
7.	Critical Temperature	**1073 K**
8.	Critical Pressure	**24.41 Bar**
9.	Critical Volume	**1045.50** cm^3/mol
7.	Elemental Analysis	**C, 66.48; H, 5.58; N, 11.08; O, 16.87**

Table 5.2 Physicochemical parameters for the mannich base

5.3 Solubility of the synthesized mannich base

The Mannich base was successfully prepared by stirring process and nature of the solubility was determined using different solvents.

S.No	Solvents	Solubility		
		Soluble	Partially soluble	Insoluble
1.	Benzene		✓	
2.	Toluene			✓
4.	Acetophenone		✓	
5.	Di chloro ethane	✓		
6.	Ethanol	✓		
7.	Methanol	✓		
8.	Water			✓
9.	CCl_4			✓
10.	DMSO		✓	

Table5.3 Solubility of Mannich base in different solvents

5.4 IR Spectra

Functional groups	Stretching Frequency
N-C-N	**1151**
N-H	**3613**
C=O	**1589**
C-N	**1437**
Aromatic C-C	**1669**
Pyridine N	**715**
Aromatic C-H	**2832, 3055**

Table 5.4 I R values of Mannich base

Newly synthesized mannich base Isonicotinic acid N-[(4-Hydroxy-3-methoxy-phenyl)-(4-methoxy-phenylamino)-methyl]-nicotinamidewas confirmed by infrared spectroscopy. Stretching frequency of N-H peak was noticed at 3613 cm^{-1}. There are many strong bands in the region 932-616 cm-1. The amide bond due to v(c=o) appears at 1589 cm^{-1} and the aromatic C-H stretching bond values are 2832 and 3055 cm^{-1}.The strong absorption at1437 cm^{-1} is attributed to C-N.Then N-C-N stretchingbond value is 1151 cm^{-1}. The aromatic C-Cstretching frequency is obtainedat 1669 cm^{-1}.

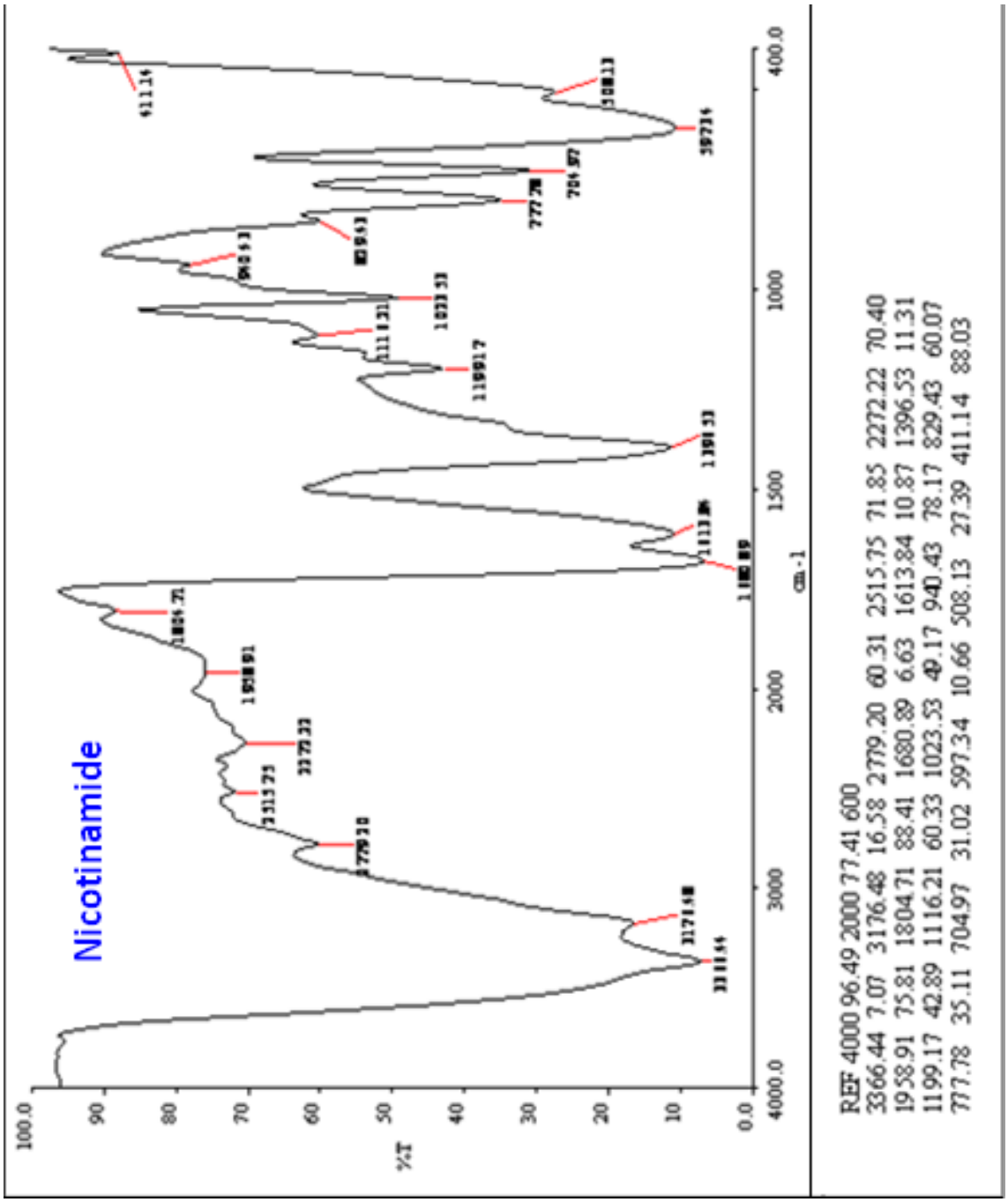


Fig 5.4.1 I R spectrum for Pure Nicotinamide

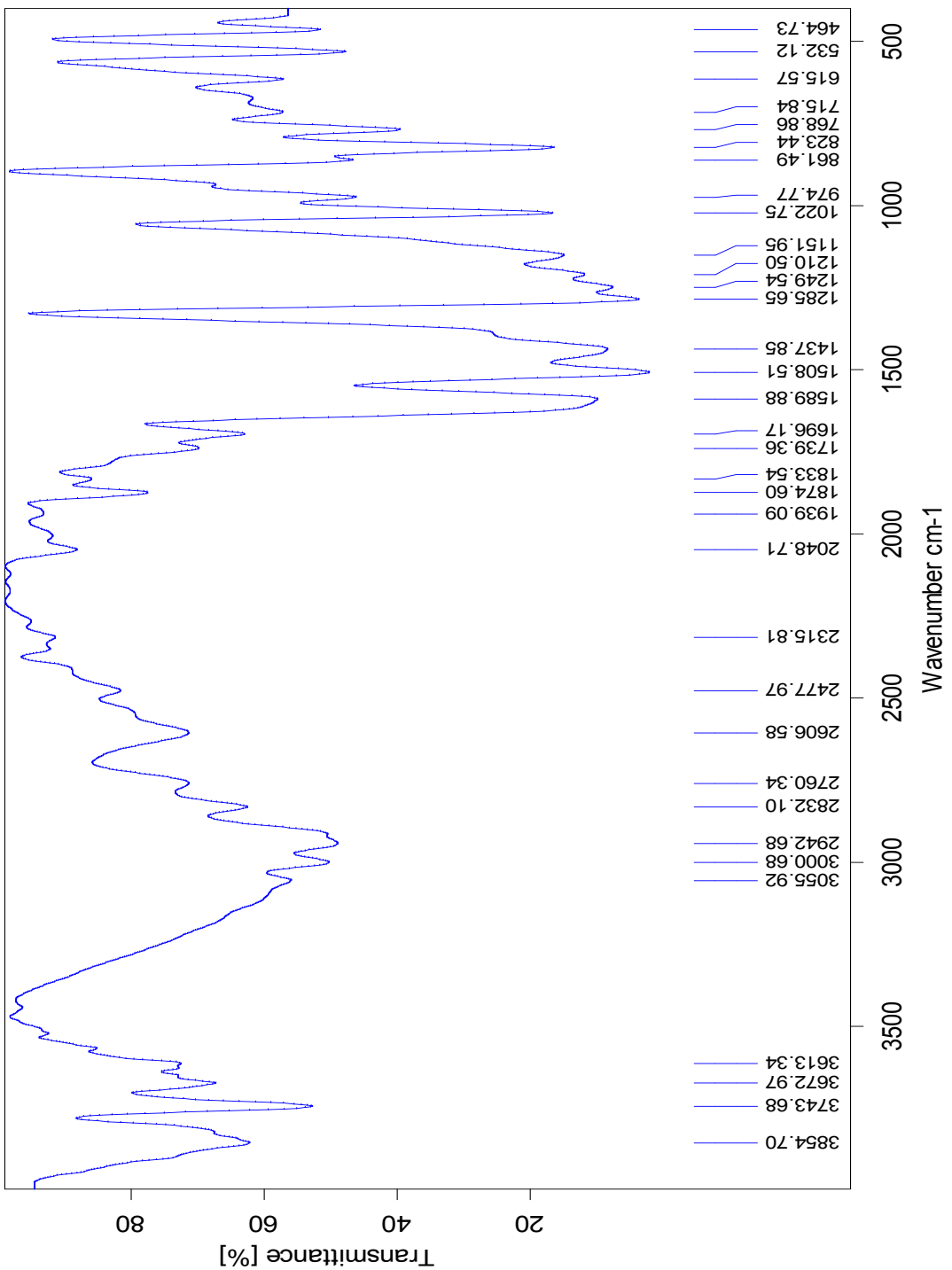


Fig 5.4.2 I R Spectrum of the Mannich base

5.5 NMR SPECTRA

1HNMR spectrum of the novel mannich base was recorded in methonal medium using TMS as an internal standard. The multiplet at 6.6-8.6 ppm due to aromatic proton, the signal δ 8.0 ppm is assigned to the aromatic amide proton, the peaks at 3.73 ppm are due to methyl carbon CH_3. The signal at δ 7. 6 ppm is attributed to the pyridine C-H proton. δ 4.00 ppm and 5.00attributed to the aromatic C-NH proton and Aromatic C-OH respectively.

Group Assignment	**Chemical shift (ppm)**
Aromatic CH	6.6-8.6
pyridine C-H proton	7.6
Aromatic C-NH proton	4.00
Aromatic C-OH	5.0
Aromatic amide N-H	8.0
Methyl CH_3	3.73

Table 5.5 NMR spectra values of Mannich base

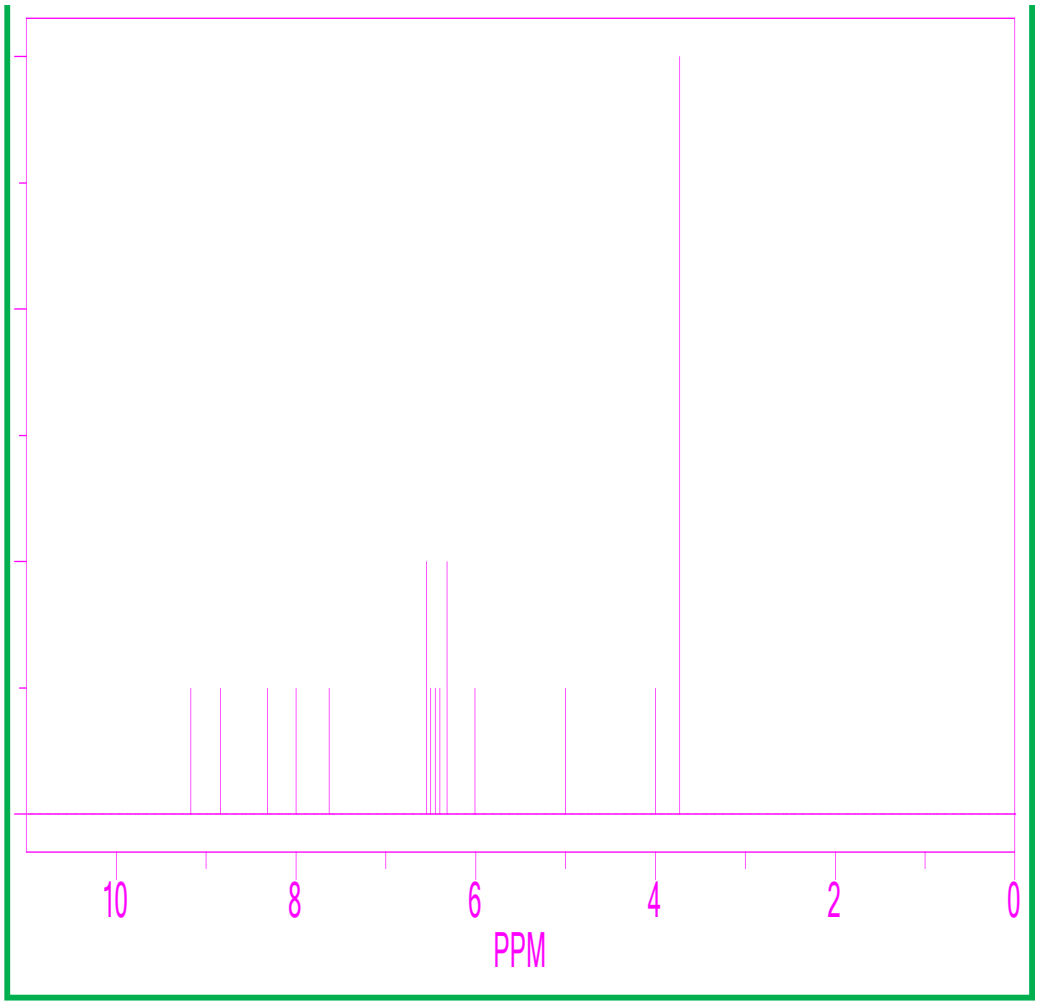


Figure 5.5 NMR peak of Mannich base

5.6 Electronic spectra

Peak value	Transitions
282	
309	

Table 5.6 Electronic spectra values of Mannich base

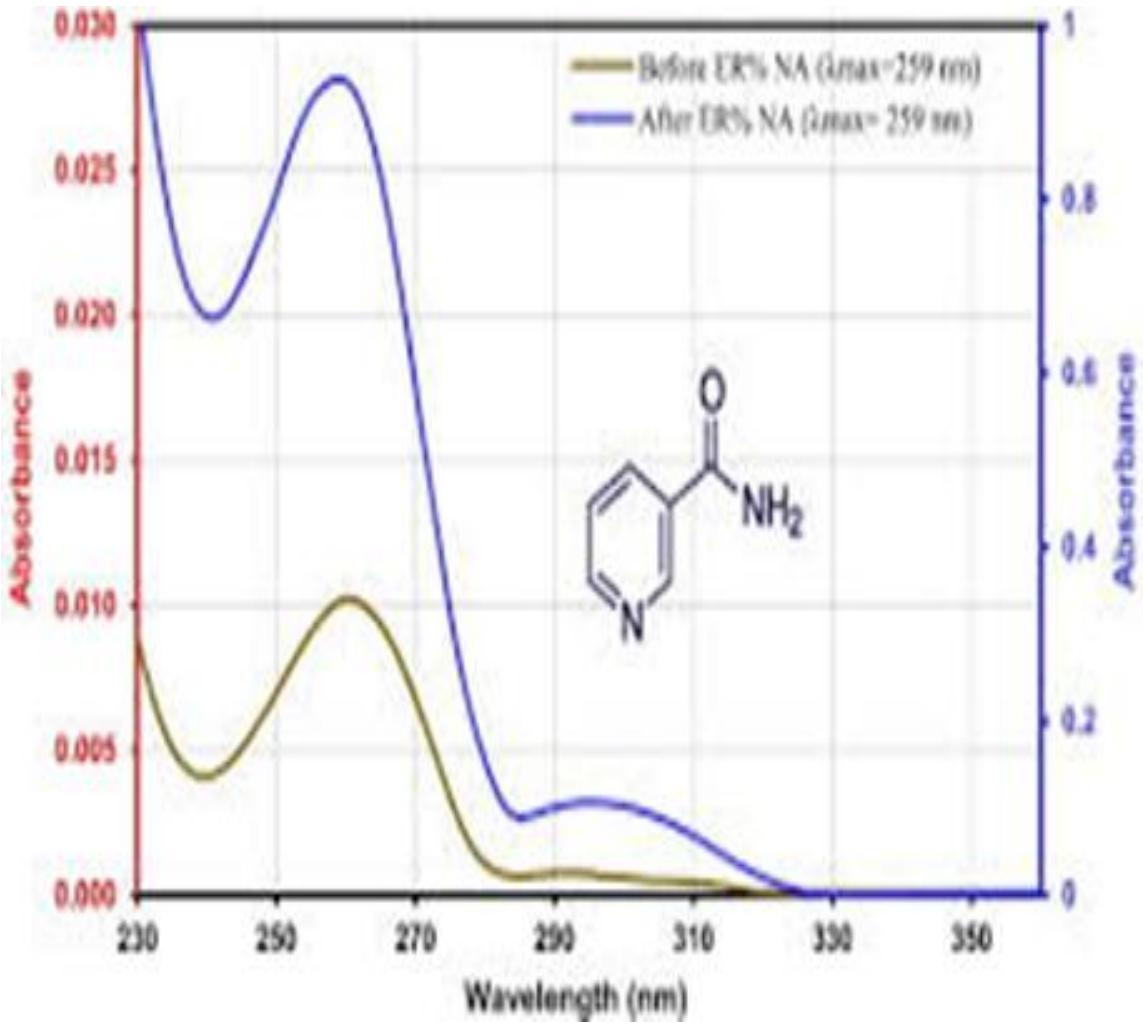


Fig 5.6 Electronic spectra of pure nicotinamide

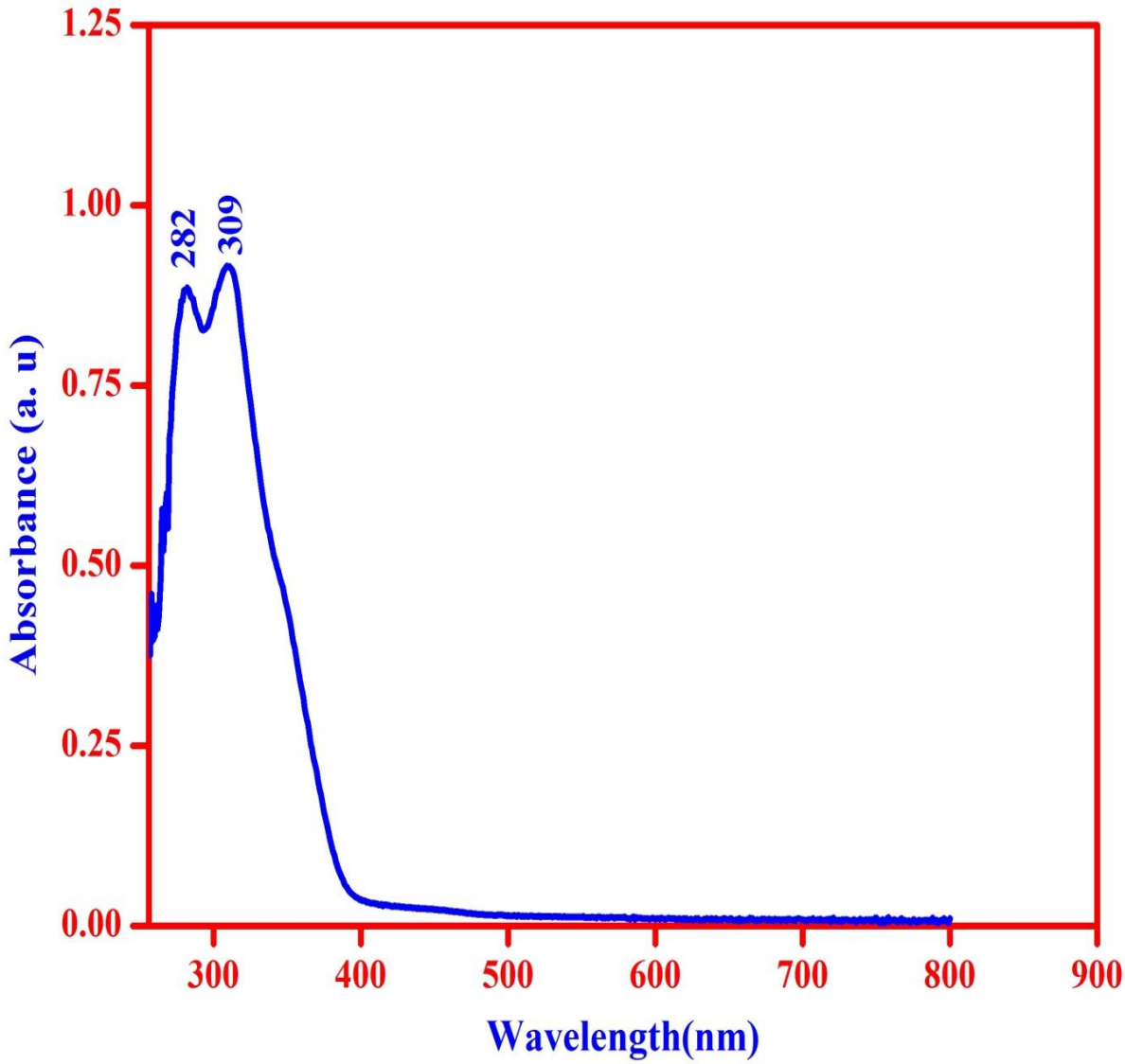


Fig 5.6.1 Electronic spectra of the mannich base

5.7 Antimicrobial activity

The antimicrobial activity for the compound was carried out by disc diffusion technique. Thecompound was tested against E.Colibacteria. Discs impregnated with different known concentration ofcompounds such as 3,4 and 5 µg were placed on agar plate that has been inoculated uniformly over theentire plate with a culture of the microorganism to be tested. The plate was incubated for 24 hours at 37 °C.During the period, the compound diffuses through the agar and prevents the growth of the organism.Effectiveness of the susceptibility is proportional to the diameter of zone of inhibition. The zone ofinhibition was measured in mm and the activities were compared with Ciprofloxacin 5 µg/disc forbacteria and Nystatin 100 units/disc for fungi as reference standard. It has been found that the compoundpossess appreciable antimicrobial activities against selected organisms. Figure.represents that the increase in concentration of compound increases the Zone formation of the microbialactivity.

Name of the micro organism	**Zone of inhibition (mm)**	**Growth of inhibition**
E.coli	**18**	**Sensitive**

Table 5.7 Anti microbial activity for newly synthesized Mannich base

The compounds possess high antimicrobial activity against the *E.Coli.sp.*

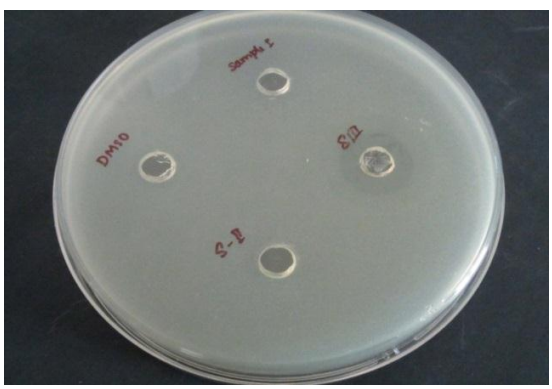


Fig 5.7 Anti microbial activity of the mannich base

CONCLUSION

Conclusion

In the present work, a novel Mannich base has been synthesized using p - Anisidine, Nicotinamide and Vanillin.

Various physico chemical parameters such as melting point, boiling point, color, yield and molecular weight have been reported.

The solubility of the newly synthesized Mannich base has been found out using various solvents and results have been tabulated.

The IR peaks of NH stretching and ν C=O indicates the formation of N-C-N bond which in turn represents the formation of Mannich base.

The presence of NMR signal at 2.0 and 5.6 indicates the NH- proton also provides information about the coordination.

The electronic spectra peaks at 282 and 309 nm correspond to the -π and transition.

The antibacterial activity of the synthesized Mannich base have been investigated against E-coli bacteria and found to possess good antibacterial activity measured from zone of inhibition.

From all these above investigations the structure and name of the newly synthesized Mannich base have been depicted.

N-[(4-HYDROXY-3-METHOXY-PHENYL) - (4-METHOXY-PHENYLAMINO) -METHYL] -NICOTINAMIDE.

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Post Graduate Project - 7

A Study on Synthesis and Spectroscopic Characterization of Cobalt (II) complex with Isoniazid Complex

Name of the Guide: Dr. A. Mushira Banu
Name of the Candidate: R. Saranya

CONTENTS

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Chapter – 1

INTRODUCTION

1.1 Coordination Complexes

Coordination complexes were known - although not understood in any sense - since the beginning of chemistry, e.g. Prussian blue and copper vitriol. The key breakthrough occurred when Alfred Werner proposed, *inter alia*, that Co(III) bears six ligands in an octahedral geometry. The theory allows to understand the difference between coordinated and ionic chloride in the cobalt ammine chlorides and to explain many of the previously inexplicable isomers.[1] He resolved the first coordination complex into optical isomers, overthrowing the theory that chirality was necessarily associated with carbon compounds. A coordination compound (or coordination complex) consists of a **metal cation** or neutral atom to which neutral or negatively charged ligands have bonded.

Ligand is an atom, ion or molecule that generally donates one or more of its electrons through a coordinate covalent bond to share its electrons through a covalent bond, or through a pi – bond with one or more central atoms or ions (these ligands act as a Lewis base). Factors that characterize the ligands are their charge, size (bulk), and of course the nature of the constituent atoms. The ligands in a complex, stabilize the central atom and dictate the reactivity of the central atom. The number of ligand atoms to which the metal center is directly bonded is the metal cation's coordination number (C.N.), and this number is always greater than the regular valence or oxidation number (O.N.) of the metal.[2]

For the last two decades, the synthesis of coordination compound with transition metals and their applications have become an attractive field because of the excellent properties such as

catalysis, ion exchange, microelectronics, nonlinear optics, porous materials, etc.[3-7] Due to the smaller size, and coordination numbers (4 or 6) of first row transition metal ions are easily coordinated with nitrogen and oxygen atoms and that's why their coordination geometric structures are simple. The mixed ligand complexes of transition metals are very important in different field of chemistry like photochemistry, analytical chemistry, magneto chemistry etc. The magnetic properties, diverse catalytic activity of such compounds is now being explored for its biological importance. Transition metal complexes are cationic, neutral or anionic species in which a transition metal is coordinated by ligands. Transition metal ions are known to play very important roles in biological processes in the human body. For example, Zn (II) and Cu (II) ions are the second and third most abundant transition metals in humans. They are found either at the active sites or as structural components of a good number of enzymes.[8-10]

Cobalt is present in vitamin B12, a co-enzyme that plays significant roles in some biochemical processes. There are numerous lists of transition metals which are effective therapeutic agents especially when coordinated to a ligand to form metal complexes. A list of metal containing compounds used in chemotherapy for treatment of diseases include platinum (anticancer), silver (antimicrobial), gold (antiarthritic), bismuth (antiulcer), antimony (antiprotozoal), vanadium (antidiabetic) and iron (antimalaria).[11-15] Nitrogen containing chiral ligands have found wide applications in chemotherapy and asymmetric catalysis. The chemistry of coordination compounds with heterocyclic ligands containing oxygen and nitrogen as donor atoms has attracted the attention of chemists in recent years. It is well known that such ligands coordinate to metal atom in different ways in different media. Transition metal ions are essential in many biological systems in nature. These metal complexes with bidentate and tetra dentate

ligands containing both hard and soft donor groups have been used extensively in coordination and organometallic chemistry.[16]

1.2 Uses of Coordination Compounds

l. Dyes and Pigments: Coordination compounds have been used from the earliest times as dyes and pigments, for example madder dye which is red, was used by the ancient Greeks and others. It is a complex of Hydroxyanthraquinone. A more modern example is the pigment copper phthalocyanine, which is blue.

2. Analytical Chemistry:

(a) Color Tests: Since many complexes are highly colored they can be used as colorimetric reagents e.g. formation of red 2,2'-bipyridyl and l,l0-phenanthroline complexes as a test for $Fe^{2+.}$

(b) Gravimetric Analysis: Here chelating ligands are often used to form insoluble complexes e.g. $Ni(DMG)_2$ and $Al(oxine)_3$.

(c) Complexometric Titrations and Masking Agents: An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution, e.g. Zn^{2+}, Pb^{2+}, Ca^{2+},Co^{2+}, Ni^{2+}, Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analyzed, e.g. Bi^{3+} in the presence of Pb^{2+}. Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

3. Sequestering Agents: Related to their use as masking agents is the use of ligands for "sequestering" i.e. for the effective removal of objectionable ions from solution in industrial processing, e.g. EDTA is used to "soften" water. The addition of EDTA to water is used in boilers etc., to prevent "scaling" or buildup of insoluble calcium salts.

4. Extraction of Metals: Sometimes certain metals can be leached from their ores by formation of stable complexes e.g. Ag and Au as complexes of cyanide ion.

5. Bio-Inorganic Chemistry: Naturally occurring complexes include hemoglobin, chlorophyll, vitamin B12 etc. EDTA and other complexing agents have been used to speed the elimination of harmful radioactive and other toxic elements from the body. (e.g. Pb^{2+}). In these cases a soluble metal chelate is formed.

6. Chemo-therapy: an example is the use of cis-$PtCl_2$ $(NH_3)_2$ as an anti-tumor drug.[17-19]

1.3 Ligands

1.3.1 Thiocyanate:

Molecular formula: CNS^-

Molar mass: 58.0824

Thiocyanate (also known as sulphocyanate or thiocyanide or rhodanide) is the anion, $[SCN]^-$. Common compounds include the colourless salts potassium thiocyanate and sodium thiocyanate. Organic compounds containing the functional group SCN are also called thiocyanates. Mercury(II) thiocyanate was formerly used in pyrotechnics.[20]

Thiocyanate is analogous to the cyanate ion, $[OCN]^-$, where in oxygen is replaced by sulphur. $[SCN]^-$ is one of the pseudohalides, due to the similarity of its reactions to that of halide ions. Thiocyanate was formerly known as rhodanide (from a Greek word for rose) because of the red colour of its complexes with iron. Thiocyanate is produced by the reaction of elemental sulfur or thiosulfate with cyanide.

$$\mathbf{8\ CN^- + S_8 \rightarrow 8\ SCN^-}$$

$$\mathbf{CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}}$$

The latter reaction is catalyzed by the enzyme sulfotransferase known as rhodanase and may be relevant to detoxification of cyanide in the body.

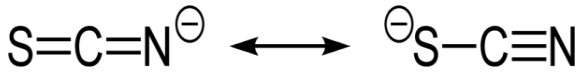

Fig 1.3.1 Resonance structures of the thiocyanate ion

Thiocyanate shares its negative charge approximately equally between sulfur and nitrogen. Consequently, thiocyanate can act as a nucleophile at either sulfur or nitrogen — it is an ambidentate ligand. $[SCN]^-$ can also bridge two (M−SCN−M) or even three metals (>SCN^- or $^-$SCN<). Experimental evidence leads to the general conclusion that class a metals (hard acids) tend to form N^- bonded thiocyanate complexes, whereas class b metals (soft acids) tend to form S-bonded thiocyanate complexes.[21] Other factors, e.g. kinetics and solubility, are sometimes involved, and linkage isomerism can occur, for example $[Co(NH_3)_5(NCS)]Cl_2$ and $[Co(NH3)_5(SCN)]Cl_2$

1.3.2 Isoniazid

Heterocyclic compounds play an important role in many biological systems, especially N- based ligand, which being a component of several vitamins and drugs. Heterocycles form by far the largest of classical divisions of organic chemistry and are of immense importance biologically and industrially. The majority of pharmaceuticals and biologically active agrochemicals are heterocyclic while various additives and modifiers used in industrial

applications ranging from cosmetics, reprography, information storage and plastics are heterocyclic in nature.[22-24]

Tuberculosis (TB) is a public health disease that produces several millions deaths annually worldwide. In developing countries is a leading cause of mortality[30]. Isoniazid, also known as isonicotinylhydrazide **(INH)**, is an antibiotic used for the treatment of tuberculosis. For active tuberculosis it is often used together with rifampicin, pyrazinamide, and either streptomycin or ethambutol. The big problem in pharmaceutical chemistry is the alarming increase of drug resistant microbial strains (MDR-TB) that makes difficult the effective control of the disease. Due to this critical situation, innovation in TB drug discovery and evolving strategies to bring new agents with best performance is a current health priority. One strategy to obtain new antimycobacterial drugs is the decobacteria activity and to obtain better resistance profiles, bioavailability and tolerability, among others. In particular, the coordination of metal cations with organic drugs is a promising development of new molecules by re-engineering old drugs with the aim to improve the antimycobacterial strategy that has been successful in many caseswith different pharmacological activities.[26]

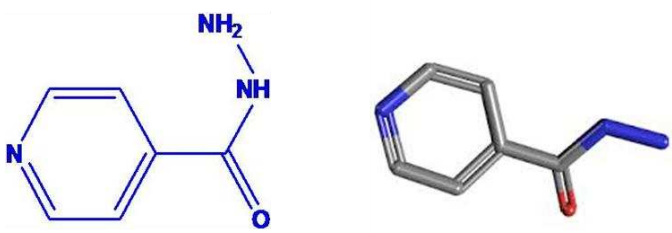

Figure 1.3.2 Structure of Isoniazid

1.3.3 Cobalt

Fig 1.3.3 Image of Cobalt

Cobalt is a silver or gray ferromagnetic metal. Pure cobalt is not found in nature, but compounds of cobalt occur naturally in many forms. Small amounts of it are found in most rocks, soil, water, plants, and animals. It is an element of atomic number 27. The Curie temperature is of 1388 K with 1.6~1.7 Bohr magnetons per atom. Common oxidation states of cobalt include +2 and +3, although compounds with oxidation state +1 are also well developed.[27]

Compounds

There is a wide variety of cobalt compounds. The +2 and +3 oxidation states are most prevalent, however cobalt(I) complexes are also fairly common. Cobalt(II) salts form the red-pink $[Co(OH_2)_6]^{2+}$ complex in aqueous solution. Adding excess chloride will also change the color from pink to blue, due to the formation of $[CoCl_4]^{2-}$. Cobalt oxides are antiferromagnetic at low temperature: CoO (Neel temperature 291 K) and Co_3O_4 (Neel temperature: 40 K), which is analogous to magnetite (Fe_3O_4), with a mixture of +2 and +3 oxidation states. The oxide Co_2O_3 is probably unstable; it has never been synthesized. Other than Co_3O_4 and the brown fluoride

CoF_3 (which is instantly hydrolyzed in water), all compounds containing cobalt in the +3 oxidation state are stabilized by complex ion formation.[28-30]

Biological role

Cobalt in small amounts is essential to many living organisms, including humans. Having 0.13 to 0.30 mg/kg of cobalt in soils markedly improves the health of grazing animals. Cobalt is a central component of the vitamin cobalamin, or vitamin B_{12}.

1.4 Antibacterial Studies

Due to outbreak of infectious diseases caused by different pathogenic bacteria and the development of antibiotic resistance, researchers are searching for new antibacterial agents. Therefore, new antimicrobial agents and nanotechnological materials have to be synthesized for the treatment of resistant bacterial diseases. The field of bioinorganic chemistry, which deals with the study of role of metal complexes in biological systems, has opened a new horizon for scientific research in coordination compounds. A large number of compounds are important from the biological point of view.

1.4.1 Bacteria

The bacteria are a large group of unicellular microorganisms. Typically a few micrometres in length, bacteria have a wide range of shapes, ranging from spheres to rods and spirals. Bacteria are ubiquitous in every habitat on Earth, growing in soil, acidic hot springs, radioactive waste, water, and deep in the Earth's crust, as well as in organic matter and the live bodies of plants and animals. There are typically 40 million bacterial cells in a gram of soil and a million bacterial cells in a millilitre of fresh water; in all, there are approximately five nonillion (5×10^{30}) bacteria on Earth, forming much of the world's biomass. Bacteria are vital in recycling

nutrients, with many steps in nutrient cycles depending on these organisms, such as the fixation of nitrogen from the atmosphere and putrefaction. However, most bacteria have not been characterized, and only about half of the phyla of bacteria have species that can be grown in the laboratory. The study of bacteria is known as bacteriology, a branch of microbiology.[31]

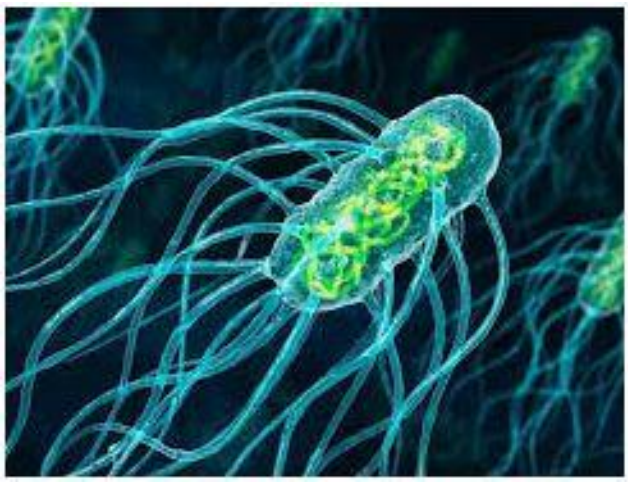

Fig 1.4.1 Structure of *E-Coli*

1.4.2 Escherichia coli

Escherichia coli is a gram negative bacterium that is commonly found in the lower intestine of warm-blooded animals. Most *E. coli* strains are harmless, but some, such as serotype O157:H7, can cause serious food poisoning in humans, and are occasionally responsible for costly product recalls. The harmless strains are part of the normal flora of the gut, and can benefit their hosts by producing vitamin K_2, or by preventing the establishment of pathogenic bacteria within the intestine.

E. coli are not always confined to the intestine, and their ability to survive for brief periods outside the body makes them an ideal indicator organism to test environmental samples for fecal contamination. The bacteria can also be grown easily and its genetics are comparatively simple and easily-manipulated, making it one of the best-studied prokaryotic model organisms, and an important species in biotechnology and microbiology. [32]

Chapter - 2

Aim and Scope

The present work aims at the preparation of the coordination complex of cobalt using Isoniazid and Ammonium thiocyanate as ligands.

To arrive at the composition and structure of the complexes, it is proposed to

1. Measure the electrical conductivity of complex and to find whether the complex is ionic or neutral.
2. Compare the infrared spectra of complex with those of parent ligand, to determine the coordination position of the ligands.
3. Record the electronic spectra of the complex, which will throw light on the probable geometry of the complex.
4. To test the antimicrobial activity of the complex and pure ligand.

Chapter- 3

Literature Survey

1. Complexation of nicotinamide with Ag+ ions in water - organic solvents was published in the Journal of inorganic chemistry, volume 51 on 30th march 2006 by M.A.Zevakin, K.V.Grazhdan, V.A.Sharnin and S.V.Dushina.

2. In 2006, thermal study of Zn(II) chlorosalicylate complex compounds with bioactive ligands such as Thiourea, nicotinamide and caffeine was published by Gyoryova Katarina, Chomic. J, Szunyogoba Eirka, Piknova Lenka, zelenak V and Vargova zuzana in the journal of thermal analysis and calorimetry.

3. The enthalpies of complex formation between nicotinamide and copper(II) percolate in aqueous ethanol and DMSO were determined calorimetrically by A.S.Kursheva, S.F. Ledenkov and V.A. Sharnin and was published in the Journal of physical chemistry on July 25th 2006.

4. Synthesis and characterization of molecular structure and properties of the generated Cu(II) and Ni(II) complexes was reported by particia A.M. Williams, Natialia Bolza and published in Indian Journal of chemistry on 15th Jan 2005.

5. Synthesis and characterization of three 5-(4-pyridyl)tetrazolato complexes obtained by reaction of 4-cyanopyridine with metal azides from aqueous solutions was

reported by Mauter Franz A., Gspan Chiristian, Gatterer Karl, Gohr Mohamed A.S. , Abuyoussey Morsy A.M., Bucher Edith and Sittle Werner in 2005 in the Journal of physical chemistry.

6. A study of copper (II) carboxylato complexes with the ligand nicotinamide was reported by Christina J.Williams, Harry Morris in 2003 was published in Journal of molecular structure.

7. In 2003, Balachandran Unni Nair and Thomas Eyhermuller was reported the preparation and structure of a dinuclear iron (II) complex with six terminally coordinated azides and published in the Central research institute of America.

8. Molecular structure and properties of copper(II), Nickel(II) complexes was published on the online.

9. Spectroscopic and Luminescence properties of an isonicotinic acid was reported by P. Starynowicz in the Journal of celal bayer university.

10. Analyses of co-operative transition in acyl carrier protein redutase upon cofactor and acyl carrier protein binding was published by N. Surolia in Jawaharlal Nehrua centre of advanced scientific research, on 17th Aug 2004.

11. A crystal structure and properties of Cu(II) complex containing azide ion was published in the Journal of coordination chemistry.

12. A Study of copper(II) carboxylato with the ligand nicotinamide was reported by Jan moncol, Milan melnik, Feder valach in the Journal of transistion metal chemistry on 24th July2003, p.53-60.

13. Michael G.Finnegan *et.al.* have reported the synthesis and UV-Visible, solution IR and EPR spectroscopy of (porphinato) iron (III) nitrite complexes.

14. Scarpellini marciele *et.al*. have reported the synthesis and characterization of the new copper (II) – nitrite complex.

15. Synthesis and structure of catena_poly[bis(nicotinamide-kN)copper(I)]-μ-thiocyanato-k^2 N:S] was reported by Christian nather and Inke Jeb in 2002 and published in acta crystallographic section c volume 58(3), P190-192-march 2002. The mixed ligand complexes have been characterized on the basic of elemental analysis, electrical conductance, magnetic susceptibility measurements, spectral and thermal studies. Probable structures have been suggested for the mixed ligand complexes on the basic of the results of elemental analysis and various physico-chemical studies.

16. Mixed ligand nickel (II), copper(II) and zinc(II) complexes of nicotinanilide and thiocyanate were prepared and their electrochemical and biological properties were

discussed [48]. Balan *et.al.* have studied the structure of nicotinanilide and thiocyanate metal complexes. He performed cyclic voltammetric studies for all the complexes and differentiated the oxidation and reduction processes and indicated that the CV studies exhibit one electron irreversible process.

17. Microwave-associated synthesis of mixed ligand complexes of Zn(II), Cd(II) and Hg(II) derived from 4- aminopyridine and nitrite ion were reported by Dhaveethu et.al [49]. Microwave assisted synthesis and structural characterization of nicotinic acid and nitrito-ko mixed ligand complexes were reported and their geometry was interpreted by various characterization techniques.

18. Foziah *et.al.* have reported the thermal studies of the alkaline earth metal nicotinamide complexes. She proposed that the complexes are non electrolytic in nature and the anions are coordinated to the central metal ion.

19. Guang *et.al.* have reported the synthesis and crystal structure of non-interpenetrating metal organic coordination networks constructed from Cd(II) with thiocyanate and nicotinic acid. By using bridging ligands instead of monodentate ligands, they are successfully extended the one dimensional chain structure into two dimensional networks through covalent or the hydrogen bonds.

20. Bio potential efficiency and DNA cleavage applications have been reported for mixed ligand complexes using nicotinamide and nitrite as primary and secondary ligands

respectively. Dilip et.al have proposed the probable structure for metal complexes with metal ions such as Ni, Co, Cu, Zn, Hg and also stated that chromium complex alone have bridged ligands and confirmed by IR spectroscopy.

21. Marijina *et.al.* reported the thiocyanate complexes of group 12 metals with pyridine-2- carboxamide and the crystal structure of the complexes have been elucidated by X-ray diffractometer. Here the thiocyanate shows a number of bonding modes with group 12 metals as terminal and bridging ligand. In the structure investigation of Zn and Hg complexes with thiocyanate, the authors proposed that both the N-donor and S-donor thiocyanate ligands can act as a bridged and terminal which are coordinated to mercury in a nonlinear fashion whereas the coordination sphere along the zinc ions are distorted tetrahedral in structure.

22. It was proposed that the nicotinamide complexes are six coordinate with a metal ion through nitrogen atom. Chandrasekaran *et.al*. have reported the synthesis and characterization of metal complexes with FCNH ligand. He proposed that the ligand coordinate to the metal as a neutral bidentate ligand and possess octahedral geometry.

23. Sabbir *et.al*. have prepared the nicotinamide complexes in aqueous medium in the ratio 2:1. They conclude that the compounds do not contain any chemically coordinated water molecules [58].

24. Lawal *et.al.* have confirmed that the nicotinamide co-ordinate to the metals ions through the pyridine ring nitrogen atom. Nicotinamide act as a chelating ligand and it possesses good antimicrobial and antifungal activity.

25. Khawla have proposed the structure of the mixed ligand complexes with isoniazid and aminoacids to be distorted octahedral. These complexes show positive activity against tuberculosis bacteria.

Chapter – 4

4 GENERAL TECHNIQUES EMPLOYED

4.1 Preparation of coordination compounds

The following methods are commonly employed for the preparation of coordination compounds.

1. By mixing the metal ion solution and ligands in suitable concentration. By evaporating or cooling the concentrated solution in an ice-salt bath, we can induce crystallization. Adding seed crystals of desired compounds and scratching inside the liquid surface often helps to induce crystallization.

2. By the addition of a solvent which is miscible with the solvent of the mixture and the techniques of cooling, seeding and scratching may be necessary to cause the preparation from the solvent mixture.

3. If the desired complex is a cation, it may be isolated by the addition of an appropriate anion with which it forms an insoluble salt. Similarly, a suitable cation may be added to the reaction mixture to precipitate anionic complexes.

4.2 CHARACTERIZATION OF COMPLEXES

Detection of complex ion in solution is related to the concentration of one of the species involved in the formation of the complex.

4.2.1 Solubility method

Sometimes the complex formation increases the solubility of sparingly soluble salts. For example, silver cyanide is sparingly soluble in water but on the addition of KCN, its solubility increases due to complex formation.

$$AgCN + KCN \rightarrow K[Ag(CN)_2]$$

$$K[Ag(CN)_2] \rightarrow K^+ + [Ag(CN)_2]^-$$

4.2.2 Conductivity method

Complex ion formation can be conveniently identified by conductivity measurements. Usually central metal atom combines with ligands (ions or molecules) to give complexes. During this process, there will be an appreciable change in the conductivity of the solution. For example, if metal ion combines with ligands to form a complex, there will be an appreciable drop in the conductivity of the solution, as the number of ions decreases during the above process. [33]

The conductance is a measure of the ease with which the current is passed through the solution. Equivalent conductance is generally used in the case in the study of electrolytic solution. However, in the case of complex compounds, molar conductance rather than the equivalent conductance is of immense importance. Molar conductance of a substance depends on the number of ions present in the solution, degree of dissociation, mobility of ions and temperature. Measurements of molar conductance, M at large dilutions gives information with regard to the number of electrical charges i.e., the sum of the charges on positive and negative

and the number of charges furnished by a molecule of complex compound. In general, the molar concentration of the order 10^{-3} M was used for the study. Accordingly, the formula of the complex whether it is associated or dissociated or polymeric might be assigned.

Molar conductance, M = 1000 K / Concentration

Where, K is the specific conductance of solution in ohm^{-}1 cm^{-}1

4.3 Spectral studies

Besides the above mentioned methods, UV, IR and NMR measurements provides information about complex formation.

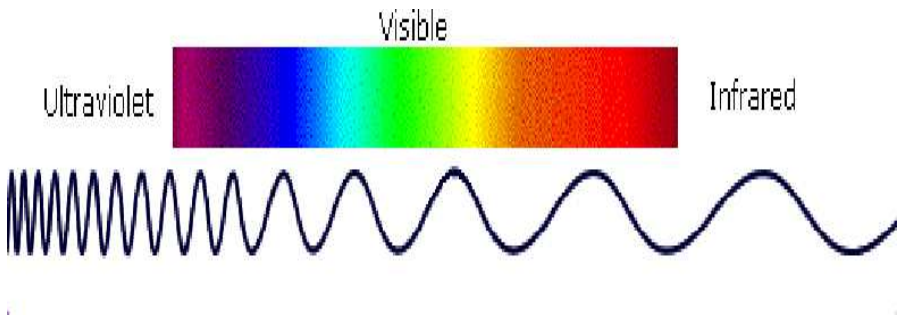

Fig 4.3 Electromagnetic spectrum

4.3.1 ELECTRONIC SPECTRA

The absorption of light in the visible region (400-800 nm) by a metal ion depends on the electronic transitions within the ion and also on the type and strength of ligand → metal bonding. Thus, the metal ions containing d-electrons (except those having 10 electrons in d- orbitals) give variable colors depending on the nature of the ligands attached with the metal ion. In many cases,

the intensity of absorption is increased and the absorption shifts to higher energies (lower λ_{max}) when coordinated water molecules are replaced by ligands which are basic than water.

4.3.2 Infra-red spectra

Vibrational rotational spectra are found in the case of those molecules which posses permanent dipole moment only. In order to study such type of spectra, the energy supplied should be sufficient so as to result transition from one vibration level to another, keeping the electronic level undisturbed. Since each vibrational change is accompanied by so many changes in the rotational energy also, absorption band consists of closely spaced line.

As the infra-red absorption bands of metal-donor atom provide information on the strength and character of the coordinate bond in a given complex, it is evident to get reliable identification of the various absorption bands to arrive at the correct structure of a complex .

When a ligand coordinates to a central metal atom, there will be changes in the bond lengths, bond angles and also interatomic forces. This means that the infra-red spectrum of a coordinated ligand differ from that of a free ligand .

There may be a change in the band position.There may occur a change in relative band intensities. This results in the appearance of new, often weak bands. Single peaks in the free ligand may undergo splitting into several, closely spaced bands in the complex.

From the above changes in the infra-red spectrum of the coordinated ligands, one may conclude whether the ligand has entered into the coordination sphere or not. The shifts in the infrared vibrational bands of the ligands on complex formation may also provide useful information about the bonding characteristics of the complex. [34]

4.3.3 NMR

Absorption of radio frequency v = 60-600 MHz brings about changes in the magnetic properties of certain atomic nuclei like ^{1H} and ^{13C}. This is called Nuclear Magnetic resonance. The hydrogen atoms of different environments of the molecules are detected and counted in the ^{1H} NMR spectrum. Similarly the different positions of carbon atoms in a molecule can be exactly known from the ^{13C} NMR spectrum of a compound.

4.3.4 Disc Diffusion method

The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of the test compounds is expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition.

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibilition by test compound (diamter)}}{\text{Zone of inhibilition by standard (diamter)}} \times 100$$

The nutrient medium was prepared by following composition like Yeast extract-5 g, Meat extract-10 g, Peptone-5 g, Sodium Chloride-5 g, Agar-20 g. The antibacterial activity of the compound was done by the disc diffusion method using DMSO as solvent. The test solutions

Figure 4.3.4 Disc diffusion method sample

were prepared by dissolving the compounds in DMSO. In a typical procedure, agar medium was inoculated with micro-organisms and it is filled with the test solution using micropipette and the plate is incubated at 35˚C for 24 to 48 hr. During this period, the test solution diffuses and the growth of the inoculated microorganism *E. Coli.*, is found to be affected. The activity developed on the plate is measured by measuring the diameter of the inhibited zone in millimeters.

5.1 Preparation of Cobalt complex

Chemicals required

- **Cobalt chloride (2.37 g)**
- **Isoniazid (1.37 g)**
- **Ammonium thiocyanate (0.76 g)**

Procedure

About 2.37 g of cobalt chloride was dissolved in pure distilled water and mixed with about 1.37 g of isoniazid in water. The mixture was heated and cooled. Then an hydrated solution of ammonium thiocyanate (0.76 g) was added in the ratio 1:2:2 and shaken well.

The precipitate was obtained and filtered through whatmann filter paper. It was dried and kept in air tight container.

5.1.1 Qualitative analysis - Cobalt

The cobalt complex was decomposed with dil. HNO_3. Added a few crystals of NH_4CNS and 10 drops of amyl alcohol. Shaken well, blue alcoholic layer indicated the presence of cobalt.

5.2 Physico-chemical properties

The physico-chemical properties of the newly synthesized complex were analyzed and conductance measurements were tabulated.

5.2.1 Electrical conductivity

The electrical conductivity of 10^{-3} M solution of each complex in was found out. This observation reveals the neutral nature (non-electrolytic nature) of the complex.

S.No	Parameters	Observation
1.	Conductance (Ω^{-1} mol^{-1} cm^2)	19
2.	Colour	Pink
3.	Yield %	74
4.	Solubility	Water
5.	Molecular formula	$C_{14}H_{14}CoN_8O_2S_2$
6.	Molecular Weight	449.4
7.	Elemental Analysis	
	C-37.42, H-3.14, Co- 13.11, N-8, O-2, S-2	

Table 5.2 Physico-chemical parameters for the complex $[Co(INH)_2(NCS)_2]$

5.3 IR Spectra

The basic theory involved is that the stretching modes of the ligand changes upon complexation due to weakening or strengthening of the bonds involved in the bond formation resulting in the subsequent change in the position of the bands appear in the IR spectrum. The changes in the structural features of the ligands are observed with the changes in the bands observed mainly in the fingerprint region 4000 – 400 cm^{-1}.

S.No	Complex	υNH_2		$\upsilon C=O$	$\upsilon C=N$	$\upsilon M-O$	$\upsilon M-N$	υCN of SCN	υCS of SCN
		Sym	Asy						
1	Isoniazid	3113	3304	1667	1556	-	-	-	-
2	$[Co(INH)_2(SCN)_2]$	3163	3431	1657	1542	474	550	2084	847

Table 5.3 IR spectral data for the Complex $[Co(INH)_2(NCS)_2]$

The structure of Isoniazid ligand and the metal complex confirmed by Infrared spectroscopy. The characteristics bonds in infrared spectrum of the ligand and its metal complex are reported in table 5.3.

The Isoniazid exhibits peaks at 3113 and 3304 cm^{-1} which corresponds to symmetric and asymmetric stretching of υNH_2 group. The nitrogen atom involves in the complexation and hence this peak seems to be broad in cobalt complex. Then NH_2 bond for isoniazid is seen at 3163 cm^{-1}

which possess positive shift in the complex The υC=O for free isoniazid has been observed at 1667 cm^{-1} whereas for cobalt complex it was shifted to 1657 cm^{-1} predicting that the metal ion is coordinated through the C=O group. These observation indicates that the isoniazid ligand acts as a bidentate ligand coordinating through both the C=O and NH_2 group. The peaks at the range of 500 cm^{-1} where attributed to υM-O vibrations similarly M-N where seen at the range of 400 cm^{-1} in cobalt complex. These frequencies were not seen in pure isoniazid ligand. The pyridine ring vibration at 695cm^{-1} for cobalt complex predicts that the pyridine ring nitrogen does not involve in coordination. In metal complexes, the thiocyanate ion acts as an ambidentate ligand at the mode of the coordination either through N atom or S atom which can be predicted by the characteristic IR peaks. The first transition series metals from M-N bonds whereas the second transition series metals form M-S bond. The mode of bonding in thiocyanate complexes can be determined by their vibrational modes of the thiocyanate ion. [35]

The υC-N of the N-bonded complexes lies in the range of 2050 cm^{-1} and near 2100 cm^{-1} for S-bonded complexes M-NCS-M bond shows the peaks >2100 cm^{-1}. υC-S for N-bonded complexes exhibits frequencies in the range 860-780 cm^{-1}, whereas for S-bonded complexes 720-690 cm^{-1}. These bonds are weak. υC-S values for $M(NCS)_2L_2$ tetrahedral complexes are high than the $M(NCS)_2L_4$ Octahedral complexes. The υC=N of bridging is higher than υC=N of terminal. The υC=N band appears at 2086 cm^{-1} indicates that the thiocyanate ligand is N-bonded. The υC=S bands at 847 cm^{-1} provides evidence for N-bonded complex. The absence of peak at 2100 cm^{-1} predicts the absence of bridging S-C-N bond**. Hence the cobalt complex will be a N-bond terminal NCS complex.**

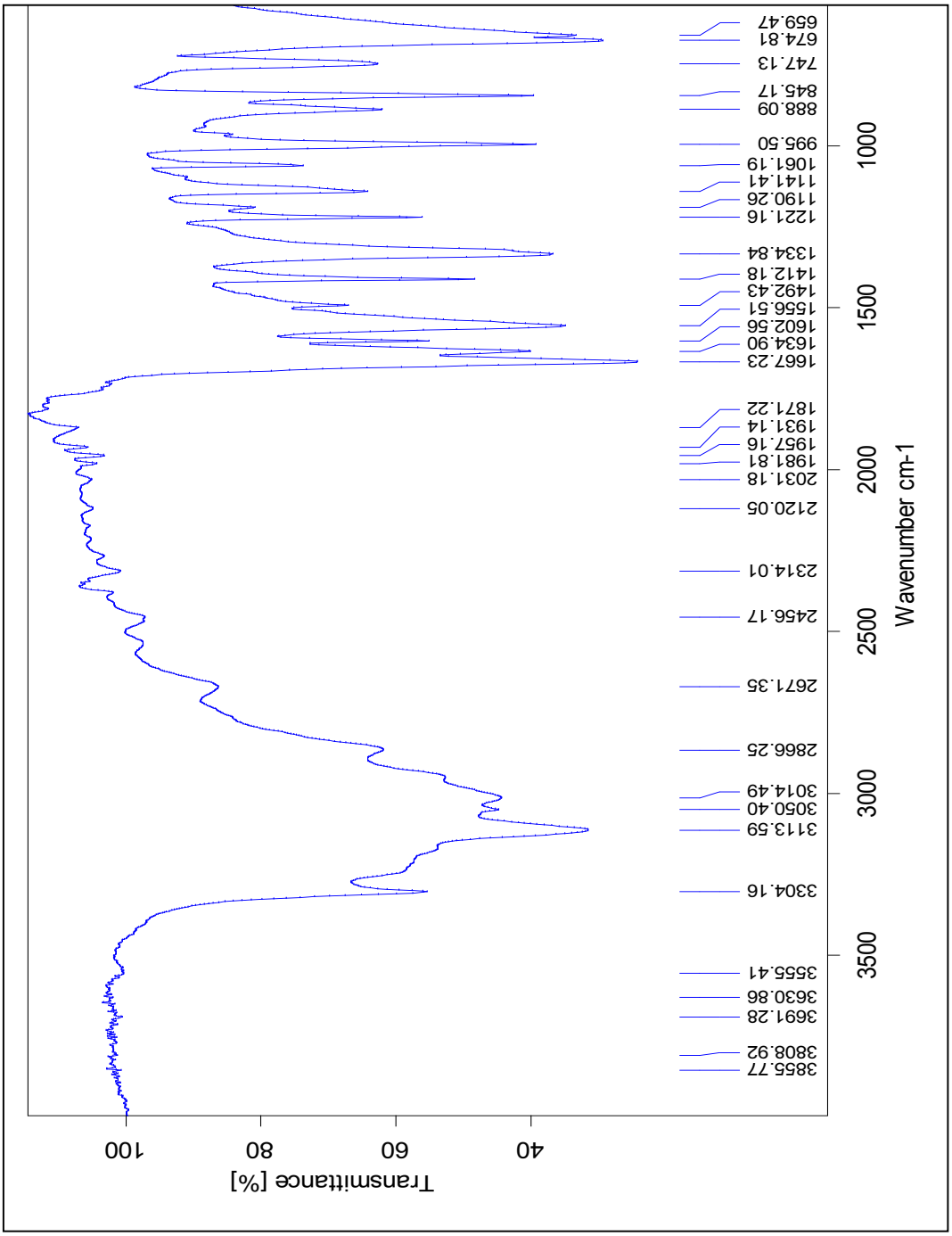

Figure. 5.3 I R spectrum of pure Isoniazid

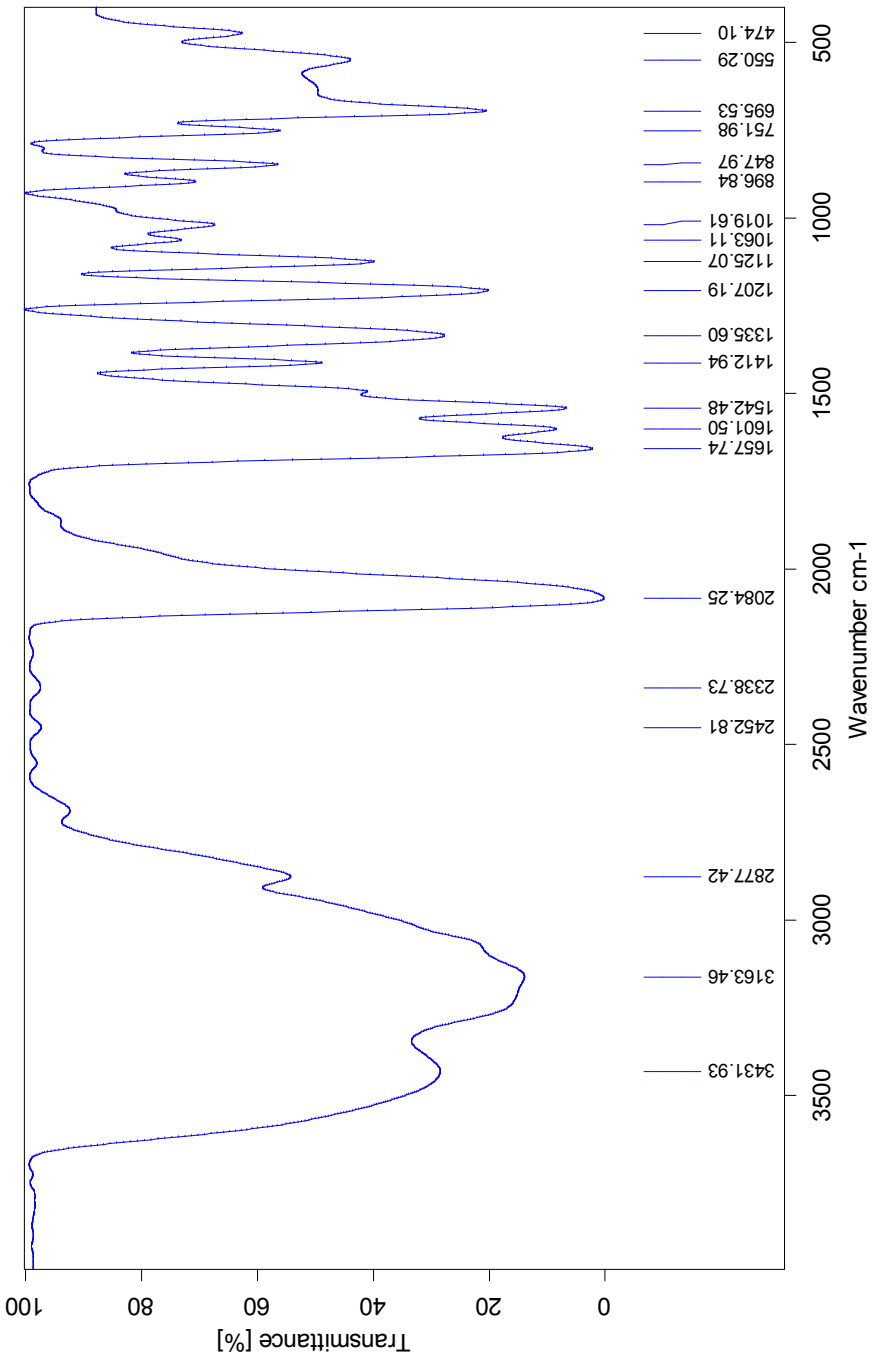

Figure. 5.3.1 I R spectrum for the complex $[Co(INH)_2(NCS)_2]$

5.4 Electronic Spectra

S.No	Complex	Absorption maxima		Transition Assignments	Probable geometry
		λ_{max} nm	cm^{-1}		
1	$Co(INH)_2(NCS)_2$	211 264 412	$47393.36cm^{-1}$ $37878.79cm^{-1}$ $24271.84cm^{-1}$	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^2E_g \rightarrow {}^2T_{2g}$	Distorted Octahedral

Table 5.4 Electronic spectral data for the complex $[Co(INH)_2(NCS)_2]$

The UV-Visible spectra of the complexes in DMF medium were obtained in the range of 200-800 nm. The absorption arising from the transfer of an electron either, from a ligand orbital to the metal orbital (L → M) or from the metal orbital to a ligand orbital (M → L) in a complex is called the charge transfer spectrum. Charge transfer (CT) transitions do not violate the usual selection rules. Charge transfer transitions, unlike d-d transitions are normally neither multiplicity forbidden nor Laporte forbidden; therefore, they produce strong absorption bands. Such strong bands enable charge – transfer absorption to be distinguished from d-d transitions in a complex. The charge transfer bands have extinction coefficients in the 500- 2000 unit range (for d-d transitions, the coefficients are below 100 unit). These bands mostly occur in the near ultraviolet region. In the spectra of some complexes, an overlap between the end for the charge-transfer band and a d-d spectrum of the complex is impossible. A CT transition is an intramolecular transition. Electronic transition from an orbital localized mainly on one atom to

an orbital localized mainly on another atom occurs. This requires much higher energies than a d-d transition . The L→ M transfer is exhibited by complexes containing the ligands O2-, Cl-, Br- and I-. The M→L charge transfer occurs in complexes containing ligands which have stable but empty orbitals. Ligands such as NO, CO and CN which are the acceptor ligands, cause such M→L absorption bands. The organic ligands, such as pyridine, bipyridine and o-phenanthroline have empty antibonding orbitals which favour M→L transfer.

Isoniazid

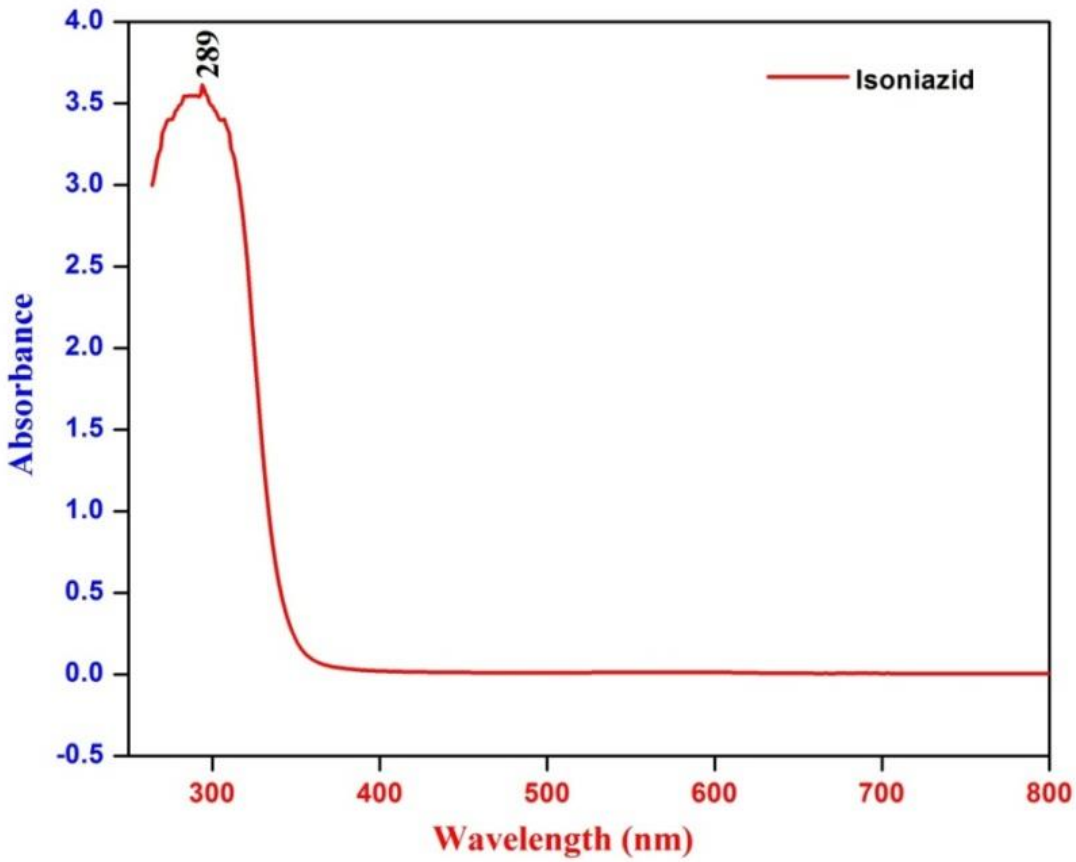

Figure. 5.4 Electronic spectrum of pure isoniazid

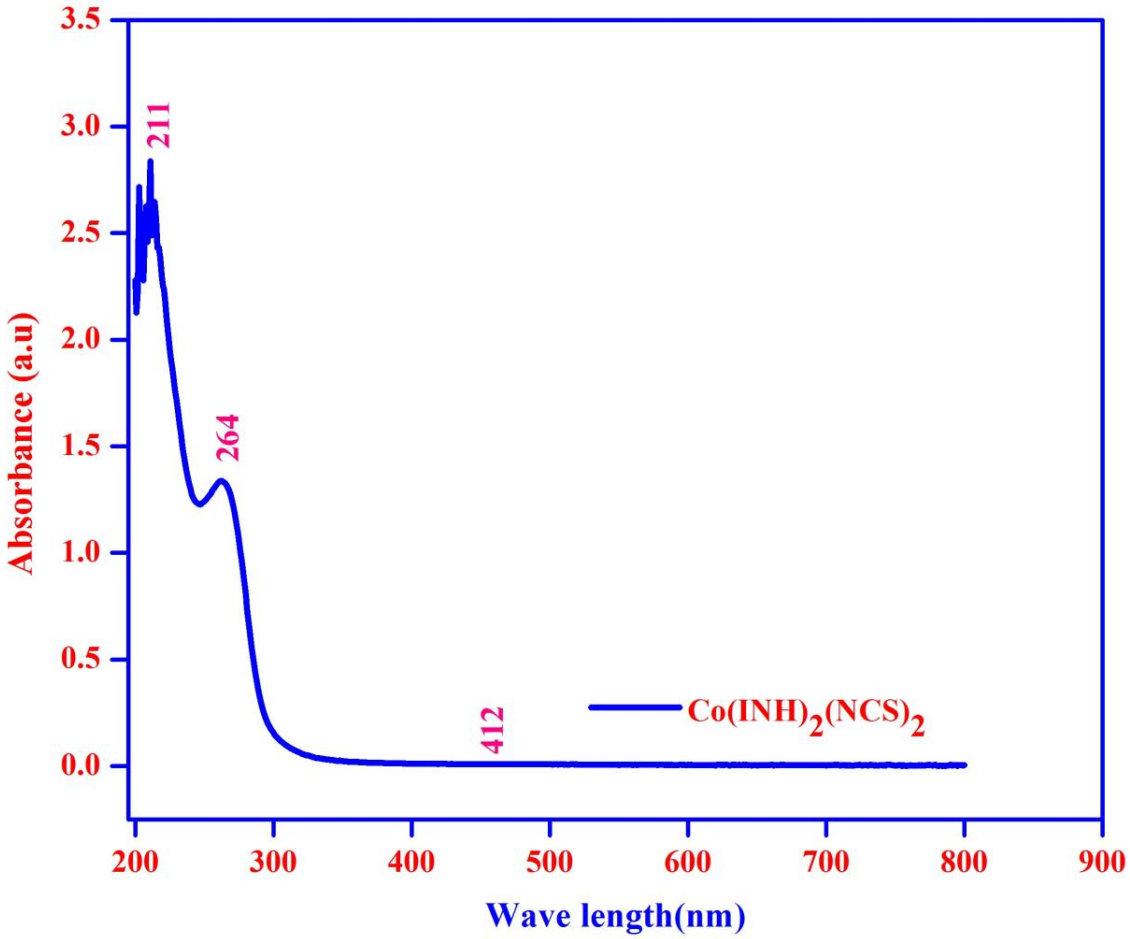

Figure. 5.5, Electronic spectrum of $[Co(INH)_2(NCS)_2]$

The electronic spectral data of the Co(II) complex was given in table. The pure isoniazid exhibits a strong peak at 289 nm. The intense higher energy peak for pyridine derivatives were seen in the range of 230-300 nm which is attributed to the $\pi \rightarrow \pi^*$ transition of heterocyclic ligands[14]. The Co complex exhibits two peaks at 211 and 264 nm in the UV region which is assigned for $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions respectively. In visible region it shows two broad peaks

at 412 nm and this may be attributed to the $^2E_g \rightarrow {}^2T_{2g}$ transition which confirmed the octahedral geometry.

5.5 ^{1}H NMR Spectra

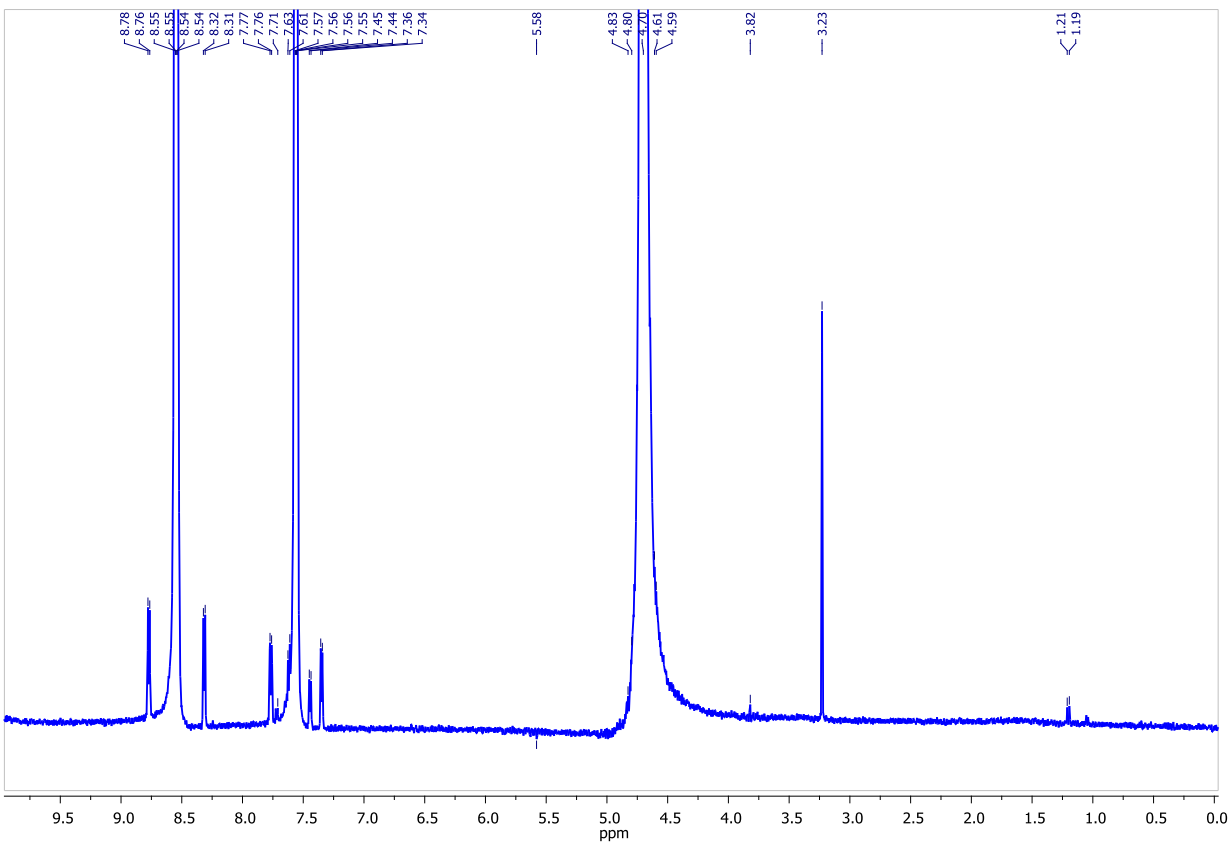

Figure. 5.5 NMR spectrum for Pure Isoniazid

A comparison of ^{1}H NMR spectra of the metal complex and their respective ligand were done. The proton peaks at δ 2.0 were assigned to NH protons of amine group. The peaks at δ 5.6

were assigned to CH protons of carbonyl group which were not seen in pure isoniazid ligand. Hence the presence of this peak shows the coordination occurs at carbonyl oxygen. The peak around δ 8.6 and 7.7 was observed in both pure isoniazid and cobalt complex which indicates that the pyridine ring protons provide the similar environment and do not involve in coordination with the cobalt. The NMR peak values for cobalt complex were given in the following table.

S. No	Peak value	Assignment
1.	2.0	N-H
2.	5.6	C-H protons of Carbonyl group
3.	7.7	Pyridine ring
4.	8.6	Pyridine ring

Table 5.5 Proton NMR values for the complex $[Co(INH)_2(NCS)_2]$

5.6 ANTIMICROBIAL ACTIVITY

The antibacterial screening of the free isoniazid and the thiocyanate complexes against *E.Coli.* are shown in Fig. The antibacterial screening was performed by disc diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of the test compounds is expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition. The antimicrobial studies showed that the ligands and their metal complexes exhibit considerable activity against the pathogenic bacterial strains. The results show that the complexes are more active than their

parent ligands against the same microorganisms and as the concentration increases the activity also increases.

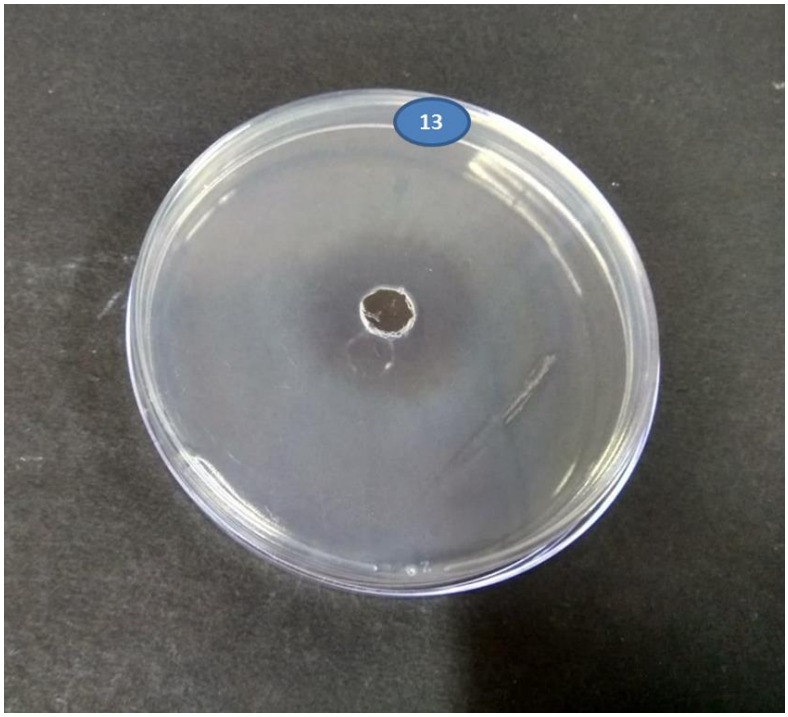

Fig 5.6 Antibacterial activity of the complex $[Co(INH)_2(NCS)_2]$

The zone of inhibition of the cobalt complex was found to be about 20mm which shows the presence of high antibacterial activity against *E. Coli*

5.7 Structure of the Complex

Based on above investigation the probable structure may be distorted octahedral in which the isoniazid acts as a bidentate ligand and Isothiocyanate co-ordinate with N-atom

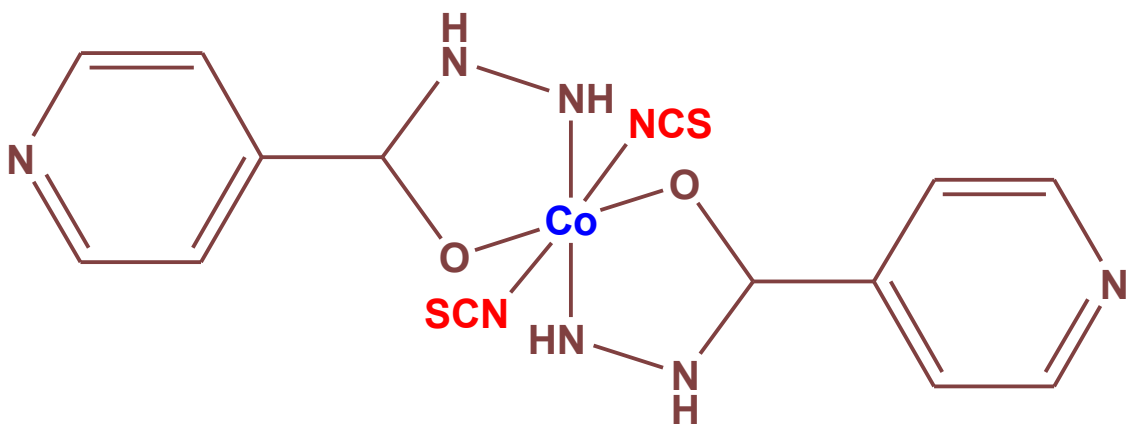

Fig 5.7 Structure of the complex $[Co(INH)_2(NCS)_2]$.

6 Conclusion

In the present study, the mixed ligand complex of cobalt has been prepared using isoniazid and thiocyanate ligands. The analytical methods and physico-chemical parameters have been found out and molar conductivity measurements predicted the non–electrolytic nature of the complex.

The UV – Visible spectra of the complex was recorded and the corresponding transitions predict the probable geometry of the cobalt complex.

The IR spectra of the pure ligand and the complex were recorded and the metal ligand coordination peaks were observed. Isoniazid acts as a bidentate ligand where both oxygen and nitrogen atoms are coordinated with the metal atom. The pyridine nitrogen does not involve in the coordination which was confirmed by the IR peaks. Though thiocyanate is an ambidentate ligand, here the coordination takes place through the nitrogen atom and hence the coordination sphere contains isothiocyanate. The complex possess good antibacterial activity.

Based on the above results and discussions, the most probable formula and geometry is given as follows.

$[Co(INH)_2(NCS)_2]$ **-** Distorted Octahedral

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Post Graduate Project - 8

Synthesis, Characterization and Biological Activity of 2-Hydroxy-3-[3-(4-Methoxy-Phenylamino)-Butyryl]-6-Methyl-Pyran-4-One

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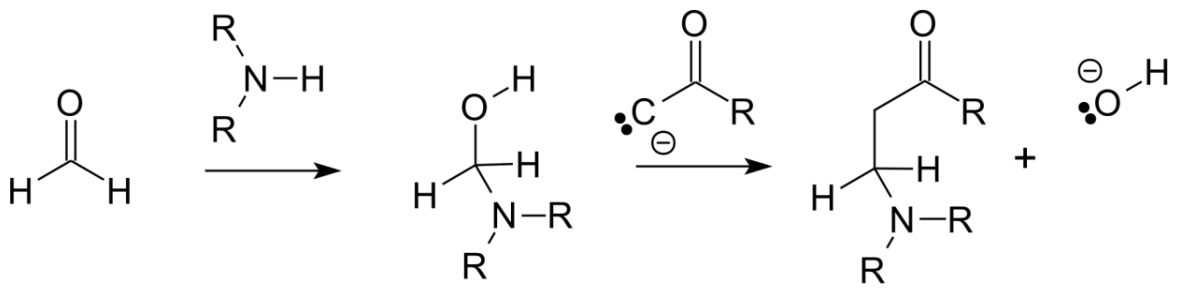
Introduction

A **Mannich base** is a beta-amino-ketone, which is formed in the reaction of an amine, formaldehyde (or an aldehyde) and a carbon acid[1].The Mannich base is an end product in the Mannich reaction, which is a nucleophilic addition reaction of a non-enolizable aldehyde and any primary or secondary amine to produce resonance stabilized imine (iminium ion or imine salt). The addition of a carbanion from a CH acidic compound (any enolizable carbonyl compound, amide, carbamate, hydantoin or urea) to the imine gives the Mannich base[2].

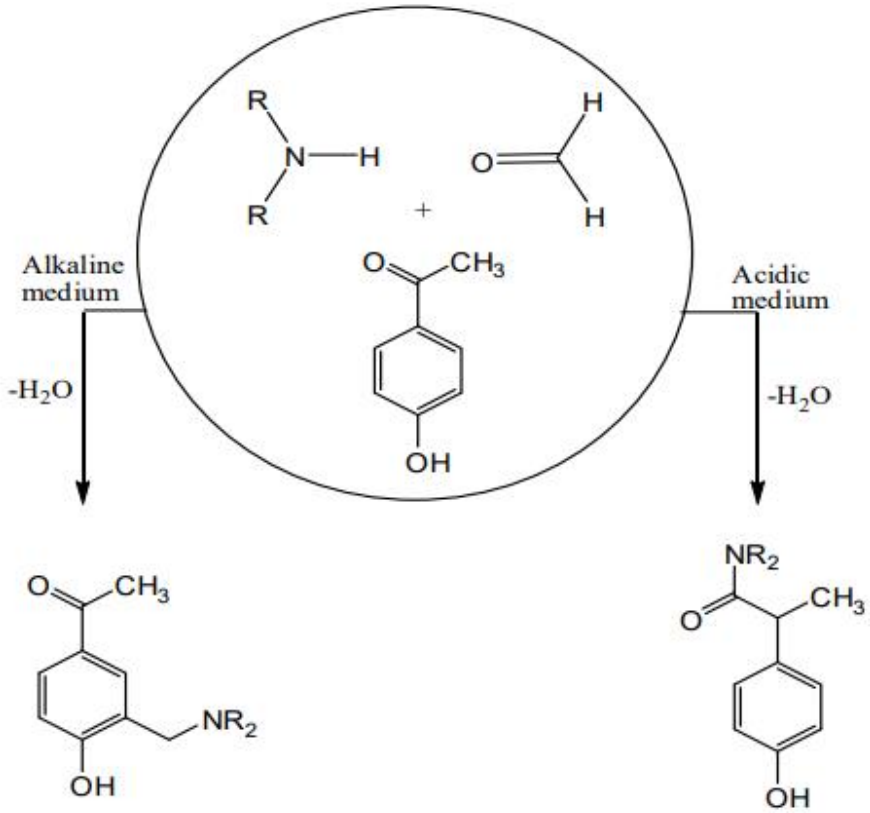


The Mannich reaction is an important, one-pot, multicomponent, C–C bond forming reaction that is widely used in the synthesis of many biologically active and natural compounds [3-7]. Originally, the Mannich product is formed through a three-component reaction containing a C–H acid, formaldehyde and a secondary amine. Recently, one of its special variations called modified Mannich reaction has gained ground, in which the C–H acid is replaced by electron-rich aromatic compounds such as 1- and 2-naphthols as active hydrogen sources [8] .At the beginning of the 20th century Mario Betti reported the synthesis of 1-aminobenzyl-2-naphthol starting from ammonia, benzaldehyde and 2-naphthol. This protocol is known as Betti reaction and the compound formed as Betti base [9-11]. Several examples have been published to extend the reaction and to synthesize various substituted aminonaphthol derivatives [12]. The relatively easy accessibility and promising biological properties have led to the resurgence of their chemistry coming again into the focus of pharmacological research. The formation of

aminonaphthols can be explained by two mechanisms. According to one possibility, first the reaction of the amine and the aldehyde yields a Schiff base and then the latter reacts with 2-naphthol in the second nucleophilic addition step. The other theory assumes the formation of an orthoquinone methide (o-QM) intermediate by the reaction of 2-naphthol and benzaldehyde. Re-aromatization, the driving force of the transformation, takes place in the second step by the nucleophilic addition of the amine component. The class of o-QMs has recently been investigated from many aspects. They are known as short-lived species playing an important role as key intermediates in numerous synthetic pathways. Reviews have recently been published about o-QM generation, applicability in organic synthesis and biological properties [13-19]. However, in this review it is likely to focus on their role in synthesis connected to Mannich base chemistry as well as their wider applicability and properties.

Mannich bases can be easily transformed into numerous compounds due to their high reactivity. Several Mannich bases are of particular interest due to their importance as precursors of valuable pharmaceuticals products and their use as synthetic building blocks [20,21]. Mannich bases have attracted more and more attention from chemists due to their specific biological activities, such as antiviral [22,23], acetylcholinesterase inhibitory [24–26], antioxidant [27,28], and antiproliferative [29,30] activity. Mannich bases are also key precursors to accessing amino alcohols, peptides, lactams, and optically active amino acids [31,32] Consequently, many researchers were attracted to investigate green protocols for the Mannich reaction during the last period [21] . The Mannich reaction is an essential reaction for the direct formation of new C–C and C–N bonds [29,33]. The products of Mannich reaction of 4-hydroxyacetophenone as substrate vary depending on the reaction conditions. Using classical conditions, such as low pH, the acetyl group undergoes reaction, producing β-amino alkyl ketone. In this case, the substrate is converted into the corresponding Mannich base through an aminomethylation process. On the other hand, under an alkaline medium, the Mannich reaction is selectively undergoes electrophilic aromatic substitution in the ortho position to the hydroxyl group (Scheme 1) [20]. The

conventional multicomponent Mannich reactions are found to have drawbacks such as a long reaction time, harsh reaction conditions, and toxic vapor and byproducts [34]. As a consequence, different reaction conditions have been widely described for Mannich reaction in the presence of a variety of catalysts [35,36]. Additionally, a continuous search for the synthetic methodologies of cleaner Mannich reactions seeking green chemistry principles includes the use of protocols in water [37] , biodegradable and reusable catalysts [38,39], ionic liquids [38,39,40], and solvent-free and/or catalyst-free media reaction conditions under microwave (MW) and ultrasound irradiation [41–47]. Microwave irradiation has been used to synthesize a lot of organic compounds. In fact, the use of microwave irradiation offers a higher reaction rate and better product in chemical synthesis [48], however few studies have been done utilizing microwave irradiation in the synthesis of Mannich bases [41,45]. These studies were done under acidic conditions using substituted acetophenones whereas the regioselectivity of the reaction was studied on the 2-hydroxy-chalcone backbone [49]. Hence, it is described herein, the first efficient, gram-scale, non-catalyzed and microwave-assisted synthetic approach of mono- and disubstituted Mannich bases of para-hydroxyacetophenone with various secondary amines.

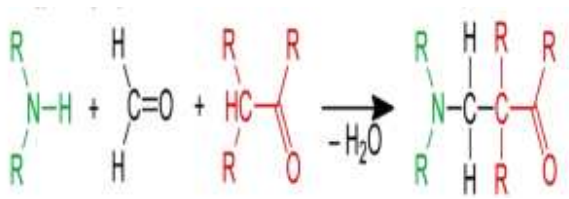


Scheme 1. Possible products of Mannich-type reaction using classical conditions.

Mannich bases, beta-amino ketones carrying compounds, are the end products of Mannich reaction [49,50]. Mannich reaction is a nucleophilic addition reaction which involves the condensation of a compound with active hydrogen(s) with an amine (primary or secondary) and formaldehyde (any aldehyde) [51]. The schematic representation of general Mannich reaction is given in Scheme 1. Mannich bases also act as important pharmacophores or bioactive leads which are further used for synthesis of various potential agents of high medicinal value which possess aminoalkyl chain. The examples of clinically useful Mannich bases which consist of amino alkyl chain are cocaine, fluoxetine, atropine, ethacrynic acid, trihexyphenidyl, procyclidine, ranitidine, biperiden [52–54], and so forth. Mannich bases are known to play a vital role in the development of synthetic pharmaceutical chemistry. The literature studies revealed that Mannich bases are very reactive and can be easily converted to other compounds, for

example, reduced to form physiologically active amino alcohols [55]. Mannich bases are known to possess potent activities like anti-inflammatory [56,57], anticancer [58, 59], antifilarial [56], antibacterial [57, 58], antifungal [58, 57], anticonvulsant [59], anthelmintic [60], antitubercular [61, 62], analgesic [63], anti-HIV [61], antimalarial [64], antipsychotic [65] , antiviral [66] activities and so forth. Along with biological activities, Mannich bases are also known for their uses in detergent additives [67], resins, polymers, surface active agents [68], and so forth. Prodrugs of Mannich bases of various active compounds have been prepared to overcome the limitations [69]. Mannich bases (optically pure chiral) of 2-naphthol are employed for catalysis (ligand accelerated and metal mediated) of the enantioselective carbon-carbon bond formation. Mannich bases and their derivatives are intermediates for the synthesis of bioactive molecules [70, 71]. Mannich reaction is widely used for the construction of nitrogen containing compounds [72]. Mannich bases have gained importance due to their application in antibacterial activity [73] and other applications are in agrochemicals such as plant growth regulators.

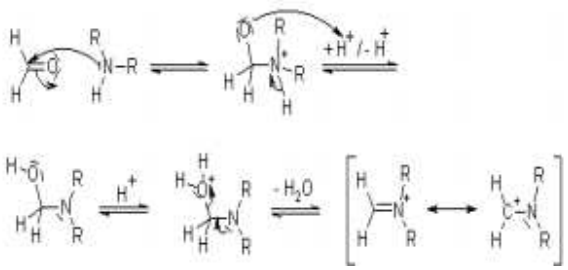
The Mannich reaction is an organic reaction which consists of an amino alkylation of an acidic proton placed next to a carbonyl functional group by formaldehyde and a primary or secondary amine or ammonia [74]. The final product is a βamino-carbonyl compound also known as a Mannich base [75]. Reactions between aldimines and α-methylene carbonyls are also considered Mannich reactions because these imines form between amines and aldehydes. The reaction is named after chemist Carl Mannich [76].



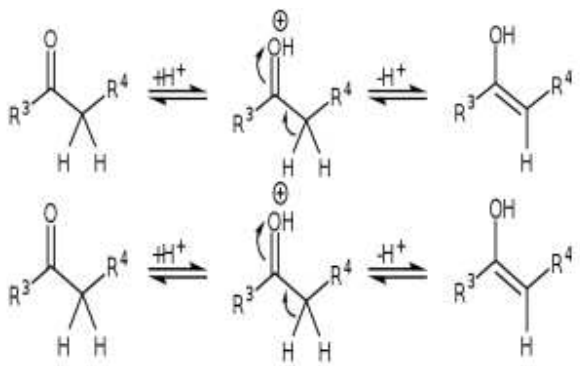
The Mannich reaction is an example of nucleophilic addition of an amine to a carbonyl group followed by dehydration to the Schiff base. The Schiff base is an electrophile which reacts in the second step in an electrophilic addition with a compound containing an acidic proton (which is, or had become an enol) [77]. The Mannich reaction

is also considered a condensation reaction [78]. In this reaction, primary or secondary amines or ammonia, are employed for the activation of formaldehyde [79,80]. Tertiary amines lack an N–H proton to form the intermediate enamine [81]. α-CH-acidic compounds (nucleophiles) include carbonyl compounds, nitriles, acetylenes, aliphatic nitro compounds, α-alkyl-pyridines or imines [82]. It is also possible to use activated phenyl groups and electron rich heterocycles such as furan, pyrrole and thiophene [83,84] . Indole is particularly an active substrate; the reaction provides gramine derivatives [85].

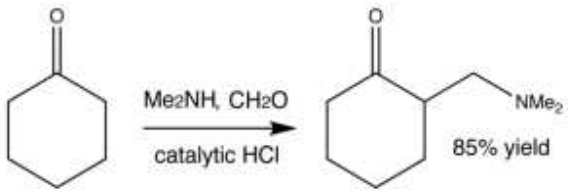
Mechanism of the Mannich Reaction:



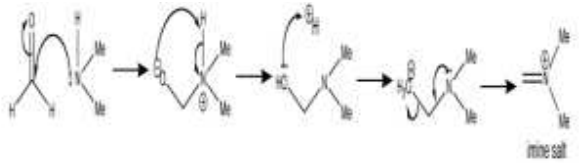
The compound with the carbonyl functional group (in this case a ketone) can tautomerize to the enol form, after which it can attack the iminium ion.



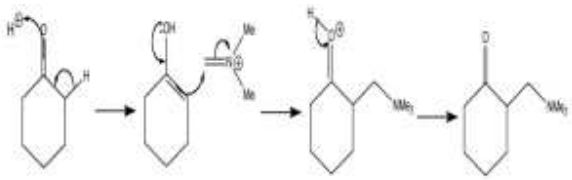
Example of a Mannich reaction: This is a typical example of Mannich reaction. It involves an enolizable aldehyde or ketone, a secondary amine, formaldehyde as its aqueous solution, and catalytic HCl. The product is an aminoketone formed from the addition of one molecule each of formaldehyde and the amine to the ketone.



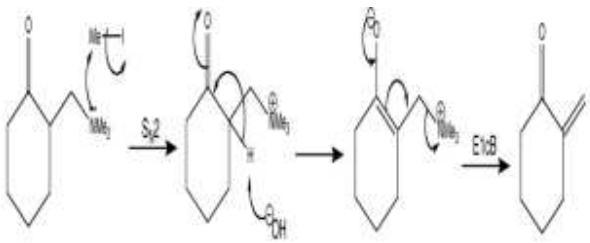
Step 1: Imine formation



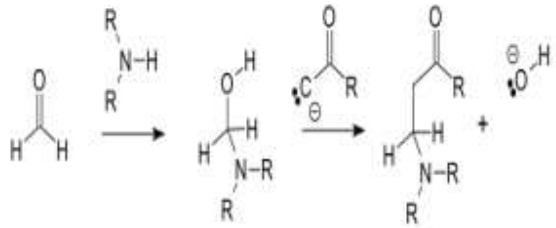
Step 2: Addition of imine salt to ketone



The Mannich products can be converted to enones. Enones such as that shown below, with two hydrogen atoms at the end of the double bond are called exomethylene compounds. Whilst they are very reactive, they cannot easily be made or stored.



Mannich Base Ketonic amines are prepared from the condensation of a ketone with formaldehyde and ammonia or a primary or secondary amine. A Mannich base can act as the equivalent of α, β unsaturated ketone in synthesis or can be reduced to form physiologically active amino alcohols.



Reactivity:

With primary or secondary amines, Mannich bases react with additional aldehyde and carbon acid to larger adducts $HN(CH_2CH_2COR)_2$ & $HN(CH_2CH_2COR)_2$. With multiple acidic hydrogen atoms on the carbon acid higher adducts are also possible. Ammonia can split off in an elimination reaction to form enals and enones.

Applications of Mannich Reaction: The Mannich reaction is employed in the organic synthesis of natural compounds such as peptides, nucleotides, antibiotics and alkaloids. The Mannich reaction is also used in the synthesis of medicinal compounds e.g. fluoxetine (antidepressant), tramadol and tolmetin (anti-inflammatory).

METHODOLOGY SYNTHESIS OF MANNICH BASE:-

p-cholorobenzaldehyde (0.397gm) dissolved in CH_2Cl_2 (5mL) stirred for ½ hr, followed by addition of $EtAlCl_2$ (0.76mL). The resulting solution was stirred for another ½ hr. A solution of p-toluidine (0.303gm) in CH_2Cl (5mL) was added to the above mixture and again stirred for ½ hr. Now acetophenone (0.33 mL) in CH_2Cl_2 (5mL) was added and reaction mixture was refluxed over water bath for 2-3 hrs. Completion of reaction was checked by TLC. The reaction mixture was now kept overnight. Reaction mixture was quenched with saturated solution of NH_4Cl and compound was extracted with CH_2Cl_2, the organic phase was washed with water and finally dried over sodium sulphate and concentrated to approximately 2 mL and left at room temperature for crystallization. Fine crystals deposited were found which were separated, washed with few drops of cold CH_2Cl_2 and finally dried.

CHROMATOGRAPHIC STUDY OF SYNTHESIZED MANNICH BASE:-

Formation of synthesized Mannich base was checked by running TLC in 5% ethyl acetate and 95% petroleum ether and viewed in Iodine chamber.

BIOLOGICAL ACTIVITY OF MANNICH BASE:-

Nutrient agar dissolved in distilled water was autoclaved at 121^0C for 30 mins at 15 Psi. Now the media was poured in petriplate in LAF. Vials were created and the bacteria were spreaded with sterile glass spreader. Compound, solvent and antibiotic (each 100µL) was incorporated into vials. Incubated the plates at 37^0C for 24 hrs, measured the zone and calculated the % activity.

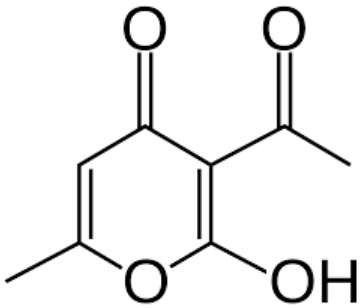
SPECTRAL STUDIES:-

- Infra red spectra of compound have been recorded using KBr discs in the range of 2000-450 cm^{-1} with Shimadzu 8300 FTIR spectrophotometer.
- 1H-NMR Spectra1H-NMR spectra were recorded on Bruker-DPX-300 at observation frequency 300-400 Hz using TMS as internal reference.

DEHYDROACETIC ACID

Dehydroacetic acid is an organic compound which has several industrial applications. The compound is classified as a pyrone derivative. It presents as an odorless, colorless to white crystalline powder, almost insoluble in water and moderately soluble in most organic solvents. It is prepared by the base-catalysed dimerization of diketene. Commonly used organic bases include imidazole, DABCO, and pyridine.

Structure



Dehydroacetic acid

Properties

Boiling point	269.9^{o}C
Melting point	109^{o}C, 228^{0}F
Appearance	White crystals
Molecular weight	168.15g/mol
Solubility	Water

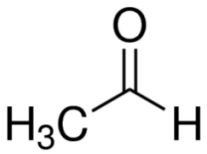
Uses:

- As a fungicide and bactericide. The sodium salt, sodium dehydroacetate, is often used in place of dehydroacetic acid because of its greater solubility in water.
- As a food preservative to prevent pickle bloating in squash and strawberries. When used as a food additive, dehydroacetic acid is referred to using the International Numbering System for Food Additives or E number 265.
- As plasticizer in synthetic resins.
- As an antienzyme in toothpastes.
- As a precursor for dimethyl-4-pyridones. The compounds are synthesized when dehydroacetic acid is exposed to aqueous solutions containing primary amines.

ACETALDEHYDE

Acetaldehyde (systematic name ethanal) is an organic chemical compound with the formula CH_3CHO, sometimes abbreviated by chemists as MeCHO (Me = methyl). It is one of the most important aldehydes, occurring widely in nature and being produced on a large scale in industry. Acetaldehyde occurs naturally in coffee, bread, and ripe fruit [10], and is produced by plants.

Structure:



Properties

Boiling point	20.2 °C (68.4 °F; 293.3 K)
Melting point	−123.37 °C (−190.07 °F; 149.78 K)
Appearance	Colourless liquid
Molecular weight	44.053 g·mol^{-1}
Solubility in water	miscible

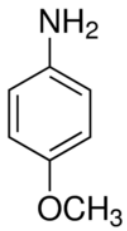
Uses:

- Acetaldehyde is also used a base in the manufacture of acetic acid, another platform chemical with many applications.
- Acetaldehyde is also used as an aromatic agent and is found naturally in fruits and fruit juices.
- Acetaldehyde occurs naturally during fermentation and is found in low levels in certain foodstuffs.

P-ANISIDINE

p-Anisidine (*para*-anisidine) is an organic compound with the formula $CH_3OC_6H_4NH_2$. Generally occurs as a white solid, commercial sample can appear grey-brown owing to air oxidation. It is one of three isomers of anisidine, methoxy-containing anilines. It is prepared by reduction of 4-nitroanisole.

Structure:



Properties

Boiling point	243 °C (469 °F; 516 K)
Melting point	56 to 59 °C (133 to 138 °F; 329 to 332 K)
Appearance	Light reddish brown solid [2]
Molecular weight	123.155 g mol^{-1}
Solubility in water	Sparingly soluble [2]
Solubility in other solvents	Soluble in ethanol, diethyl ether, acetone, benzene

Uses:

- It is used as a reagent for the detection of oxidation products such as aldehydes and ketones in fats and oils.
- It has a role as a reagent and a genotoxin.

PRINCIPLES OF SPECTROSCOPY:

All organic compounds interact with electromagnetic radiation that is they absorb energy. When a molecule absorbs energy, a transformation occurs that may be either

temporary or permanent. Lower energy radiation may cause the promotion of electrons to higher energy levels or bond cleavage.

Whether the transformation involves molecular rotation, bond vibration or electronic transition, the molecule absorbs only the wavelength of radiation with exactly the energy necessary for the transition.

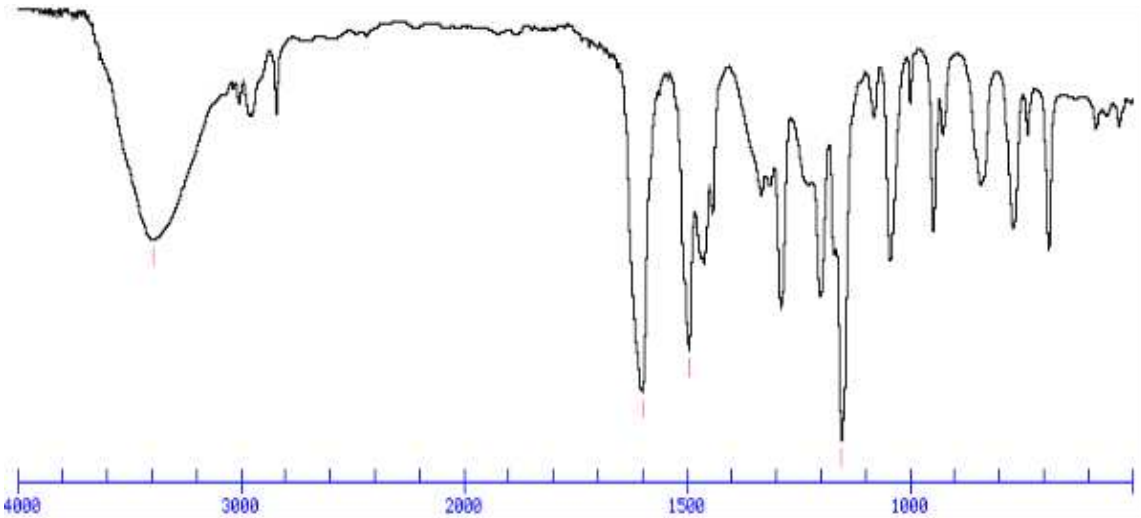
The absorption of wavelengths of radiation is selective for a particular transition which depends on the structure of the molecule. By measuring the absorption spectra of known compounds, we can correlate the wavelengths of energy absorbed with characteristic structural features. This information is then used to determine the structure of unknown compounds.

Infrared spectroscopy:

Theory:

Infrared spectroscopy is an absorption method in the wavelength region of 1 to 100 μm in that extends the region of the visible light to longer wavelengths and smaller frequencies/energies. The energy of infrared light is no longer sufficient to induce transitions of valence electrons. Instead, infrared radiation excites vibrational and rotational motions in molecules.

However, infrared spectra are usually presented by a plot of the percentage of transmission is the wave number in cm^{-1} (as opposed to a plot of absorbance vs the wavelength in nm in UV/VIS spectroscopy). A typical IR spectrum is therefore recorded from about 4 000 to 10 000 cm^{-1}(upper limit) to about 100-800 cm^{-1} (lower limit).



An Example IR Spectrum

Because each inter atomic bond may vibrate in several different motions (stretching or bending), individual bonds may absorb at more than one IR frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar types of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibrations do not cause absorption of IR radiation. For example, neither of the carbon-carbon bonds in ethene or ethyne absorbs IR radiation.

Regions of the IR Spectrum:

Over time organic chemists have recorded and catalogued the types and locations of IR absorptions produced by a wide variety of chemical bonds in various chemical environments. These data can be quickly referenced through tables of IR absorption ranges and compared to the spectrum under consideration. As a general rule, the most important factors determining where a chemical bond will absorb are the bond order and the types of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore the same or similar functional groups in different molecules will typically absorb within the same, specific frequency ranges. Consequently tables of IR absorptions are arranged by functional group.

In IR absorption tables, signal intensities (height) are usually denoted by the following abbreviations: w = weak, m = medium, s = strong, v = variable. A broad signal shape is sometimes indicated by br. occasionally absorption frequency is given as a single approximation denoted with an approximately rather than a range.

Table of IR Absorptions:

These trends in absorption can be further summarized into the following categories

3600 - 2700 cm^{-1}	X-H
2700 - 1900 cm^{-1}	X=Y
1900 - 1500 cm^{-1}	X=Y
1500 - 500 cm^{-1}	X-Y

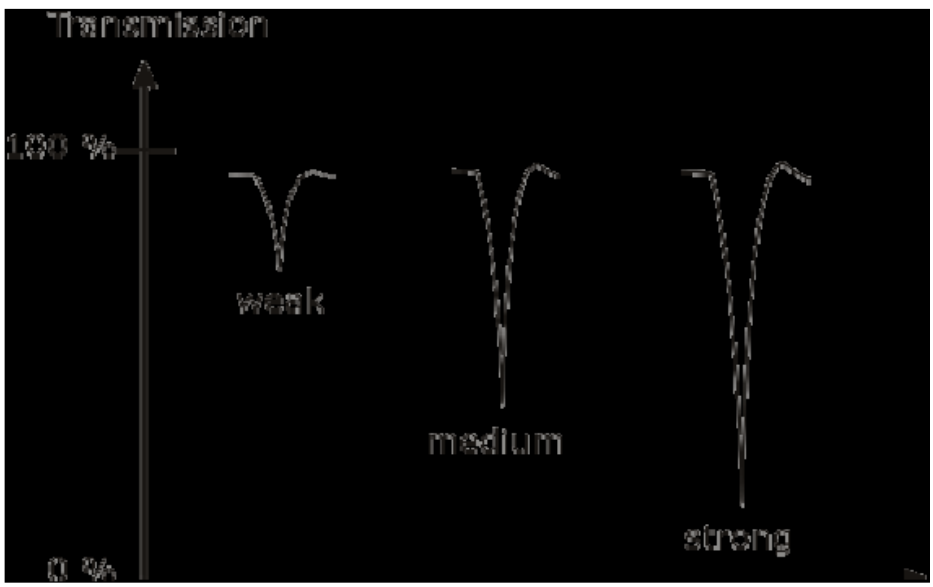
Upon first inspection, a typical infrared spectrum can be visually divided into two regions. The left half, above 2000 cm^{-1}, usually contains relatively few peaks, but some very diagnostic information can be found here. First, alkane C-H stretching absorptions occurs just below 3000 cm^{-1} demonstrate the presence of saturated carbons, and signals just above 3000 cm^{-1} demonstrate unsaturation. A very broad peak in the region between 3100 and 3600 cm^{-1} indicates the presence of exchangeable protons, typically from alcohol, amine, amide or carboxylic acid groups. The frequencies from 2800 to 2000 cm^{-1} are normally void of other absorptions, so the presence of alkyne or nitrile groups can be easily seen here.

In contrast, the right half of the spectrum, below 2000 cm^{-1}, normally contains many peaks of varying intensities, many of which are not readily identifiable. Two signals which can be seen clearly in this area is the carbonyl group, which is a very strong peak around 1700 cm^{-1}, and the C-O bond with can be one or two strong peaks around 1200 cm^{-1}. This complex lower region is also known as the "fingerprint region" because

almost every organic compound produces a unique pattern in this area. Therefore identity can often be confirmed by comparison of this region to a known spectrum.

Classification of IR bands

IR bands can be classified as strong (s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the *y*-axis. A medium band falls to about half of the *y*-axis, and a weak band falls to about one third or less of the *y*-axis.



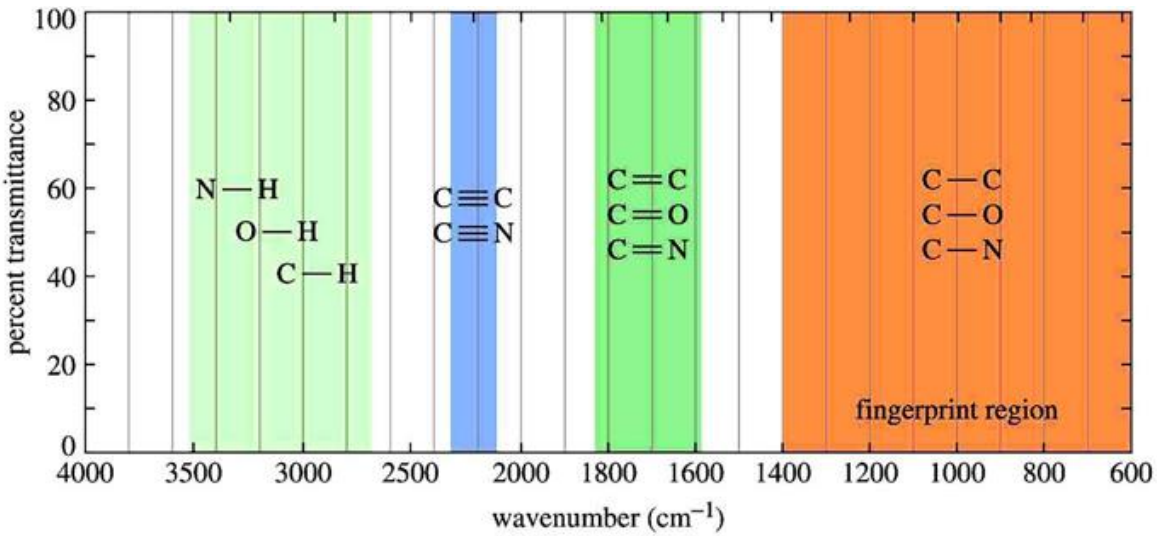
Infrared active bonds

Not all covalent bonds display bands in the IR spectrum. Only polar bonds do so. These are referred to as IR active. The intensity of the bands depends on the magnitude of the dipole moment associated with the bond in question:

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.

IR absorption range

The typical IR absorption range for covalent bonds is 600 - 4000 cm^{-1}. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around 2200-2400 cm^{-1} would indicate the possible presence of a C-N or a C-C triple bond.



Nuclear Magnetic Resonance (NMR)

Excitation of the nucleus of atoms through radiofrequency irradiation provides extensive information about molecular structure and atom connectivity.

^{1}H NMR Spectroscopy:

This important and well established application of nuclear magnetic resonance spectroscopy will serve to illustrate some of the novel aspects of this method. To begin with the NMR Spectrometer must be in turn to a specific nucleus, in this case the proton. The nucleus of hydrogen atom (proton) behaves as a spinning bar magnet. Because it posses both electric and magnetic spin. Like any other charged body, the nucleus of a hydrogen atom also generates a magnetic field. The actual procedure for obtaining the spectrum varied but the simplest is referred to as the continuous wave (cw) method.

The number of signals in an NMR spectrum tells the number of sets of equivalent protons in a molecule. The positions of signals in the spectrum help us to know the nature of protons via aromatic, aliphatic, acetylenic, vinylic adjacent to some electron attracting or electron releasing group etc. Shift in the position of NMR absorptions which arises due to the shielding (or deshielding) of protons by the electrons are called chemical shifts.

For measuring the chemical shift of various protons in a molecule, the signal of tetramethylsilane (TMS) is taken as a reference. This difference in the absorption position of the proton with respect to TMS signal is called chemical shift (δ-value).

TLC:

TLC is a simple, quick and inexpensive procedure to confirm the formation of the product. TLC is also used to analyze the purity of the compound. To prepare the TLC plate, slurry of silica gel prepared by adding chloroform and methanol in the ratio 1:9 to silica powder was uniformly coated on a thin glass plate.

AIM AND SCOPE OF THE WORK

- The aim of this project is to synthesize, characterize and to establish the structure through the IR spectral study of the newly synthesized Mannich base.

- The compounds containing nitrogen and sulphur present in the ring and chloro group are found to be biologically important and also behave as potential donor. On account of this, compound containing hetero atom such as 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-oneare used for synthesis of mannich base.

- The synthesized compounds are taken and characterized by analytical and spectral methods.

- To analyse antibacterial activity of the synthesised compound.

EXPERIMENTAL METHODS

The melting point was determined in open capillary and was uncorrected. The purity of the compound was checked by TLC on silica gel "G" coated glass plates. IR spectra were recorded in KBr on shimadzu FT-IR 8300 spectrophotometer, ^{1}H NMR spectra on a Bruker DRX-400 MHZ. Many experimental techniques are briefly discussed below:

1. IR spectra were recorded in St. Joseph College, Trichy-20.
2. ^{1}H NMR and ^{13}C NMR spectra were recorded in Alagappa University, Karaikudi.
3. The biological activity has been studied in Department of Biotechnology, Mohamed Sathak College of Arts and Science College, Sholinganallur, Chennai.

ANALYTICAL METHODS:

1. **Lassaigne's test:**

   A small piece of sodium metal was fused in fusion tube and some portions of the sample were added. The tube was heated to red hot and quickly plunged into 5 ml of water. The solution was boiled and filtered. Then this filtrate was divided into two portions and tested. One portion was mixed with few ml of freshly prepared $FeSO_4$ solution and then acidified with dilute sulphuric acid. The appearance of the blue colour indicates the presence of nitrogen in the compound.

2. **Dye test for primary amines:**

   0.1g of the compound was dissolved in 3ml of dilute HCl and cooled in tap water and 1ml sodium nitrite solution was added. Then it iwas added to β-naphthol dissolved sodium hydroxide solution. A scarlet red precipitate appeared indicating presence of primary amine.

EXPERIMENTAL PROCEDURE:

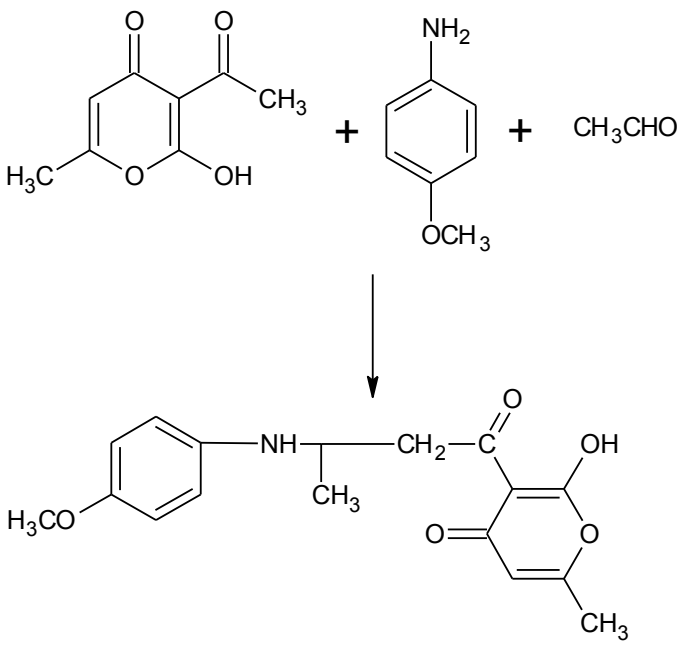
Synthesis and characterisation of 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

Chemicals Required:

2-chloro-5-acetyl pyridine	(0.01m)	: 1.5 g
2-aminobenzothiazole	(0.01m)	: 1.5 g

2-aminobenzothiazole and 2-acetyl5-chloropyridine were taken in 1:1 ratio. 2-aminobenzothiazole and 2-acetyl5-chloropyridine were dissolved in ethanol and taken in round bottom flask with constant stirring for three hours, using a magnetic stirrer under ice cold condition. Then the yellow solid substance was separated out. It was washed several times with cold distilled water. The crude sample was recrystallized from ethanol. The scheme of the reaction is given below.

Scheme



2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

RESULTS AND DISCUSSION

The compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

- Was prepared from mannich base.
- The structure of the compound was confirmed by IR, ^{1}H and ^{13}C NMR.
- The physical characterisation of the synthesized compound is given in the table-I.

TABLE-I

PHYSICAL CHARACTERIZATION

Physical characterization of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

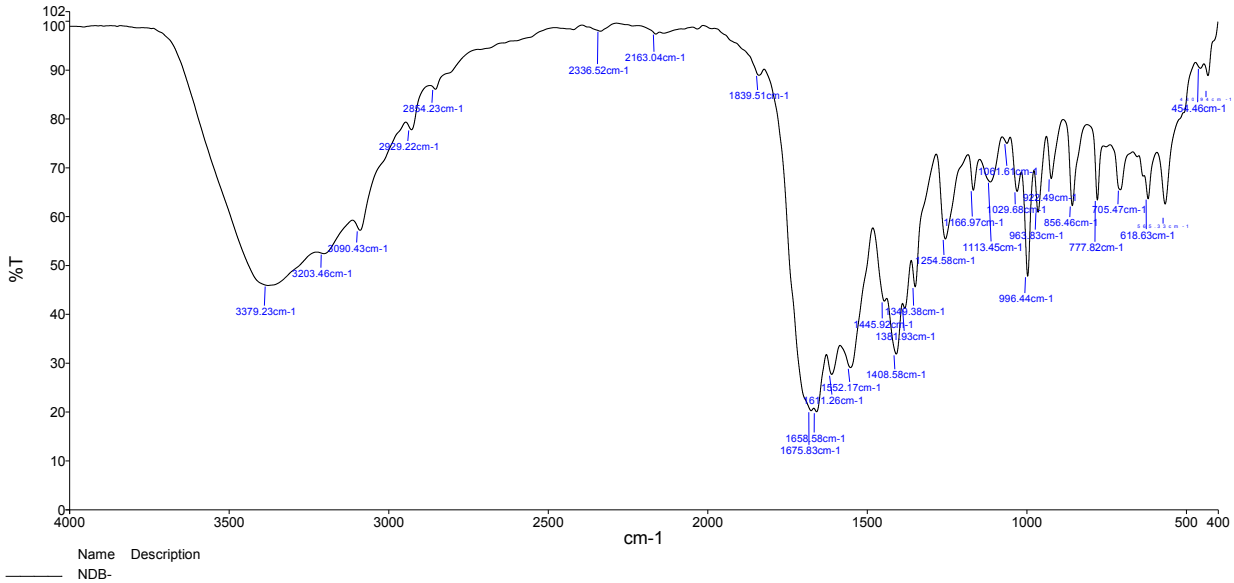
Molecular Formula	Molecular Weight	Melting Point(^{0}C)	Elemental analysis (%) Found (calculated)			Solubility
			C	H	N	
$C_{17}H_{19}NO_5$	317.33		77.33%	5.45%	24.67%	Methanol, Ethanol, Chloroform

TABLE-II

IR SPECTRAL DATA

IR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

Frequency (cm^{-1})	Functional group
3379	NH
3090	Aromatic CH
2929	Aliphatic CH
1675	C=O



IR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

IR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one was recorded to predict the functional groups present in the compound.

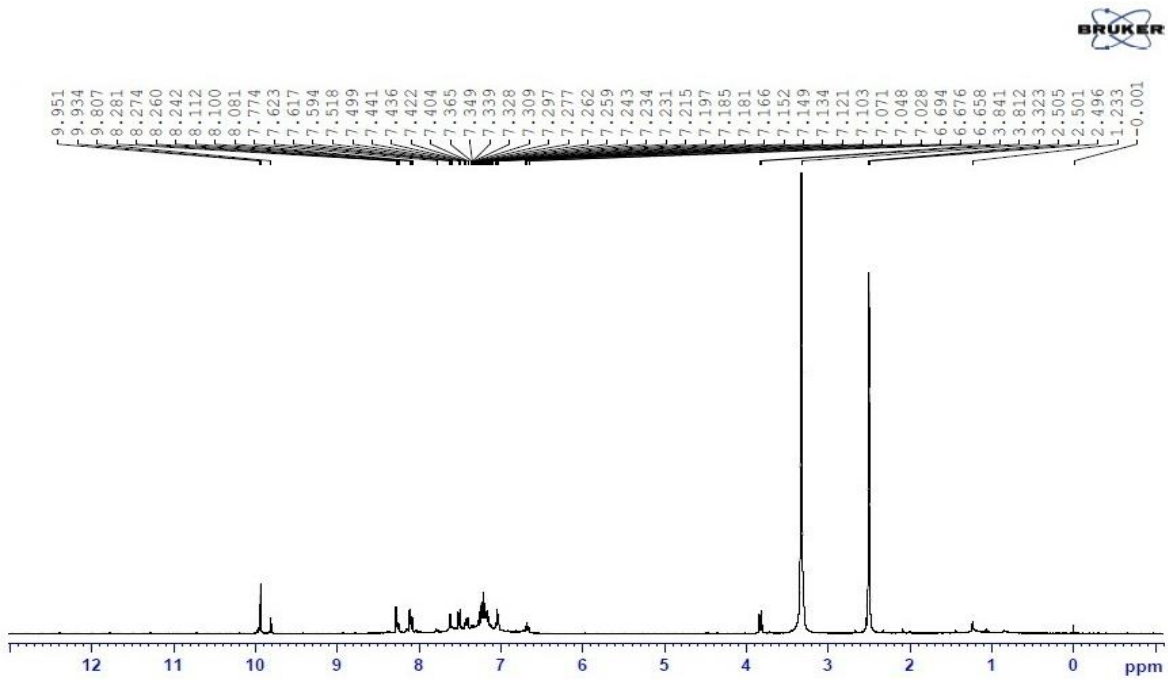
- The sharp band at 3090 cm^{-1} indicates that the presence of aromatic C-H.
- The medium banded attributed at 3379 cm^{-1} indicates the presence of N-H.
- The band at 2929 cm^{-1} shows the presence of Aliphatic C-H.
- The band at 1675 cm^{-1} indicates that the presence of C=O.

TABLE-III

^{1}H NMR SPECTRAL DATA

^{1}H NMR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

Chemical shift(ppm)	Assignment
9.95	OH proton
6.65-6.69	Aromatic protons
3.84	NH proton
3.81	methoxy proton
3.32	methylene proton
1.23	methyl proton



[1]H NMR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

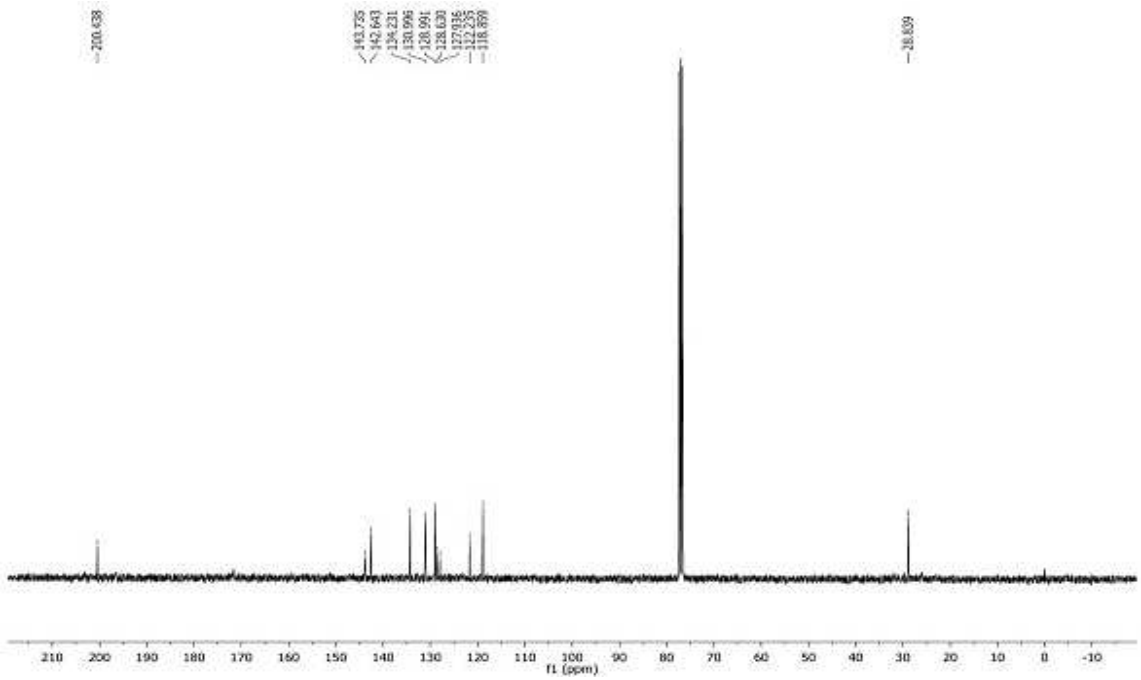
[1]H NMR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

- The OH proton shows chemical shits value at 9.95 δ
- The aromatic proton shows chemical shifts value at 6.65-6.69 δ.
- The NH proton shows chemical shifts value at 3.84δ.
- The OH proton shows chemical shits value at 9.95 δ
- The methoxy proton shows chemical shits value at 3.81δ
- The methylene proton is obtained at chemical shifts value at 3.32δ.

TABLE-IV

^{13}C-NMR SPECTRAL DATA

^{13}C-NMR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one



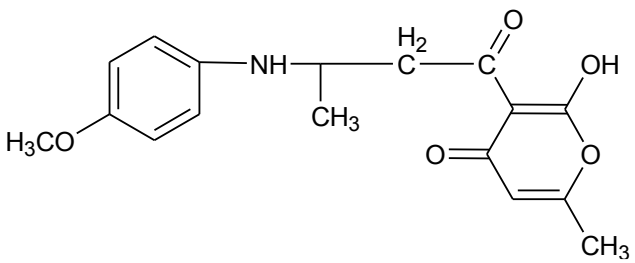
^{13}C-NMR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

^{13}C-NMR spectral data of the compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

- The chemical shift value at 200.4 ppm corresponds to Carbonyl carbon
- The peak at δ 128.6-128.9 shows the presence of the aromatic carbon.
- The methoxy carbon is assigned to the chemical shift value of 143.7ppm.
- The methylene carbon is assigned to the chemical shift values at 118.8ppm.
- The methyl carbon is assigned to the chemical shift values at 28.8ppm.

Structure of compound

Based on the above spectral studies, the following structure has been proposed for the compound



2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one

BIOLOGICAL ACTIVITY

Biological assay depends upon a comparison of the inhibition of growth of microorganism. For the antimicrobial study the invitro disc diffusion method has been employed. In this study the compound is tested for their effect on certain human pathogenic bacteria, both Gram positive (Staphylococcus aurous) and Gram negative (Escherichia coli).

PROCEDURE:

Nutrient agar is used as a medium for studying the antimicrobial activity. The following reagents are required for the preparation of nutrient and agar medium.

Yeast extract	=	5 g
Meat extract	=	10 g
Peptone	=	5 g
Sodium Chloride	=	5 g
Agar	=	20 g

All the above reagents were dissolved in 1000 ml of distilled water in clean conical flask and the pH was maintained at 7. The solution was boiled to dissolve the medium completely and sterilized by autoclaving at 7 kg pressure (121˚C) for 15 minutes.

After sterilization, 20 ml media was poured into the sterilized Petri plates. These Petri plates are kept at room temperature for some time.

After few minutes, the medium gets solidified in plates. Then it was incubated for 12hrs. After the incubation this was inoculated with microorganisms using sterile swabs. All these manipulations were carried out with utmost care under aseptic conditions.

The antibacterial activity of the compound was done by the disc diffusion method using $CHCl_3$ as solvent. The test solutions were prepared by dissolving the compounds in $CHCl_3$. In a typical procedure, a well made on the agar medium was inoculated with microorganisms and it was filled with the test solution using micropipette and the plate was incubated at 35˚C for 24 to 48 h. During this period, the test solution diffuses and the growth of the inoculated microorganisms such as Staphylococcus aurous, and Escherichia coli were found to be affected. The activity developed on the plate was measured by measuring the diameter of the inhibited zone in millimetres.

BIOLOGICAL ACTIVITY

In Vitro Antibacterial Screening

The synthesis and characterization of biological activity compound were evaluated for their in vitro antibacterial activity against staphylococcus aureus and Escherichia coli by agar dilution method were performed using Mueller- Hinton agar (hi-media) each compounds and standard were tested at a concentration of 100µ/mg in DMSO, the zone of inhibition was measured after 24hr incubation at 37^{o}c. After the incubation period the diameter of clear zone around each well were measured in mm, clearing zone of variable size were visible well of each compound. Ciprofloxacin was chosen as a standard antibacterial measurement.

The potato dextrose agar PDA is used as a medium for antifungal activity, the nutrient agar is prepared by dissolving 20g of potato extract 20g of agar and 20g of dextrose in one litre of dissolving distilling water in a clean conical flask. The solution is boiled to dissolve the media completely and sterilized by autoclaving with 7kg pressure (121^{o}c) for the 30 minutes after the sterilization 20 ml media poured in to the sterilized Petri plate. These Petri plate are kept at room temperature for some time. After a few minutes, the medium get solidifies in plate. DMSO (0.5µL) is used as solvent and clotrimazole (10µg/disc) as control in a typical procedure, a well made on the agar medium is inoculated with microorganism and it is filled with test solution using a micro pipette (50µL) and the plate is incubated at 35oc for 72 h. During this period the test solution diffuses and affects the growth of the inoculated microorganism. A zone is developed on the plate and the inhibition zones are measured by measuring the diameter of inhibited zone in mm. The zone of inhibition value is given in the table- 4.

Table-IV

Antibacterial Activity of Compounds

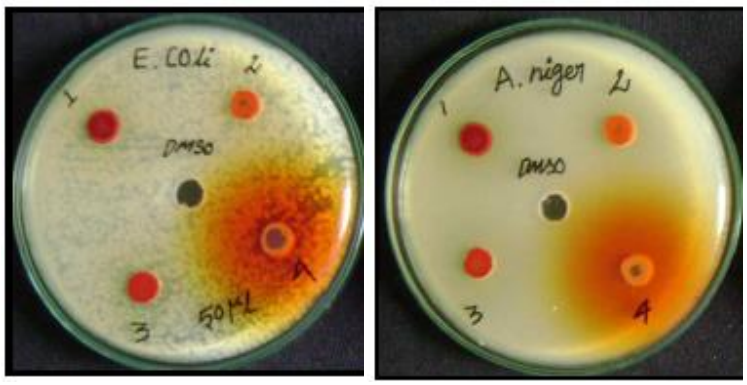
ORGANISM	Concentration of DMSO extract added and Zone of inhibition (mm/ml)				
	25 µl	50 µl	75 µl	100 µl	Control
Staphylococcus aureus	9	11	12	14	11
A. nigers	11	13	15	18	14

Result and discussion for antibacterial activity:

Antibacterial activity of the compound has activity against Staphylococcus aureus and A.nigers at various concentrations.

Photo Graphical Evidence

The zone inhibition of the compound is shown below:



CONCLUSION

- The compound 2-Hydroxy-3-[3-(4-methoxy-phenylamino)-butyryl]-6-methyl-pyran-4-one was synthesized using Mannich method.

- The synthesized compound was characterized using IR, ^{1}H and ^{13}C NMR.

- The synthesized compound was screened for antibacterial activity.

- The compound is highly active against both Staphylococcus aureus and A. nigers in anti bacterial activity.

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Post Graduate Project – 9

Corrosion Inhibition of Mild Steel in 1.0 M HCl by Artabotrys Hexapetalus Leaves Aqueous Extract

Name of the Guide: Dr. A. SamsathBegum
Name of the Candidate: S. Akshaya

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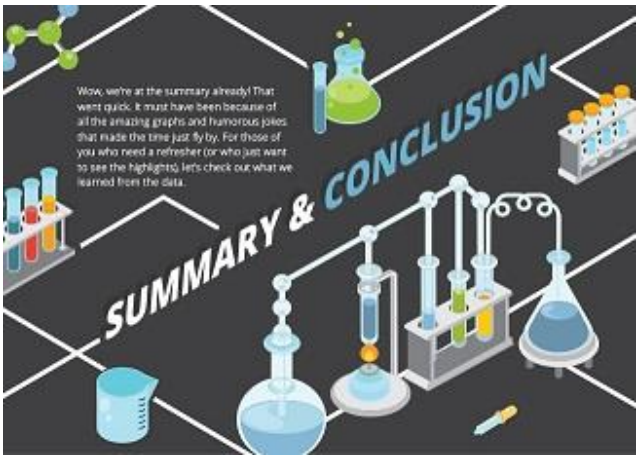
Results and discussion

CHAPTER-V



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CHAPTER-1

INTRODUCTION

CORROSION

Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Both the type of metal and the environmental conditions, particularly gasses that are in contact with the metal, determine the form and rate of deterioration.

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment.

Figure -1: Deterioration on metal surface

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media.

Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its location. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media. The present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

DEFINITION OF CORROSION

- Corrosion is the irreversible damage or destruction of living tissue or material due to a chemical or electrochemical reaction. A prime example of corrosion is rusting of iron or steel.
- Corrosion is a natural process, which converts refined metal to a more chemically stable form, such as its oxide, hydroxide or sulfide. It is the gradual destruction of materials (usually metals) by chemical or electro chemical reaction with their environment.
- Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species.
- Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment. Corrosion is the destructive attack on a metal through interaction.

THEORIES OF CORROSION

- **Homogeneous theory**

A corroding metal irrespective of the presence or absence on its surface of any micro heterogeneity can be regarded as single electrode on which reactions take place. Metal becomes unstable due to the charge transfer reaction taking place at the interface. Hence, it is necessary that the potential difference across the interface be more negative than the equilibrium potential for the metal dissolution (anodic) reaction or more positive than the equilibrium potential for the electronation (cathodic) reaction.

- **Heterogeneous theory**

According to this theory, corrosion is caused by local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity. Corroding metal consists of an electron sink area, where de-electronation reaction occurs. b. an electron source area, where electronation reaction occurs in an ionic conductor to keep the current flowing.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday‟s Laws, being determined by the total flow of electrons from anodes to cathodes which is called the “corrosion current”, I_{corr}. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a “mixed electrode” since simultaneous anodic and cathodic reactions are proceeding, on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

The most common and important electrochemical reactions in the corrosion of iron are

Anodic reaction (corrosion)

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Cathodic reactions (simplified)

$$2H^+ + 2\,e^- \longrightarrow H_2$$

$$H_2O + 1/2O_2 + 2e^- \longrightarrow 2\,OH^-$$

This reaction is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

MECHANISM OF CORROSION

Although several mechanisms have been proposed for the corrosion process, corrosion is mainly electrochemical in nature and hence in this chapter, the electrochemical mechanistic aspects have been discussed. According to this approach, the corrosion reaction can be considered as taking place by two simultaneous reactions; the oxidation of a metal at an anode (a corroded end releasing electrons) and the reduction of a substance at a cathode (a protected end receiving electrons). In order for the reaction to occur, the following conditions must exist:

- A chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition).
- An electrolyte must be present to provide solution conductivity and act as a source of material to be reduced at the cathode.
- An electrical path through the metal or between metals must be available to permit electron flow.

The below diagram illustrates the typical electrochemical corrosion of iron in contact with water.

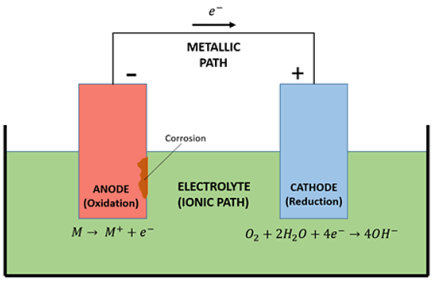

Figure -2: Electrolyte corrosion cell

In a nearly neutral or slightly acid environment, the water is dissociated into hydrogen ions (H^+) and hydroxyl ions (OH^-) as

$$H_2O \rightleftarrows H^+ + OH^-$$

When metal is placed in contact with a liquid, surface ionization occurs, because of the electric charge difference at the solid-liquid interface. For example, iron dissolves in water in the form of positively charged ferrous ions (Fe^{++})

$$Fe \rightleftarrows Fe^{++} + 2e^-$$

Electrochemically, a chemical substance is "oxidized", when it loses electrons to a second substance. The electrode at which the oxidation takes place is called as the "anode". A chemical substance is "reduced", when it acquires electrons. The electrode at which reduction takes place is called the "cathode". Hence, oxidation reaction results in the formation of positive charge ferrous ions at the anode. Ferrous ions moving away from the metal surface are further oxidized to ferric ions (Fe^{++}) as follows

$$Fe^{++} \rightleftarrows Fe^{+++} + e^-$$

The positively charged ferric ions are attracted to the negatively charged hydroxyl ions and form the corrosion product $Fe(OH)_3$

$$Fe^{+++} + 3(OH)^{-} \rightleftarrows Fe(OH)_3$$

The rust consists of iron hydroxide or iron oxide hydrates in various states, depending on the degree of oxidation and dehydration.

The reduction reaction at the cathode must take place concurrently in order to continue the corrosion process. Several reactions are possible and the one that occurs is determined by the environment. Without the presence of air or oxygen, hydrogen ions can be reduced by the excess of electrons at the cathode surface and evolve as molecular hydrogen by

$$2H^{+} + 2e^{-} \rightleftarrows H_2$$

If hydrogen is not removed from the surface, the cathodic reaction decreases and the corrosion rate is reduced. With the presence of air, the more likely reaction is the reduction of oxygen. Two possible reactions occur:

$$O_2 + 4H^{+} + 4e^{-} \rightleftarrows 2H_2O$$

$$O_2 + 2H_2O + 4e^{-} \rightleftarrows 4(OH)^{-}$$

Hydrogen evolution or oxygen reduction with the formation of water is likely to occur in acid media. On the other hand, oxygen reduction with the formation of hydroxyl ions is more dominant in a neutral or alkaline environment. In either case, there is an increase in the alkalinity of the solution at the cathode.

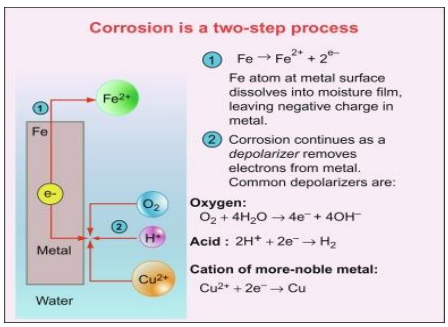

Figure -3: Two step process of corrosion

In summary, corrosion occurs when metal atoms detach themselves from the metal surface at the anode and enter the solution as ions, leaving behind electrons in the metal. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen ions that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In

solutions, where hydrogen tends to evolve too slowly, oxygen is reduced and combines with hydrogen ions or water to form hydroxyl ions.

TYPES OF CORROSION

They are many different types of corrosion, each of which can be classified by the cause of the metals chemical deterioration.

The metal corrodes at the same rate over the entire surface for the former and only small areas are affected in localized corrosion. Classification by appearance is manifested by the morphology of the corrosion attack and this can be visualized either by naked eye or magnification. The schematic in the given below diagram illustrates some of the most common forms of corrosion.

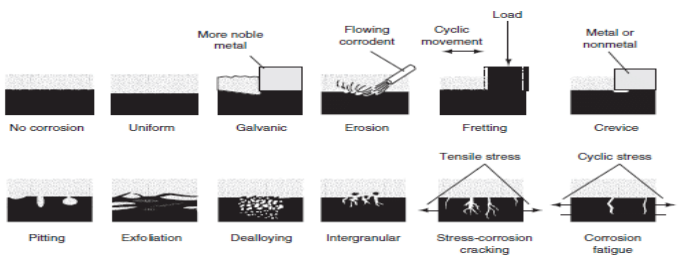

Figure -4: Schematics of the common forms of corrosion

General attack corrosion

It is also known as uniform attack corrosion. General attack corrosion is the most common type of corrosion and is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal. Ultimately, the metal deteriorates to the point of failure.

Figure -5: Uniform Corrosion

General attack corrosion accounts for the greatest amount of metal destruction by corrosion but is considered as a safe form of corrosion, due to the fact that it is predictable, manageable and often preventable.

Localized Corrosion

Unlike general attack corrosion, localized corrosion specifically targets one area of the metal structure. Localized corrosion is classified as one of three types:

Pitting

Pitting results when a small hole, or cavity, forms in the metal, usually as a result of de-passivation of a small area. This area becomes anodic, while part of the remaining metal becomes cathodic, producing a localized galvanic reaction. The deterioration of this small area penetrates Crevice corrosion: Similar to pitting, crevice corrosion occurs at a specific location. This type of corrosion is often associated with a stagnant micro-environment, like those found under gaskets and washers and clamps. Acidic conditions or a depletion of oxygen in a crevice can lead to crevice corrosion.

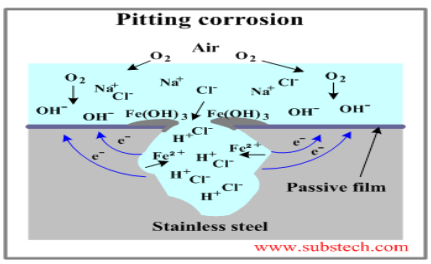

Figure -6: Pitting corrosion

Filiform Corrosion

Occurring under painted or plated surfaces when water breaches the coating, filiform corrosion begins at small defects in the coating and spreads to cause structure. This form of corrosion is often difficult to detect due to the fact that it is usually relatively small and may be covered and hidden by corrosion-produced compounds.

Galvanic Corrosion

Galvanic corrosion or dissimilar metal corrosion occurs when two different metals are located together in a corrosive electrolyte. A galvanic couple forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly.

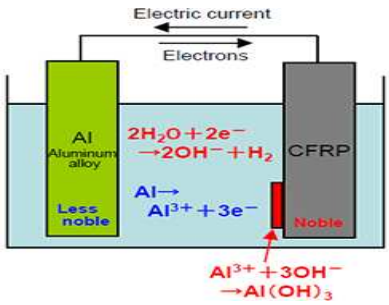

Figure -7: Galvanic corrosion

Three conditions must exist for galvanic corrosion to occur:

- Electrochemically dissimilar metals must be present
- The metals must be in electrical contact
- The metals must be exposed to an electrolyte

Environmental Cracking

Environmental cracking is a corrosion process that can result from a combination of environmental conditions affecting the metal. Chemical, temperature and stress-related conditions can result in the following types of environmental corrosion:

Figure -8: Environmental cracking

- Corrosion cracking
- Corrosion fatigue
- Hydrogen-induced racking
- Liquid metal embrittlement

Flow-Assisted Corrosion (FAC)

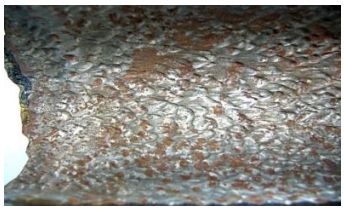

Figure -9: Flow-Assisted corrosion

- Flow-assisted corrosion, or flow-accelerated corrosion, results when a protective layer of oxide on a metal surface is dissolved or removed by wind or water, exposing the underlying metal to further corroding and deteriorate
- Erosion-assisted corrosion
- Impingement
- Cavitation

Intergranular Corrosion

Figure -10: Intergranular corrosion

Intergranular corrosion is a chemical or electrochemical attack on the grain boundaries of a metal. It often occurs due to impurities in the metal, which tend to be present in higher contents near grain boundaries. These boundaries can be more vulnerable to corrosion than the bulk of the metal.

De-Alloying

De-alloying, or selective leaching, is the selective corrosion of a specific element in an alloy. The most common type of de-alloying is de-zincification of unstabilized brass. The result of corrosion in such cases is a deteriorated and porous copper.

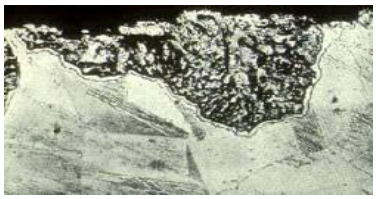

Figure -11: De-Alloying corrosion

It is the removal of one solid element from alloy by corrosion processes. De alloying corrosion is also called de-zincification.

The most common example is de-zincification which is selecting removal of zinc in brass alloy. Similar processes occur in other alloy systems in which aluminium, Iron, Cobalt, Chromium and other elements are removed**.**

Fretting Corrosion

Fretting corrosion occurs as a result of repeated wearing, weight and/or vibration on an uneven, rough surface. Corrosion, resulting in pits and grooves, occurs on the surface.

Figure -12: Fretting corrosion

Fretting corrosion is often found in rotation and impact machinery, bolted assemblies and bearings, as well as to surfaces exposed to vibration during transportation.

High-Temperature Corrosion

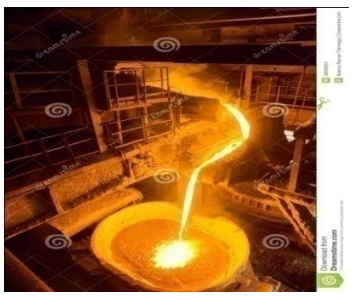

Figure -13: High-Temperature corrosion

High-temperature corrosion is a mechanism of corrosion that takes place in gasturbines, diesel engines, furnaces or other machinery coming in contact with hot gas containing certain contaminants. Fuel sometimes contains vanadium compounds or sulfates which can form compounds during combustion having a low melting point. These liquid melted salts are strongly corrosive for stainless steel and other alloys normally inert against the corrosion and high temperatures. Other high-temperature corrosions include high-temperature oxidation, sulfidation and carbonization**.**

Crevice Corrosion

Figure -14: Crevice corrosion

Crevice corrosion is also a localized form of corrosion and usually results from a stagnant microenvironment in which there is a difference in the concentration of ions between two areas of a metal.

Crevice corrosion occurs in shielded areas such as those under washers, bolt heads, gaskets, etc. a stagnant solution builds, pH shifts away from neutral. This growing imbalance

between the crevice (micro environment) and the external surface (bulk environment) contributes to higher rates of corrosion, where oxygen is restricted. These smaller areas allow for a corrosive agent to enter but do not allow enough circulation within, depleting the oxygen content, which prevents re-passivation. As. Crevice corrosion can often occur at lower temperatures than pitting. Proper joint design helps to minimize crevice corrosion.

Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is a result of the combination of tensile stress and a corrosive environment, often at elevated temperatures. Stress corrosion may result from external stress such as actual tensile loads on the metal or expansion/contraction due to rapid temperature changes.

Figure -15: Stress corrosion cracking

It may also result from residual stress imparted during the manufacturing process such as from cold forming, welding, machining, grinding, etc. In stress corrosion, the majority of the surface usually remains intact; however, fine cracks appear in the microstructure, making the corrosion hard to detect. The cracks typically have a brittle appearance and form and spread in a direction perpendicular to the location of the stress. Selecting proper materials for a given environment (including temperature and management of external loads) can mitigate the potential for catastrophic failure due to SCC.

Caustic Agent Corrosion

Figure -16: Caustic Agent corrosion

Caustic agent corrosion occurs when impure gas, liquids, or solids wear a material down. Although most impure gases do not damage metal in dry form, when exposed to moisture they dissolve to form harmful corrosive droplets. Hydrogen sulfide is an example of one such caustic agent.

Microbial Corrosion

Figure -17: Microbial corrosion

Microbial corrosion, commonly referred to as microbiologically influenced corrosion (MIC) is caused by microorganisms. It applies to both metallic and non-metallic materials with or without oxygen. When oxygen is absent, sulfate-reducing bacteria are active and produce hydrogen sulfide causing sulfide stress cracking. When oxygen is present, some bacteria may directly oxidize iron to iron oxides and hydroxides. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

Filiform Corrosion

Filiform corrosion: It is basically a special type of crevice corrosion, sometimes termed as “under film” corrosion. This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating.

Figure -18: Filiform corrosion

Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided unless absence of an adverse effect has been proven by field experience.

Cavitation Damage

Figure -19: Cavitation Damage

Cavitation damage is a special form of erosion corrosion caused by the formation of vapour bubbles and their collapse in the liquid near a metal surface. This form of damage occurs in hydraulic turbines, pump impellers, and other surfaces that are in contact with high-velocity liquid flow along with high pressures.

Erosion Corrosion

Figure -20: Erosion corrosion

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities. Erosion corrosion can be controlled by the use of harder alloys (including flame-sprayed or welded hard facings) or by using a more corrosion resistant alloy

Concentration cell Corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. Concentration cell corrosion is associated with gaskets, joints, scale, debris, loose protective films, etc.

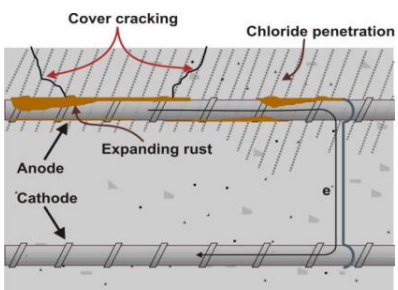

Figure -21: Concentration cell corrosion

Corrosion attack is accelerated, where the oxygen concentration is least. Metal at the area of low oxygen availability becomes anodic to other areas. As the cathodic area is large compared to the anodic area, the intensity of attack is usually more severe on surrounding areas of the same surface. This condition can be eliminated by sealing the faying surfaces in a manner to exclude moisture. Proper protective coating application with inorganic zinc primers is also effective in reducing faying surface corrosion.

Corrosion fatigue

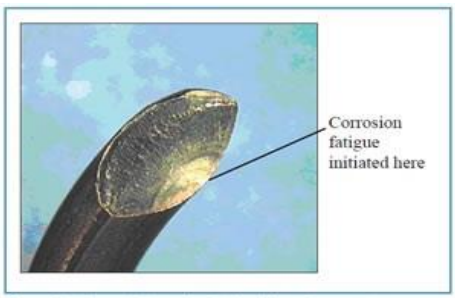

Figure -22: Corrosion fatigue

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment. Control of corrosion fatigue can be accomplished by either lowering the cyclic stresses or by corrosion control by using protection methods.

Direct chemical Corrosion (or) dry Corrosion

This type of corrosion occurs mainly through the direct chemical action of environment/atmospheric gases such as oxygen, halogens, hydrogen sulphide, nitrogen or anhydrous liquid sulphur dioxide with metal surface in immediate proximity. The extent of corrosion depends upon the following factors:

- Chemical affinity between the corrosive environment and solid metals
- Ability of reaction product on metal surface to form a protective film.

FACTORS AFFECTING RATE OF CORROSION

Nature of the metal

Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum , silver. Whereas metal with lower electrode potentials, readily undergo corrosion. e.g., metals like zinc, magnesium, aluminium. When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion. For e.g., the potential l difference between the iron and copper is 0.78V which is more than that between iron and tin is 0.30V. Therefore, iron corrodes faster when in contact with copper than that with tin. On this account, the use of dissimilar metals should be avoided wherever possible. For example, bolt and nut or screw and washer should make by the same metal (or alloy) to avoid galvanic corrosion.

Ratio of cathodic to anodic region

The rate of corrosion is influenced by relative size of cathodic to anodic area. If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio decreases corrosion rate further increases. This is because at anode electrons are liberated. Which are consumed at cathodic region. If cathodic region is larger the liberated electrons are rapidly consumed at cathode. This further enhances, the anodic reactions leading to increase in overall rate of corrosion. When two dissimilar metals are in contact, Corrosion is more rapid and severe, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank), If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode. An intense localized corrosion occurs at the exposed small anodic surface. On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas.

Nature of the corrosion product

The corrosion product formed like metal oxide may act as protective film, if it is stable, insoluble, and non-porous. If it acts as protective film it prevents further corrosion by acting as barrier between metal surface and corrosion medium. On the other hand if corrosion product is

Unstable, porous, and soluble, it further enhances corrosion in oxidizing environments, metals like aluminium, chromium, titanium, etc., are highly passive as their oxides as corrosion products form protective films on the metal surface, preventing further corrosion. Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments

pH of the medium

In general rate of corrosion is higher in acidic pH than in neutral and alkaline pH.In case of iron, at very high pH protective coating of iron oxide is formed which prevents corrosion. Whereas at low pH, severe corrosion takes place. But for metals like aluminium, corrosion rate is high even at high. pH

Temperature

The rate of corrosion increases with increasing temperature. This is due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

Effect of Oxygen

Oxygen plays an important corroding medium. If the metal is exposed to different concentration of oxygen, differential aeration corrosion takes place. The region which is less 0exposed to oxygen acts as anode hence undergoes corrosion and region exposed to high oxygen Concentration acts cathode hence doesn't undergo corrosion.

Hydrogen Over Voltage

The metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. Since at lower hydrogen over voltage, the liberation of hydrogen gas is easy. Therefore cathodic reaction is very fast, which in turn makes anodic reaction very fast. Thus increasing the rate of corrosion. Higher the over voltage lesser is the corrosion.

PREVENTION OF CORROSION

Rust and other corrosion forms can lead to safety issues and ruin the integrity of your equipment and supplies. Even routine maintenance to remove and repair corrosion can drive up costs. Fortunately, there are a variety of measures you can take to minimize corrosion. Herewe‟ll highlight four of these methods based on cost and effectiveness

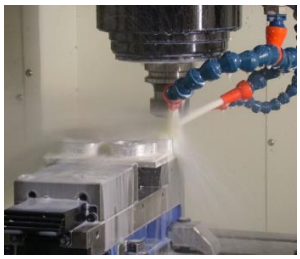

Figure -23: Prevention of corrosion

Barrier Coatings

One of the easiest and cheapest ways to prevent corrosion is to use barrier coatings likepaint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film. Plastic and waxes are often sprayed onto metal surfaces. Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds. Today‟s paint systems are actually a combination of different paint layers that serve different functions. The primer coat acts as an inhibitor, the intermediate coat adds to the paint‟s overall thickness, and the finish coat provides resistance to the environmental factors.

The biggest drawback with coatings is that they often need to be stripped and reapplied. Coatings that aren‟t applied properly can quickly fail and lead to increased levels of corrosion. Coatings may also contain volatile organic compounds, which can make them vulnerable to corrosion.

Hot-Dip Galvanization

This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection.

The process has been around for more than 250 years and has been used for corrosion protection of things like artistic sculptures and playground equipment. Compared to other corrosion prevention methods, galvanization is known for lower initial costs, sustainability, and versatility. Unfortunately, galvanization can‟t be done on-site, meaning companies have to pull equipment out of work to be treated. Some equipment may simply be too large for the process, forcing companies to abandon the idea altogether. In addition, if the process isn't done properly, the zinc can chip or peel. And high exposure to environmental elements can speed up the process of zinc wear, leading to increased maintenance check-ups. Lastly, the zinc fumes that release from the galvanizing process are toxic.

Alloyed Steel (Stainless)

Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product. Corrosion-resistant nickel, for example, combined with oxidation-resistant chromium results in an alloy that can be used in oxidized and reduced chemical environments. Different alloys provide resistance to different conditions, giving companies greater flexibility.

Despite its effectiveness, alloyed steel is very expensive. Companies with limited financial resources will likely have to turn to other methods. Monitoring surface conditions arecritical, as cracks or scratches can result in an increase of corrosion. Companies also need to Make sure the agents used in maintenance don‟t include corrosion properties.

Cathodic Protection

Cathodic protection protects against galvanic corrosion, which occurs when two different metals are put together and exposed to a corrosive electrolyte. To prevent this, the active sites on the metal surface need to be converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

While cathodic protection is highly effective, anodes need to be checked often which can drive up costs of maintenance. They also increase the weight on the attached structure and aren‟t always effective in high-resistivity environments. Finally, anodes lead to increased water flow on ships and other underwater equipment.

Coatings

Coatings provide physical barriers that do not allow corrosive materials to come in contact with the structure that is being protected. Mainly, coatings are used on the exterior of pipelines to protect from external factors and are not used to directly protect the pipeline from CO_2 corrosion. The most common type of coatings are painting and platting which both provide effective corrosion protection and aesthetic appearance. Painting: Painting is an effective way to protect pipelines from external environmental factors. Although when looking at CO_2 corrosion on the interior of the pipeline, it is not ideal because painting the inside of a pipeline is impractical. The paint will breakdown over time, either through chemical reactions with the flowing fluid or the erosion due to turbulent or transient flow. Once the coating has broken down it leaves unprotected sections of the pipe when fluid induced localized corrosion occurs.

Plating

Plating involves using electric currents to coat a metal with a thin layer of another metal that acts as a protective barrier. Plating an entire pipeline is very uncommon as it is expensive; however, it can be done when dealing with high pressures and high amounts of H_2S and CO_2. One drawback of plating is if the plating fails in a small section (either an imperfection or a scratch) then highly localized corrosion occurs. Another factor to consider is if the plating is more noble than the pipeline (for example, chromium on steel), the steel will act as a sacrificial anode for the chromium. This causes the exposed area to corrode much more rapidly than an un-plated surface would.

CORROSION INHIBITORS

An inhibitor is a chemical substance or combination of substances which when added in very low concentrations in a corrosive environment effectively prevents or reduces corrosion without significant reaction with the components of the environment. Concentrations of

Corrosion inhibitors can vary from 1 to 15,000 ppm (0.0001 to 1.5 wt %). Corrosion inhibitors can be solids, liquids and gases, and can be used in solid, liquid and gaseous media. Solid media can be concrete, coal slurries or organic coatings (paints). Liquids may be water, aqueous solutions or organic solvents. A gaseous medium is an atmosphere or water vapor. Corrosion inhibitors are selected on the basis of solubility or dispersibility in fluids which are to be inhibited. For instance, in a hydrocarbon system, a corrosion inhibitor soluble in hydrocarbon is used. Two phase system composed of both hydrocarbons and water is utilized as oil soluble water- dispersible inhibitor.

Corrosion inhibitors have been found to be effective and flexible means of corrosion mitigation. The use of chemical inhibitors to decrease the rate of corrosion processes is quite variable. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment and product additive industries. In the oil extraction, processing and chemical industries, corrosion inhibitors have always been considered to be the first line of defense. A great number of scientific studies have been devoted to the subject of corrosion inhibitors.

Inhibitors find major use in closed environmental systems that have good circulation so that an adequate and controlled concentration of inhibitor is ensured. Such conditions can be met, for instance in cooling water recirculation systems, oil production, oil refining, and acid pickling of steel components. One of the more recognizable applications for inhibitors is in antifreeze for automobile radiators. The application of inhibitors must be viewed with caution by the user because inhibitors may afford excellent protection for one metal in a specific system but can aggravate corrosion for other metals in the same system. Inhibitors can be organic or inorganic compounds and they are usually dissolved in aqueous environments. Some of the most effective inorganic inhibitors are chromates, nitrites, silicates, carbonates, phosphates and arsenates. The organic inhibitors include amines, heterocyclic nitrogen compounds, sulfur compounds such as thioethers, thioalcohols, thioamides, thiourea and hydrazine. Chromates and zinc salts are used increasingly less due to their toxicity and are nowadays largely replaced by organic inhibitors. Thus practical criteria for the selection of corrosion inhibitors from the great variety of inorganic and organic substances with inhibiting properties are not only their inhibition efficiency but also safety of use, economic constraints and compatibility with other chemicals in the system, and environmental concerns.

In order to avoid or reduce the corrosion of metallic materials, inhibitors used in cooling system must satisfy the following criteria.

- ❖ It must give good corrosion protection at a very low concentration of inhibitor. It must protect all efficient exposed materials from the attack of corrosion.
- ❖ It must remain in extreme operating conditions (higher temperature and velocity. In case of an under or over dosage of inhibitor, corrosion rate should not increase drastically.
- ❖ The inhibitor or reaction products of the inhibitor should not form any deposits on the metal surface particularly at locations where heat transfertakes place.
- ❖ It should suppress both uniform and localized corrosion. It should have long range effectiveness. It should not cause toxicity and pollution problems.

CLASSIFICATION OF CORROSION INHIBITORS

A common classification of inhibitors is based on their effects on the electrochemical reactions involved in the corrosion process.

Passivating Inhibitors

Passivating inhibitors cause a large anodic shift of the corrosion potential forcing the metallic surface into the passivation range. There are two types of passivating inhibitors.

- ❖ The oxidizing anions such as chromates, nitrites and nitrates that can passivate steel in the absence of oxygen.
- ❖ The non-oxidizing ions such as phosphates, tungstates and molybdates that require the presence of oxygen to passivate steel.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential to monitor the inhibitor concentration.

Volatile Inhibitors

Volatile corrosion inhibitors (VCIs) also called vapor phase inhibitors (VPIs) are compounds transferred in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing the acidic carbon dioxide or by shifting the surface pH towards less acidic. If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors.

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Liquid phase inhibitors (LPIs)

LPIs are in wide scale use to combat CO_2 corrosion in pipelines. The inhibitor is that is injected into the pipeline is transported in low concentrations and adsorbs onto the surface of the steel. Because the inhibitor is in the liquid phase only the interior of the pipeline needs to be in contact with the liquid either continuously or semi-continuously. One of the main benefits in using inhibitors to protect from CO_2 corrosion is that it can continuously be added to the flow to provide continuous protection.

Cathodic Inhibitors

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. For example, calcium, magnesium and zinc ions will precipitate as hydroxides on cathodic sites as the local environment becomes more alkaline due to the reduction reaction at these sites. cathodic inhibitors are effective when they slow down the cathodic reaction rate. Arsenic, bismuth and antimony which are referred to as cathodic poisons reduce the hydrogen reduction reaction rate and thus lower the overall corrosion rate. Other cathodic inhibitors remove reducible species from the environment. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through.

- The use of oxygen scavengers such as sodium sulfite and hydrazine which react with the oxygen and remove it from the solution.
- vacuum de-aeration or boiling to lower the dissolved oxygen concentrations.

Anodic Inhibitors

Anodic inhibitors such as chromates, phosphates, tungstates and other ions of transition elements with high oxygen content are those that stifle the corrosion reaction occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface forming a protective film or barrier, thereby reducing the corrosion rate. Anodic inhibitors build a thin protective film along the anode and increasing their potential and thus slow down the corrosion reaction. Chromates, nitrates, tungstate and molybdates are some examples of anodic inhibitors. Although, this type of control is affected, yet it may be dangerous since severe local attack can occur, if certain areas are left unprotected by depletion of the inhibitors.

Mixed Inhibitors

Some substances inhibit corrosion by reducing simultaneously the rate of anodic and cathodic reactions involved in the corrosion process and are therefore called mixed inhibitors. They are typically film forming compounds that cause the formation of precipitates on the

surface blocking both anodic and cathodic sites indirectly. Anodic inhibitors are, for the most part, dangerous inhibitors, especially if their concentrations are too less. But cathodic inhibitors are generally safe. Mixed inhibitors are less dangerous than pure anodic inhibitors, and in number of cases they may not increase the corrosion intensity. The most common inhibitors of this category are the silicates and the phosphates.

Synergistic Inhibitors

It is very rare that a single inhibitor is used in systems such as cooling water systems. More often, a combination of inhibitors (anodic and cathodic) is used to obtain better corrosion protection properties. The blends which are produced by mixing of multi-inhibitors are called synergistic blends. Examples include chromate-phosphates, polyphosphate-silicate, zinc-tannins, and zinc-phosphates.

Precipitation Inhibitors

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust. In aerated hot water systems, sodium silicate protects steel, copper and brass.

GREEN CORROSION INHIBITORS

Extracts of plant materials contain a wide variety of organic compounds. Most of them contain hetero atoms such as P, N, S and O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented.

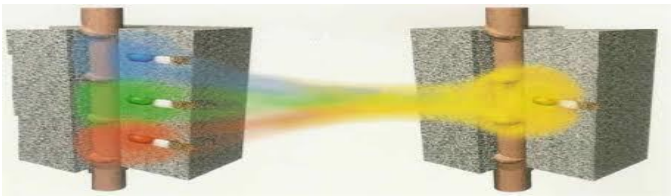

Figure -24: Migrating corrosion inhibitors

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties. The term "green inhibitor" or "eco-friendly inhibitor" refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of "inhibitors", "green inhibitors" can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

Organic green inhibitors

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from natural sources like plants. It also includes synthetic compounds with negligible toxicity. Some of the notable developments on organic green inhibitors especially plant extracts are discussed here.

Plant extracts

The authors have so far investigated the application of plant extracts, as well as other organic inhibitors against corrosion of steel in acidic fluids. Loto had reported the application of the extract of Mangifera indica (Common name: mango, indigenous area: India and other tropical regions) leaves and bark for corrosion of mild steel in diluted sulphuric acid (H_2SO_4) medium. The weight loss measurements and electrochemical impedance spectroscopic studies were used to determine the inhibition efficiency of the inhibitors. Though the extract of leaves

and bark showed a significant effect on the corrosion rate separately, the combination of these two extracts exhibited rather higher efficiency.

The inhibitive effect of Zenthoxylum alatum (Winged Prickly Ash, East and South Asian Countries) fruit extract was reported for corrosion of mild steel in phosphoric acid medium at temperatures ranging from 50–80^{0}C. The surface analysis using X-ray photoelectron spectroscopy (XPS) revealed the layer formation of the plant extract on the surface of mild steel. And the results were indicated the possible formation of iron phosphate that was catalyzed by the formation of the iron-plant extract organo-metallic complex.

Satapathy et al studied the methanol extract of Justicia gendarussa (Willow-leaved justicia, India, Indonesia) leaves for corrosion inhibition of mild steel in hydrochloric acid medium (HCl). The authors have made an attempt to characterize the organic compounds present in the methanol extract by means of gas chromatography- mass spectrometric technique. The results showed that the compounds present in the methanol extract were difficult to separate, since the retention times of majority of the compounds were close to each other. The electron spectroscopy for chemical analysis and atomic force microscopywere employed to obtain the information about the film formation on the surface of the mild steel specimen.

Inorganic Green Inhibitor

A number of inorganic elements (minerals) are essential for the growth of living things. Mineral elements in wide variety are present in trace amounts in almost all foodstuffs. The higher concentrations of many metals cause toxicity to all forms of lives. Chromates are among the most common substances used as inhibitors or incorporated in anticorrosive pretreatments of aluminums alloys. The corrosion of galvanized steel was inhibited by the formation of cerium-rich film. The film contains Ce^{4+}which was formed by the cerium oxides and hydroxide

IMPORTANCE OF GREEN INHIBITOR

- Inhibitors are a great method of preventing corrosion and are easy to apply. Has application in a wide range of sectors.
- The knowledge of the method of the action,facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects.

- ❖ It is important in the choice of inhibitor, ascertain the subsequent effects of this towards the environment
- ❖ .The search for environmental friendly inhibitors has shown excellent results, outperforming conventional inhibitors.Reference organic inhibitors newly developed. Inhibitors play a vital role in providing protection against corrosio.
- ❖ The selection of the inhibitor is important for environmental protection not all inhibitors are eco-friendly.
- ❖ There is a growing trend to use plant extracts and pharmaceutical compounds as corrosion inhibitors. Most of these compounds are environmentally-friendly.

ECO-FRIENDLY INHIBITORS FOR CORROSION CONTROL OF MILD STEEL (MS)

In recent years several researchers have indicated the use of eco-friendly corrosion inhibitors for mild steel in different media. They forms complexes with metal ion onto the metal surface and thus forming a protective coating on the metal surface and protecting them from corrosive agents in different media. Inhibition efficiency of these inhibitors in different media have been evaluated by employing different investigational techniques like weight loss method, electrochemical studies, Raman spectroscopy, gasometric techniques, potentiodynamic polarization, electrochemical impedance, polarization method, SEM, FTIR etc. are being used.

CHAPTER-II

AIM AND SCOPE OF THE PRESENT WORK

Green compounds represent a potential class of corrosion inhibitors. There is a wide range of studies regarding corrosion inhibition by hetero atoms containing green compounds. Green compounds containing lot of hetero atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulfur. The corrosion-inhibiting property of these compounds is attributed to their molecular structure.

Acid solutions are widely used in industries for pickling, acid cleaning of boilers, rescaling and oil well as acidizing. Corrosion inhibitors are widely used in order to control the corrosion of metallic materials by cleaning acids. 1.0 M HCl is employed in such purposes. Most of the earlier studies on inhibition of corrosion of metals in acids have been related to the performance of organic compounds containing hetero groups.

Recently, environmental friendly inhibitors have attracted several researchers. Natural products are non-toxic, biodegradable and readily available. They have been widely used as inhibitors. Corrosion inhibition of mild steel by various types of plant extracts has been studied.

Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly, and acceptable and possess no threat to the environment. The present work in undertaken:

1. To evaluate the inhibition efficiency of an aqueous leaves extract of *Artabotrys hexapetalus* in controlling the corrosion of mild steel in 1.0 M HCl medium.
2. To analyse the best fit isotherm for corrosion inhibition.
3. To understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization and impedance analysis.
4. To propose a suitable mechanism for corrosion inhibition.

CHAPTER-III

EXPERIMENTAL METHOD

The experimental studies related to the inhibition action of *Artabotrys hexapetalus* leaves extract on mild steel in 1.0 M HCl have been present here. Such studies include weight loss, polarization and impedance studies.

Artabotrys hexapetalus

Artabotrys hexapetalus is a genus of plants in the *Annonaceae* family. There are over 100 species in the old world tropics, with 31 species in Africa. It is part of the clustered apple family (Annonaceae). All species are small trees or shrubs with a tendency to climb. Leaves are simple and alternate, without hairs. Bisexual flowers are borne singly or in clusters opposite the leaves. The 6-pettalled flowers are scented, and the plant bears fleshy fruits.

Artabotrys hexapetalus is indigenous in southern India and Sri Lanka but later introduced throughout the Old World tropics. It is commonly cultivated in southern China, Indo-China, the Philippines and also in Java.

Artabotrys hexapetalus

Figure -25: Artabotrys hexapetalus

Properties

Botanical name : *Artabotrys hexapetalus*

Family : Annonaceae

Kingdome : Plantae

Order : Magnoliales

Genus : Artabotrys

Division : Magnoliphyta

Tamil name : Manoranjitham

Therapeutic uses: The flowers of *Artabotrys hexapetalus* are tonic and stimulant. The fruits and the bark are used to treat fever, diarrhea, skin diseases, wounds, ulcers, inflammation, cough, asthma and bronchitis. The leaves extract has antibacterial, antifertility and antifungal activities.

Pharmacological action: Anti-inflammatory, anti-oxidant, anti-osteoporatic, anti -bacterial activity.

Collection of the plant material: The leaves were collected from the area Elur, Namakkal (DT), Tamilnadu. Fresh leaves were authenticated and identified by Dr. John Britto, The Rapient Herbarium and centre for Module systematics, St, Joseph'Hs College, Trichirappalli, Tamil nadu, India.

Preparation of Extract

The leaves were collected, shade dried and powdered. An aqueous extract was prepared by refluxing 10 gm of powdered *Artabotrys hexapetalus* leaves in double distilled H_2O. The extract was cooled, filtered and made up to 100 ml with distilled water. From that, various distributions were prepared.

Preparation of the specimens

Mild steel specimen (0.026%-S, 0.06%-P, 0.4%-Mn, 0.1%-C and the rest iron) of the dimensions 1x5x0.2 cm were polished to mirror finished. They are decreased with acetone and used for the weight loss method, polarization and impedance studies.

Materials and chemicals used

For polarization, cylindrical mild steel rod embedded in Teflon with an exposed area of 1 cm^2 was used. The electrodes were polished with emery papers of 0/0, 2/0, 3/0, and 4/0 grades and degreased with acetone, dried and used.

Acid

HCl was used of G.R. Grade (MERCK CHEMICALS)

TABLE-1

Phytochemical screening of aqueous extract of *Artabotrys hexapetalus* leaves extract

Phyto-constituents	Chemical Test	Aqueous extract
Alkaloids	Wagners	-
Coumarin	Anthraquinones	+
Tannins	$FeCl_3$	+
Flavonoids	Lead acetate	+
Sterols	Libermann	-
saponins	Sodium hydroxide	+
Phenols	$FeCl_3$	+
Quinones	Alcoholic KOH	-
xanthoproteins	HNO_3	+

(Note: + : Presence; - : Absence)

Weight loss method

Weight loss measurements were performed in 1.0 M HCl medium with and without the presence of different volumes of inhibitor by using the formula, inhibition efficiency were calculated.

Inhibition efficiency (%) = W_0-W_i/W_0*100

Where

W_0= Weight loss in plain acid

W_i = Weight loss in inhibited acid

Potentiodynamic polarization studies:

Potentiodynamic polarization studies were performed for mild steel specimen in the presence and the absence of the inhibitors. Polarization measurements were performed to evaluate the corrosion current, corrosion potential and the Tafel‟s slope.

The electrode used was a mild steel rod of the same composition embedded in araldite and with an exposed area of 1cm^2. The polarization cells contain a three electrode assembly. A rectangular foil was used as the counter or auxiliary electrode. The area of the counter electrode is much larger compared to the area of the working electrode. This will exert a uniform potential field on the working electrode. The reference electrode is Hg/$HgCl_2$/1N H_2SO_4 for HCl solution.

A solution quantity of 100 ml of the test solution was taken in a polarization cell. The working electrode was polished with 0/0, 1/0, 2/0, 3/0, and 4/0 emery papers successively and degreased with acetone. The working electrode, reference and auxiliary platinum electrodes were assembled and connections were made.

Stirring was provided to the test solutions to avoid for the system the volume polarization before start of experiment. A time interval of about 15 minutes was given for the system to attain steady state and open circuit potential was recorded. Polarization measurements were made carried out from 800mV to 250mV at a constant identical to weight loss measurements.

Polarization measurements were made from mild steel specimens in 1.0 M HCl in the presence and absence of the inhibitor. Current in mA and potential in mV were plotted. From the graph, the Tafel slope (in mV/decade) and the corrosion potential (in mV/decade) were calculated.

Impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell setup was the same as that used for polarization measurements.

The real part and imaginary part of the cell impedance were measured in ohms at varies frequencies. The value of charge transfer resistance, R_t , and the double layer capacitance, C_{dl} were calculated.

CHAPTER-IV

RESULTS AND DISCUSSION

It is a well known fact that research activities leading to the development of corrosion inhibitors based on natural products have immense scope in several industries, because of their non-toxicity, biodegradable nature and are also easily available. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly and possess no threat to the environment.

The efficiency of an extract as a corrosion inhibitor can be attributed to the number of mobile electron pairs present, π-orbital character of free electrons and the electron density around the hetero atoms. In the present study, inhibition efficiency of *Artabotrys hexapetalus* leaves extract in 1.0 M HCl medium has been evaluated using weight loss measurements and its potentiodynamic polarization and impedance studies. The effect of this extract on the extent of inhibition of corrosion of mild steel in 1.0 M HCl medium by this extract can be explained in terms of its adsorption on the metal surface. This extract gets adsorbed on the metal surface by means of, when mild steel is immersed in the acid solution the phyto-components diffuses from the bulk of solution towards the metal surface.

The inhibitive influence of *Artabotrys hexapetalus* on the corrosion of mild steel in 1.0 M HCl leaves was studied by weight loss method, polarization and impedance measurements. The inhibition efficiency values determined by these techniques showed closed agreement. The maximum inhibition efficiency was found to be 96.8%.

The corrosion decreased with increase in addition of *Artabotrys hexapetalus* probably due to the progressive adsorption of the inhibitor on the metal surface.

The percentage of inhibition efficiency increases with increase in the inhibitor volume. The corrosion inhibition by *Artabotrys hexapetalus* leaves extract is attributed to the adsorption of the additive onto the mild steel surface.

The values obtained from the weight loss technique for the studied inhibitor fit well into the Temkin and El-awady adsorption isotherm. The values of free adsorption process indicate that both physisorption and chemisorption studied for the mild steel surface.

The leaves of *Artabotrys hexapetalus* prevent the corrosion due to the presence of any of the phytochemical components shifting the corroded metal into the noble. The polarization study also shown an agreement with inhibitor efficiency obtained from weight loss studies.

Weight loss studies

Table-2 gives the inhibition efficiency of different volume of *Artabotrys hexapetalus* 1.0 M HCl medium. The inhibition depends upon the nature and mode of adsorption of the metal surface. The adsorption is assumed to be quasi-substitution process between the water molecules on the surface and any of the natural components present in the inhibitor.

The inhibition of heterocyclic compound present in the plant extract with the metal surface may occur through any of the phyto-components present in the inhibitor and also to the interaction of π-electrons of ring with metal surface, thereby enabling the compound to get adsorbed on the metal surface.

Adsorption isotherm

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Temkin, Flory-Huggins, Frumkin, and the recently formulated thermodynamic/kinetic model of El-awady et al. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clue to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs as the interaction energy between molecules and metal surface is higher than that between the H_2O molecules and the metal surface.

Langmuir adsorption isotherm

Adsorption isotherms are very important to determine the mechanism of phyto-electrochemical reaction. The adsorption isotherm values are shown in **table-3**.

Langmuir adsorption isotherm is

$$\Theta = K_{ads}.\ C/1 + K_{ads}\ .C$$

$$\Theta\ (1+K_{ads}.C) = K_{ads}\ .C$$

$$\Theta = K_{ads}.\ C - K_{ads}\ .C\Theta$$

$$\Theta = (1-\Theta)\ K_{ads}\ .C$$

$$\Theta/1-\Theta = K_{ads}\ .C$$

The plot of 3+ logs (Θ/1-Θ) against 3+logC is a straight line as shown in **figure-26**. Thus the Langmuir isotherm is valid for the inhibitor.

Temkin adsorption isotherm

It is given by the expression;

$$\Theta = -2.303 \log K/2a.-2.303 \log C/2a$$

Where "K" is the adsorption equilibrium constant, "a" is the lateral interaction parameter. The plot of Θ against log V is shown in **figure-27**. The linear plot indicates that Temkin adsorption isotherm was obeyed and negative, value of "a" indicated repulsion exist in the adsorption layer. The results are shown in **table -4.**

Florry-Huggins adsorption isotherm

It is given by the expression

$$\log \Theta/C = \log K + x \log (1-\Theta)$$

Where „x" is the size parameter and it is a measure of the number of adsorbed water molecules substituted by an inhibitor molecule. The adsorption parameter is shown, in **table-5.** The plot of log Θ/C against log (1-Θ) is linear as shown in **figure-28.**

El-awady isotherm

It is given by the expression:

$$\log (\Theta/1-\Theta) = \log K + y \log C$$

Here K_{ads} the equilibrium constant of adsorption process is calculated by the relationship, K_{ads} = 1/k. A plot of 2 + log (1-Θ) Vs. 2+ logC is linear as shown in **figure-29**. The calculated K_{ads} and 1/y values are given. The adsorption isotherm values are shown in **table-6.**

Frumkin Isotherm

$$K_{ads}\, C = (\ /1-\Theta)e^{-2a}$$

Take logarithm on both sides of the equation, it can be rearranged as given below.

$$\log K_{ads} + 2a = \log(\ /(1-\Theta)C)$$

where, K_{ads} is the adsorption desorption equilibrium constant, V is the inhibition volume and „a" is the interaction parameter describing the lateral interaction among inhibitor molecular in the absorbed layer on the metal surface. Linear plots of **log(/(1- Θ)C)** Vs. Θ is shown in **figure -30.** obtained. The values for the Frumkin adsorption parameters are shown in **table-7.**

Free energy change

ΔG^0_{ads} of inhibitor on mild steel surfaces related to the constant of the adsorption according to equation. The

$$\Delta G^0_{ads} = -2.303RT\log (K_{ads} \times 55.5)$$

From the results, shown in **table-8**, most of the values of ΔG^0_{ads} were found to be negative and were below the threshold value of -40 kJ/mole indicating that the adsorption of *Artabotrys hexapetalus* leaves extract, on mild steel susrface is spontaneous and thatmechanism of physical adsorption is applicable.

Potentiodynamic polarization studies

Table-9 and **figure**s **31, 32, 33, & 34** gives the values of potentiodynamic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}) and the cathodic Tafel slopes (b_c and b_a) for the different volume shown in the green inhibitor understudy. It can be seen that the phyto-components diffuse from the bulk of the solution and gets absorbed on metal surface.

AC impedance study:

Table-10 and **figures 35, 36, 37 & 38** shows the AC impedance value for different volume of the inhibitor. The R_t value increases and C_{dl} value decreases with inhibitor volume. This implies the formation of protective film on the metal surface. It can be also seen from **table-11** that there is a close agreement between the values of inhibition efficiencies obtained from weight loss measurements, polarization and impedance studies.

TABLE-2

Inhibition effect on corrosion of mild steel in 1.0 M HCl medium by *Artabotrys hexapetalus* leaves extract using weight loss method

Concentration, (%)	Weight loss	Inhibition Effect (%)	Rate of corrossion
2	0.018	71.8	7.5×10^{-4}
4	0.013	79.6	5.4166×10^{-4}
6	0.008	87.5	3.3333×10^{-4}
8	0.007	89.0	2.9166×10^{-4}
10	0.006	96.8	2.5×10^{-4}

TABLE-3

Langmuir adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium by *Artabotrys hexapetalus* leaves extract

Concentration, (%)	Θ	1-Θ	Θ/1-Θ	LogΘ/1-Θ	3+Log Θ/1-Θ	3+LogC
2	0.718	0.282	2.546	0.4058	3.4058	3.301
4	0.796	0.204	3.901	0.5911	3.5911	3.6020
6	0.875	0.125	7.0	0.8450	3.845	3.7781
8	0.89	0.11	8.090	0.9079	3.9079	3.9030
10	0.968	0.032	30.25	1.4807	4.4807	4.000

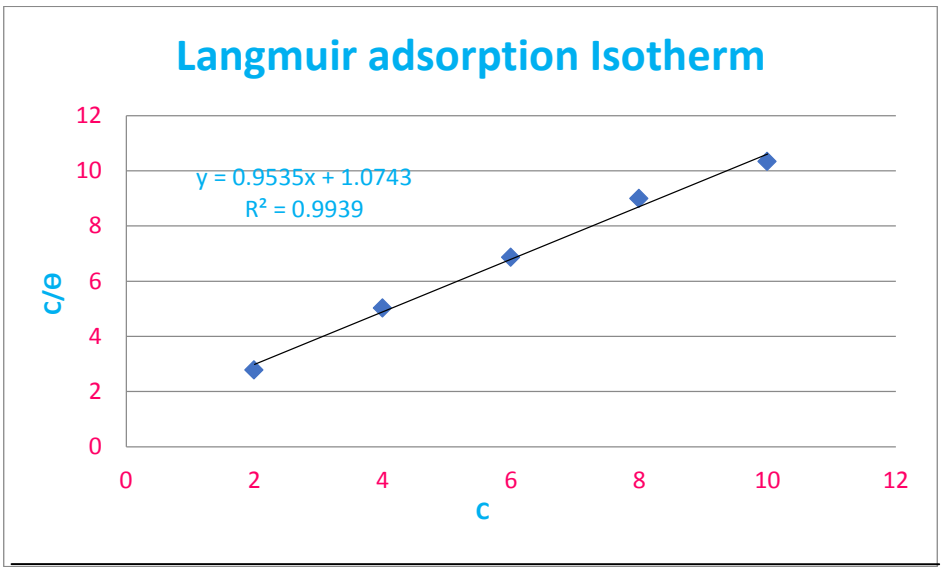

Figure-26 : Langmuir adsorption isotherm for the inhibition of corrosion mild steel in 1.0 M HCl medium using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = 1.074

Kads = 0.9310

ΔG^0ads = -9.9415

Slope = 0.953

R^2 = 0.993

1/y = 1.0493

TABLE-4

Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium by *Artabotrys hexapetalus* leaves extract

Concentration (%)	**Log C**	**2+Log C**	Θ
2	0.3010	2.301	0.718
4	0.6020	2.602	0.796
6	0.7781	2.778	0.875
8	0.9030	2.903	0.89
10	1.00	3.00	0.968

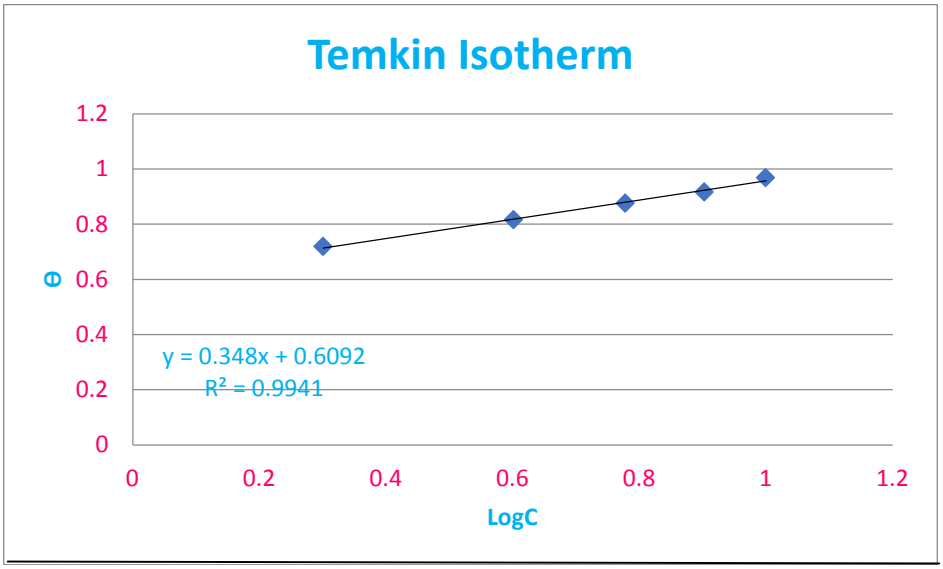

Figure -27: Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = 0.609

Kads = 56.2211

ΔG^{0}_{ads} = -20.2736

Slope = 0.609

R^2 = 0.994

1/y = 2.8735

A = -3.3002

TABLE-5

Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium by *Artabotrys hexapetalus* leaves extract

Ɵ	**Concentration (%)**	**Ɵ/C**	**Log Ɵ/C**	**4+LogƟ/C**	**1-Ɵ**	**Log (1-Ɵ)**	**4+Log(1-Ɵ)**
0.718	2	0.359	-0.4449	3.5551	0.282	-0.5497	3.4503
0.796	4	0.199	-0.7011	3.2989	0.202	-0.6903	3.3097
0.875	6	0.1458	-0.836	3.164	0.125	-0.9030	3.097
0.89	8	0.1112	-0.9538	3.0462	0.11	-0.9586	3.0414
0.968	10	0.0968	-1.0141	2.9859	0.032	-1.4948	2.5052

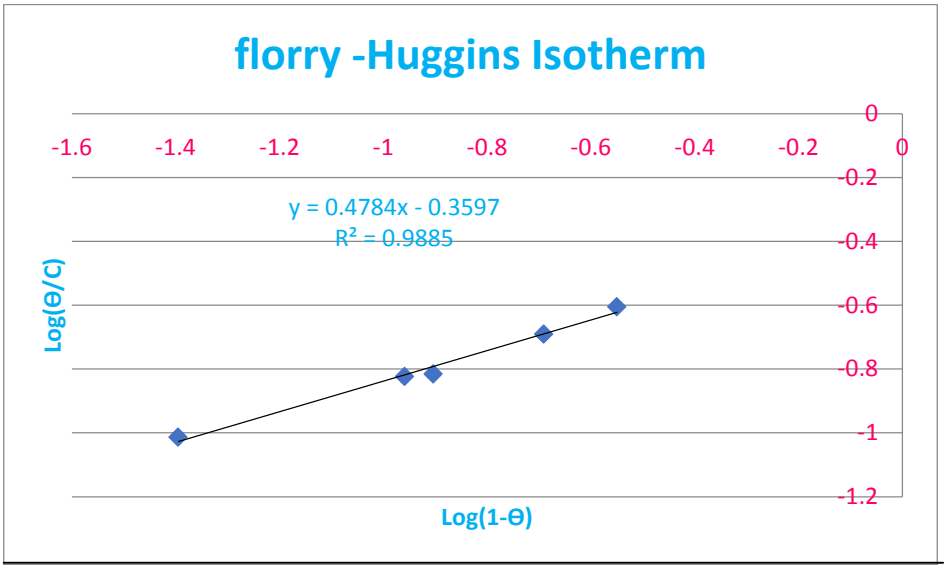

Figure -28: Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = -0.359

Kads = 0.4375

ΔG^{0}_{ads} = -8.0369

Slope = -0.359

R^2 = 0.988

1/y = 2.0920

TABLE – 6

El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl medium by *Artabotrys hexapetalus* leaves extracts

Concentration (%)	2+Log C	Θ	1-Θ	Θ/1-Θ	2+Log (Θ/1-Θ)
2	2.301	0.718	0.282	2.5460	4.546
4	2.602	0.796	0.204	3.9019	5.9019
6	2.778	0.875	0.125	7.0	9.0
8	2.903	0.89	0.11	8.0909	10.0909
10	3.00	0.968	0.032	30.25	32.25

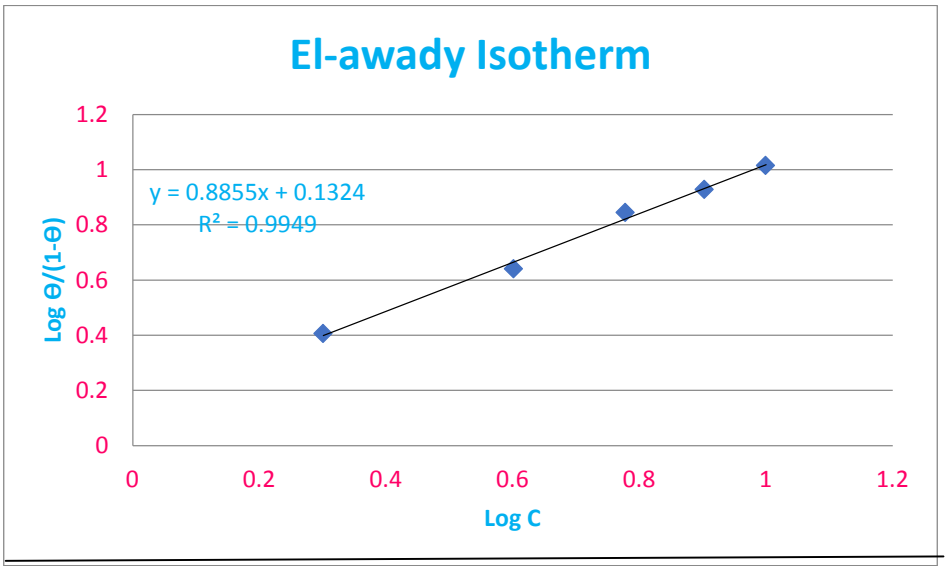

Figure 29: El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M HCl using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = 0.132

Kads = 1.4096

ΔG^0_{ads} = -10.9864

Slope = 0.885

R^2 = 0.994

1/y = 1.1299

TABLE – 7

Frumkin adsorption isotherm for the inhibition of mild steel in 1.0 M HCl medium by *Artabotrys hexapetalus* leaves extract

Concentration (%)	**Θ**	**(1-Θ) C**	**LogΘ/(1-Θ)C**
2	0.718	0.564	0.1048
4	0.796	0.816	-0.0108
6	0.875	0.750	0.0669
8	0.89	0.88	4.8800
10	0.968	0.320	0.4807

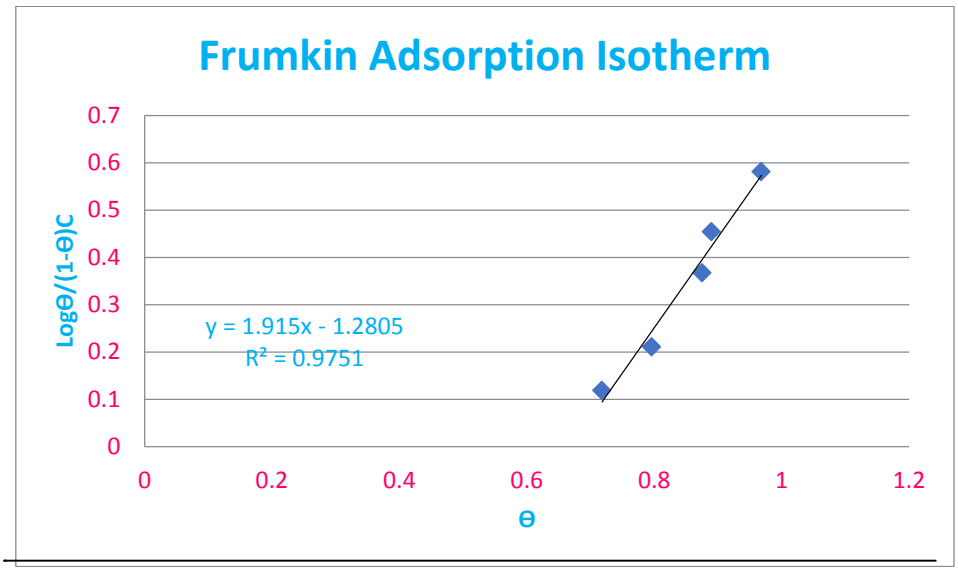

Figure 30: Frumkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0M HCl using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = -1.280

Kads = -0.6620

ΔG^{0}_{ads} = -9.0829

Slope = -1.280

R^2 = 0.975

1/y = 0.5221

A = 0.9575

TABLE – 8

Adsorption isotherm parameters for the inhibition of the corrosion of mild steel in 1.0M HCl by *Artabotrys hexapetalus* leave extract

Isotherm	$-\Delta G^0_{ads}$	Slope	R^2	A	1/y
Langmuir Isotherm	-9.9415	0.953	0.953	-	1.0493
Temkin Isotherm	-20.2730	0.348	0.994	-3.3089	2.8735
Florry-Huggins Isotherm	-8.0369	0.478	0.998	-	2.0920
El-awady Isotherm	-10.9864	0.885	0.994	-	1.1299
Frumkin Isotherm	-9.0829	1.915	0.925	0.9575	0.5221

The R^2 value shows that **Temkin, Florry-Huggins & El-awady** are the best fit isotherms.

TABLE – 9

Corrosion parameters obtained from polarization curves for mild steel in 1.0 M HCl medium in the presence and absence of inhibitor

SYSTEM	[Inhibitor], (%)	I corr., mV	-E corr., mV	ba, mV dec^{-1}	bc, mV dec^{-1}	Inhibition Efficiency (%)
Blank	-	779.758	-491.966	90.836	180.905	-
Artabotrys hexapetalus leaves extract	2	587.581	-484.131	99.285	314.412	24.645
	6	329.168	-452.508	83.791	195.336	57.7858
	10	116.663	-451.192	61.901	172.752	85.0385

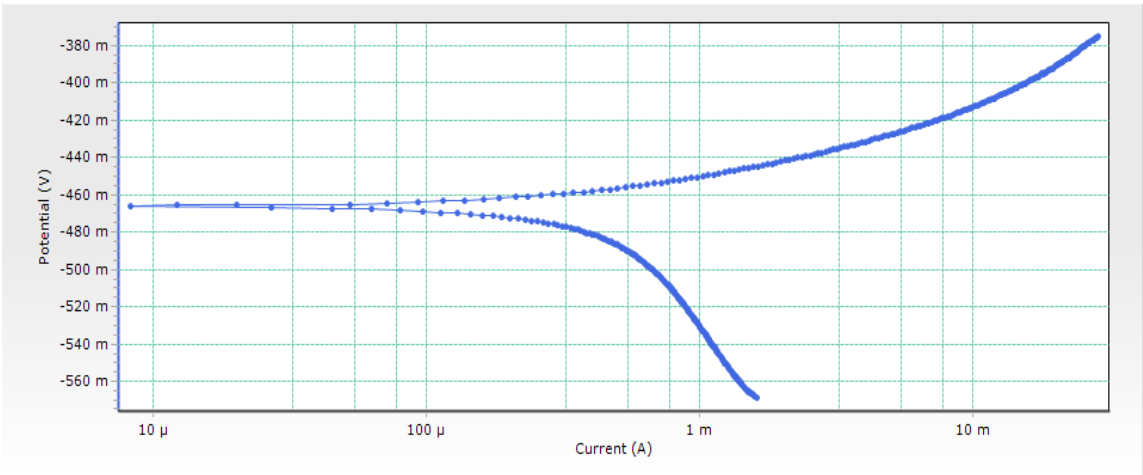

Figure -31: Potentiodynamic polarization curve for mild steel in 1.0 M HCl

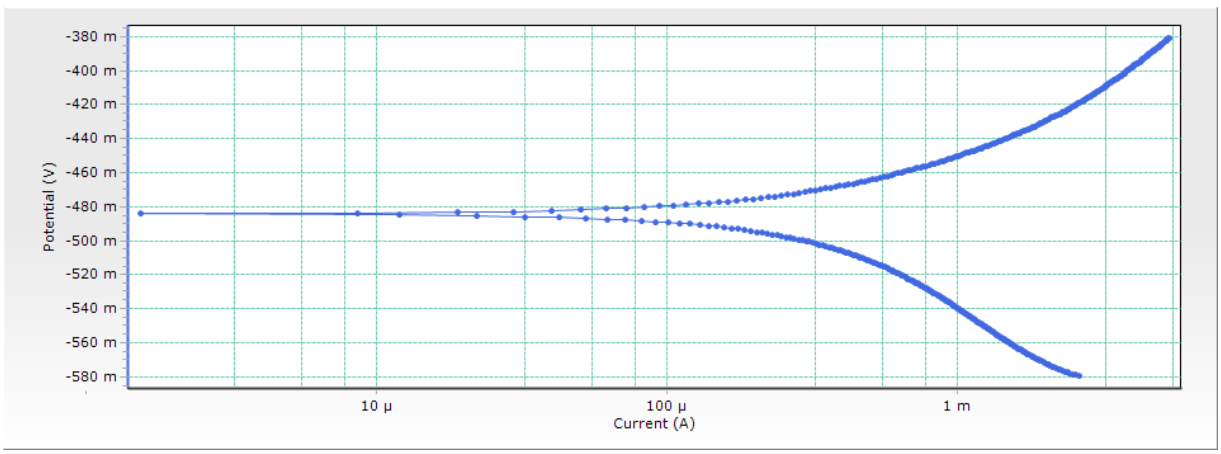

Figure-32: Potentiodynamic polarisation curve for mild steel in 1.0 M HCl solution in the presence of 2 % of *Artabotrys hexapetalus* leaves extract

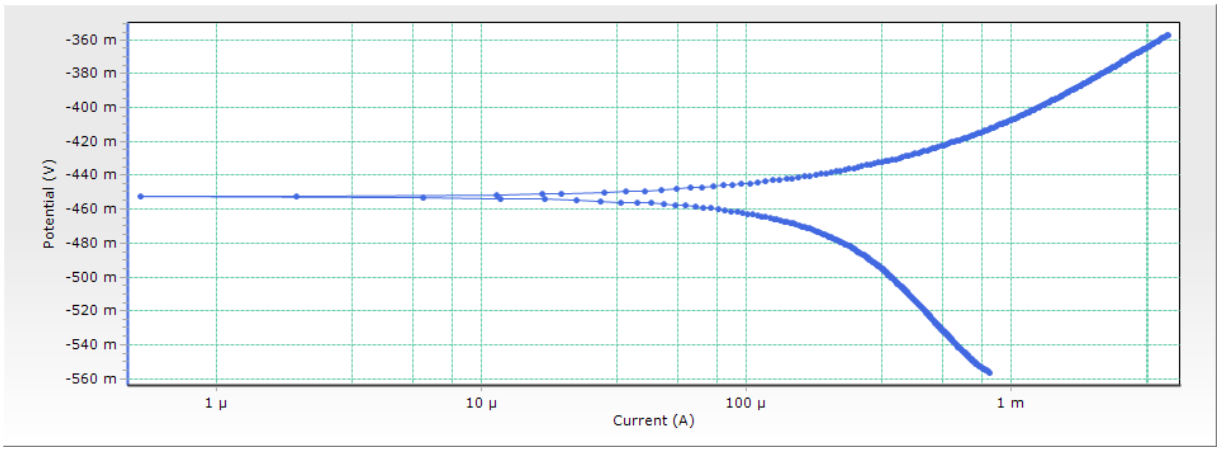

Figure-33: Potentiodynamic polarisation curve for mild steel in 1.0 M HCl solution in the presence of 6 % of *Artabotrys hexapetalus* leaves extract

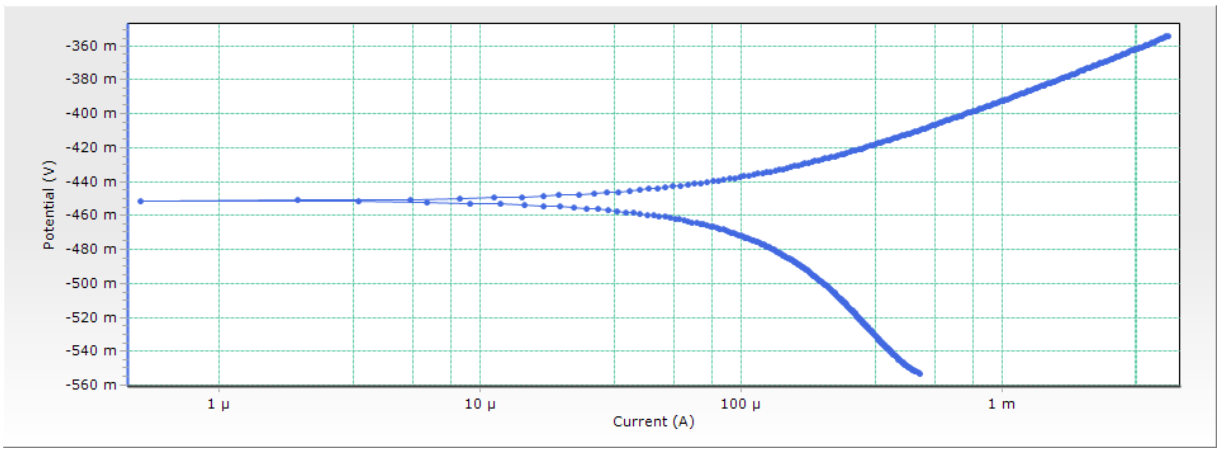

Figure-34: Potentiodynamic polarisation curve for mild steel in 1.0 M HCl solution in the presence of 10 % of *Artabotrys hexapetalus* leaves extract

TABLE – 10

Corrosion parameters obtained from impedance curve for mild steel in the presence and absence of inhibitor in 1.0 M HCl medium

[Inhibitor], (%)	**R_t , Ohm.cm^2**	**C_{dl}, F/cm^2**	**Inhibition Efficiency (%)**
Blank	66	2.4955	-
2	88	1.8716	25
6	144	1.1437	54.16
10	140	0.2764	52.85

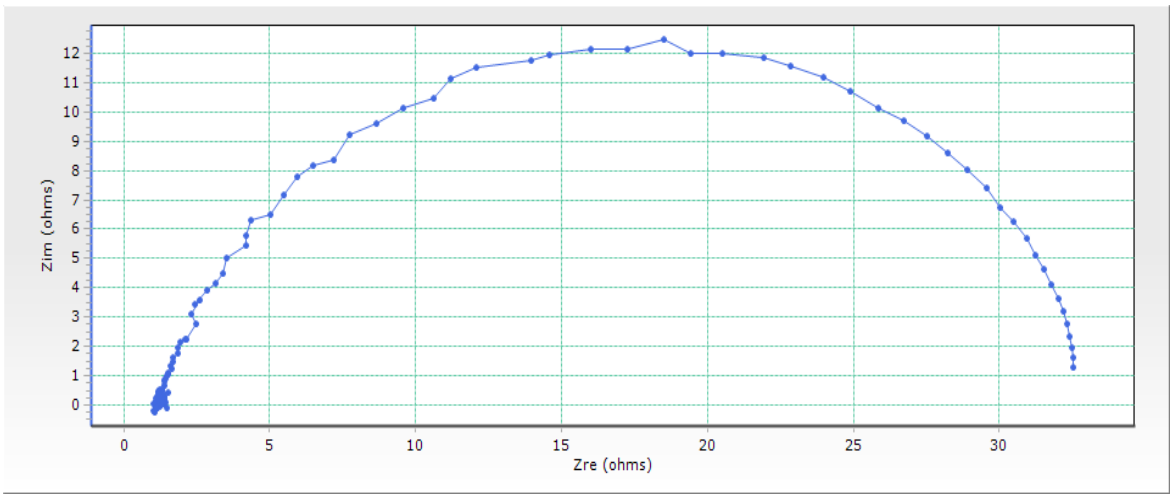

Figure -35: Impedance diagram for mild steel in 1.0 M HCl

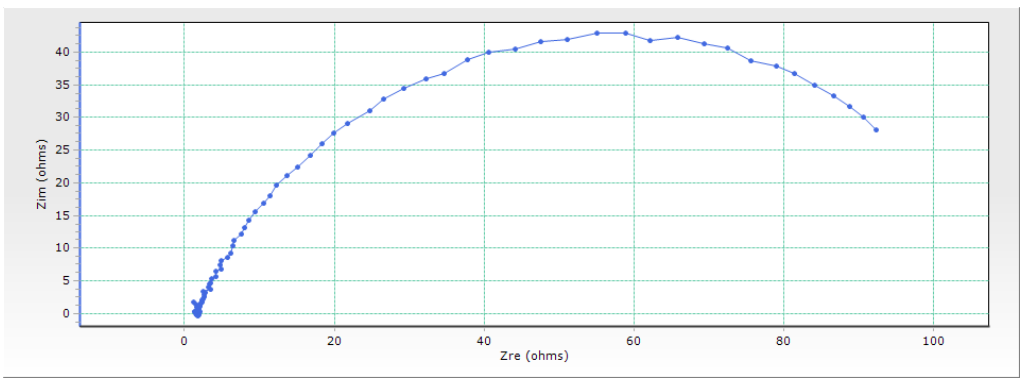

Figure -36: Impedance diagram for mild steel in 1.0 M HCl solution in the presence of 2% concentration of *Artabotrys hexapetalus* leaves extract

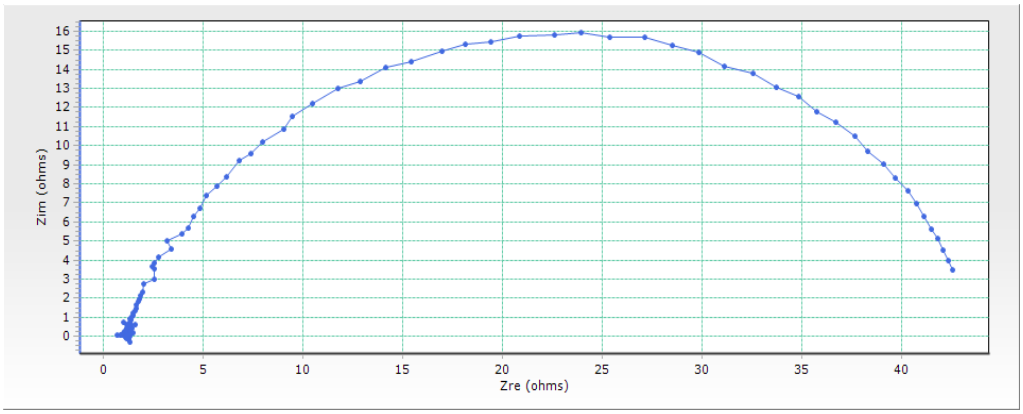

Figure -37: Impedance diagram for mild steel in 1.0 M HCl solution in the presence of

6 % concentration of *Artabotrys hexapetalus* leaves extract

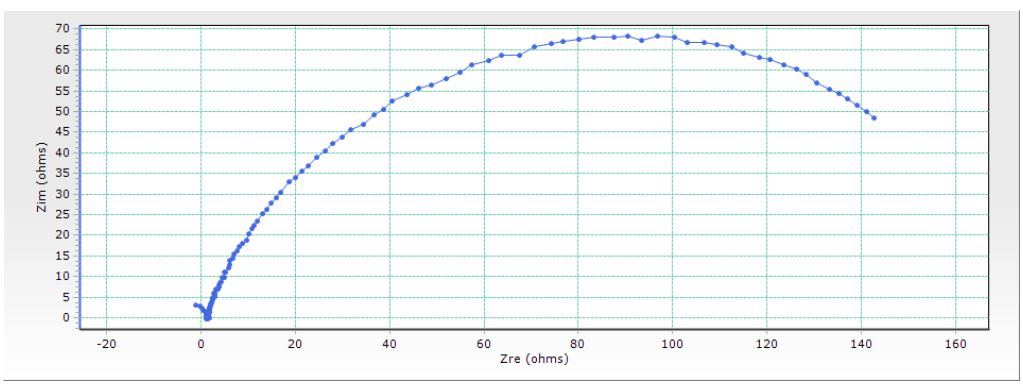

Figure -38: Impedance diagram for mild steel in 1.0 M HCl solution in the presence of 10% of *Artabotrys hexapetalus* leaves extract

TABLE-11

Comparison of inhibition efficiency measured by Weight loss, Polarization method and Impedance method

[Inhibitor], (%)	Inhibition efficiency		
	Weight loss studies	**Polarization Studies**	**Impedance Studies**
Blank	-	-	-
2	25.8	24.6457	25
6	55.3	57.7858	54.16
10	82.8	85.0385	88.9

CHAPTER-V

SUMMARY AND CONCLUSION

The inhibitive influence of leaves of *Artabotrys hexapetalus* on the corrosion of mild steel in 1.0 M HCl medium was studied by weight loss method, polarization and impedance measurements. The corrosion is decreased with increase in the addition of *Artabotrys hexapetalus* leaves extract probably due to the progressive adsorption of the inhibitor on the metal surface. The maximum inhibition efficiency was found to be 96.8%.

- The corrosion of mild steel in 1.0 M HCl solution is inhibited by the addition of leaves extract of *Artabotrys hexapetalus*.
- The percentage of inhibition efficiency increases with increase of the inhibitor concentration.
- The corrosion of mild steel inhibited by leaves extract of *Artabotrys hexapetalus* is attributed to the adsorption of phytochemical components present in the inhibitor onto the mild steel surface.
- The values obtained from the weight loss technique for the studied inhibitor fit well into the Temkin & El-awady adsorption isotherm. The values of free energy for the adsorption process indicate that the adsorption of the inhibitor on the mild steel surface occurs spontaneously.
- The leaves of *Artabotrys hexapetalus* prevent the corrosion of mild steel due to the presence of phytochemical components shifting the corrosion into the noble.
- The polarization and impedance study also shows an agreement with inhibitor efficiency obtained from weight loss studies.
- The results obtained suggest that the *Artabotrys hexapetalus* leaves extract is a good corrosion inhibitor for mild steel in 1.0 M HCl medium and it can be preferentially useto replace toxic and non-biodegradable inhibitor.

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Post Graduate Project – 10

Synthesis, Characterization And Biological Activity Of 2-Methoxy-4-{(Z)-[(4-Methoxyphenyl)Imino]Methyl}Phenol

Name of the Guide : Dr. B. Arifa Farzana
Name of the Candidate : Z. Sulaika

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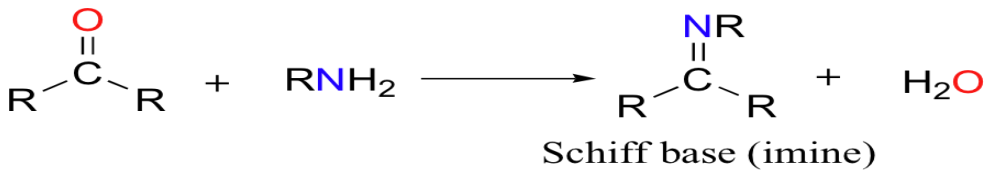
SCHIFF BASE

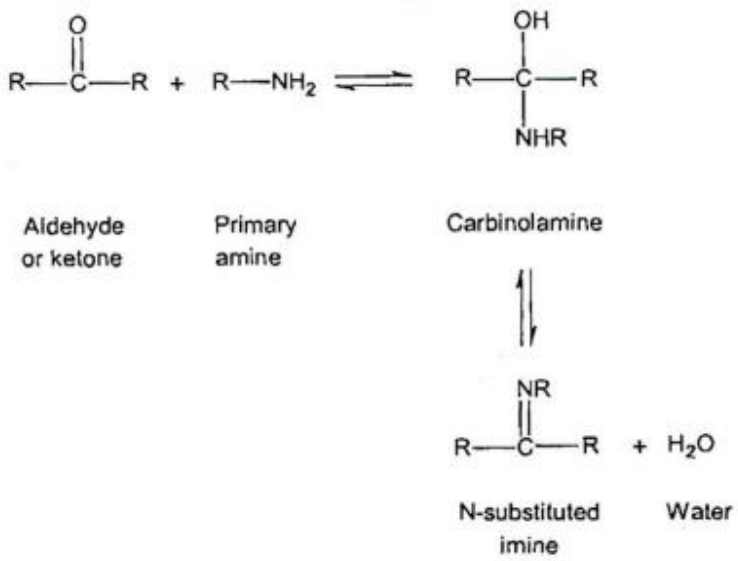
A Schiff base is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by C=N-R group. It is usually formed by condensation of an aldehyde or ketone with a primary amine according to the following scheme



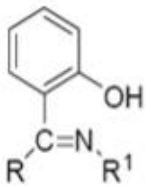
Schiff base (imine)

Where R may be an alkyl or an aryl group. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those which contains alkyl substituents are relatievely unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable [1,2] while those aromatic aldehydes having effective conjugation are more stable [3-6].

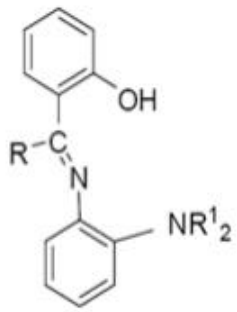
The formation of a Schiff base from an aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating.



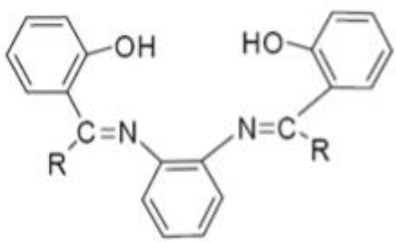
Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerisable, while those of aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehyde. Schiff bases are generally bidentate (1), tridentate (2), tetradentate (3) or polydentate (4) ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion.



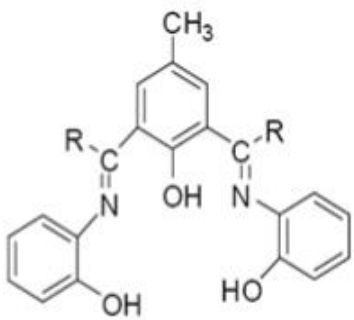
Bidentate (**1**)



Tridentate (**2**)



Tetradentate (**3**)



Pentadentate (**4**)

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, eg., biological, inorganic and analytical chemistry [3,4]. Applications of many new analytical devices require the presence of organic reagents as essential compounds of the measuring system.

Transition metal complexes with Schiff bases have expanded enormously and embraced wide and diversified subjects comprising vast areas of organometallic compounds and various aspects of biocoordination chemistry [5]. The design and synthesis of symmetrical Schiff bases derived from the 1:2 step wise condensation of carbonyl compounds, with alkyl or aryl diamines and a wide range of aldehyde or ketone functionalities, as well as their metal (II) complexes have 3 been of interest due to their preparative accessibility, structural variability and tunable electronic properties allowing to carry out systematic reactivity studies

based ancillary ligand modifications. In recent years much effort has been put in synthesis and characterization of mono- and bi-nuclear transition metal complexes [6].

Schiff bases are used in optical and electrochemical sensors, as well as in various chromatographic methods to enable detection of enhanced selectivity and sensitivity [7-9]. Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties [10]. Schiff bases are widely applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed utilizing the variation in their spectroscopic characteristics following changes in pH and solvent [11]. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions [12]. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds.

BIOLOGICAL IMPORTANCE OF SCHIFF BASES

Many biologically important Schiff bases have been reported in the literature possessing antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumour and anti HIV activities [13-16]. Another important role of Schiff base structure is in transamination [17]. Transamination reactions are catalysed by a class of enzymes called transaminases. Transaminases are found in mitochondria and cytosal of eukaryotic cells. Schiff base formation 4 is also involved in the chemistry of vision, where the reaction occurs between the aldehyde function of 11-cis-retinal and amino group of the protein (opsin) [18]. The biosynthesis of porphyrin, for which glycine is a precursor, is another important pathway, which involves the intermediate formation of Schiff base

between keto group of one molecule of δ-aminolevulinic acid and ε-amino group of lysine residue of an enzyme.

Schiff base ligands may contain a variety of substituents with different electron-donating or electron-withdrawing groups and therefore may have interesting chemical properties. They have attracted particular interest due to their biological activities [19] eg, acting as radio pharmaceuticals for cancer targeting [20]. They have also been used as model systems for biological macromolecules. Besides the biological activity, solid-state thermochromism and photochromism are an another characteristic of these compounds leading to their application in various areas of materials science such as the control and measurement of radiation intensity, display systems and optical memory devices [21].

Schiff bases derived from the salicylaldehydes with two or more donor atoms are well known as polydentate ligands, coordinating in deprotonated or neutral forms. The ability of metal ions to control the oxidation potentials of organic molecules by complexation has a significant role in biological electron transfer processes, molecular electronics and also in catalysis [22]. Schiff bases are used as corrosion inhibitor e.g. fluorinated Schiff base derived from 3, 4-difluorobenzaldehyde and 4, 4′-benzidine were used as inhibitor in steel.

SCHIFF BASE METAL COMPLEXES

Transition metals are known to form Schiff base complexes and Schiff bases have often been used as chelating ligands in the field of coordination chemistry. Their metal complexes 5 have been of great interest for many years. It is well known that N, O and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [23]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications [24-26]. They serve as models for biologically important species and find applications in biomimetic

catalytic reactions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities.

There are certain metallo-elements without which the normal functioning of living organism is inconceivable. Among these metallo-elements so called, 'metals of life', four members form an island. These are Na, Mg, K and Ca the transition elements are V, Cr, Mn, Fe, Co, Ni, Cu and Zn. These elements are present at trace and ultra trace quantities and play vital roles at the molecular level in a living system. These transition elements are known to form Schiff base complexes. Schiff base metal complexes have been known since the mid nineteenth century [27] and even before the general preparation of the Schiff base ligands themselves.

Schiff base metal complexes have occupied a central place in the development of coordination chemistry after the work of Jorgensen and Werner [28]. Ettlings isolated a dark green crystalline product from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia. Schiff prepared complexes of metal-salicylaldehyde with primary amines [29]. Subsequently, Schiff [30] prepared complexes from the condensates of urea and salicylaldehyde. Delephine prepared complexes [31] by reacting metal acetate, salicylaldehyde and a primary amine in alcohol and demonstrated a 2:1 stoichiometry. However, there was no comprehensive, systematic study until the preparative work of Pfeiffer and associates [32]. Pfeiffer and his coworkers [33] reported a series of complexes derived from Schiff bases of salicylaldehyde and its substituted analogues.

The study of binuclear and polynuclear complexes of transition metal ions has received a growing attention in recent years. It has been an interesting area for chemists, physicists and biologists, since these complexes form the basis of several research fields such as bioinorganic chemistry, magneto chemistry,

material science, catalysis, super conductivity and multi electron redox chemistry etc., [34-35].

The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configurations and structural labiality and are sensitive to the molecular environment. 2-hydroxy Schiff base ligands and their complexes derived from the reaction of derivatives of salicylaldehyde with amines have been extensively studied in great details for their various crystallographic, structural and magnetic features [36-38].

Particularly, a large number of transition metal complexes of Schiff base ligands derived from the condensation of salicylaldehyde and 2-hydroxyl-1-naphthaldehyde with various primary amines became the topic of contemporary research [39,40]. These Schiff base ligands may act as bidentate N,O-, tridentate N,O,O-, N,O,N-, N,O,S-, tetradentate N,N,O,O-, hexa dentate N,N,O,O,S,S- donor ligands [41] etc., which can be designed to yield mononuclear or binuclear complexes or one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) metal-organic frame works [42].

Although several kinds of metal ions are found, metallo proteins with transition metal ions are numerous. The main reason for the preference of transition metal ions over the other 7 metal ions is ultimately due to their unique features such as the flexibility to adopt more than one-coordination geometries and the ability to exist in multiple oxidation states. Natural systems utilize one or both of these features for their feasible biological transformations.

A rational control of the nuclearity of transition metal complexes is important to design systems with the desired properties as some of these applications require the presence of more than one metal centre in the particular complex. Indeed, binuclear complexes may have different reactivity than mononuclear counterparts, thereby enabling transformations inaccessible to single

metal ions [43]. For instance, nucleic acid hydrolysis is postulated to be facilitated by the cooperative action of two metal ions [44].

Schiff base ligands that are able to form binuclear transition metal complexes are useful to study the relation between structures and magnetic exchange interactions [45], and to mimic bimetallic biocides in various proteins and enzymes [46]. The complexes thus play an important role in developing the coordination chemistry related to catalysis, enzymatic reactions, magnetism and bioinorganic modeling studies [47]. In this regard, there is much interest in designing dinucleating ligands and their transition metal complexes.

Metal ions play an important role in living system both in growth and in metabolism. The active sites of the biomolecules [48] are coordination complexes comprising of one or more metal ions. The potential relation and those of synthetic coordination complexes has contributed significantly to the emergence of interdisciplinary field of bioinorganic chemistry. The bioinorganic chemistry [49] forms the molecular basis of all possible interactions between the biological molecules and metal ions which is in turn applied in the field of medicine, biology, 8 environmental sciences, catalysis and technology. So the research activities have been grouped as follows.

1. Study of the metal coordination environment in metallo proteins, nucleic acids, carbohydrates, membranes [50, 51].

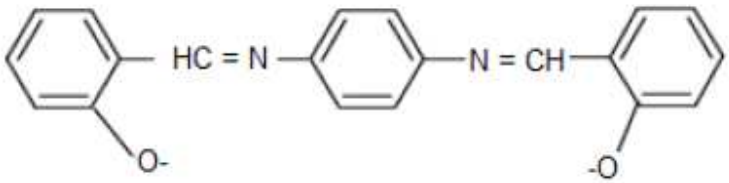
2. Study of the mechanism of reactions occurring at a metal center in enzyme [52].

3. Study of synthetic analog for the active sites in metallo proteins (design, synthesis, structure, spectroscopy and applications like catalytic reactions and metal sequestering from waste water and deposits) [53].

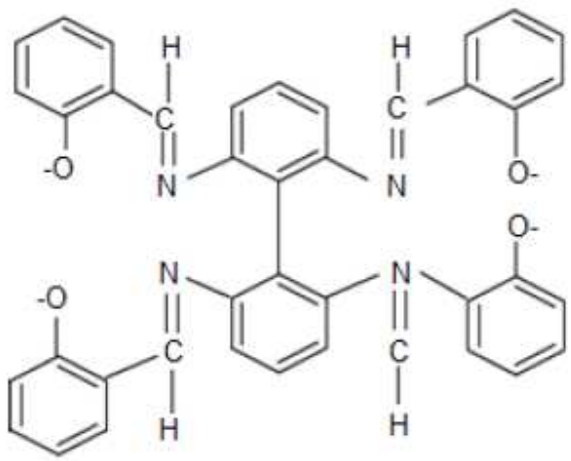
4. Design and study of metal containing drugs to cure or prevent diseases (36 g) (synthesis and mechanism of action)

5. Removal of metal ions and metal compounds from the living system (detoxification) [54]. In all these fields, both the metal and the ligands are of important for the structure, the stability and the process that are regulated and catalysed by the metal species.

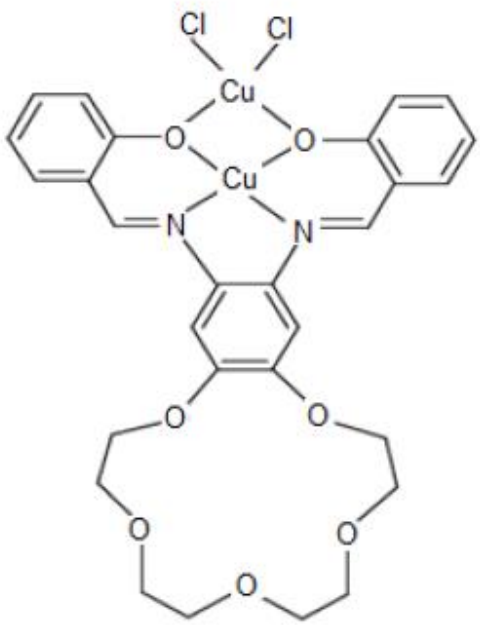
Hasty *et al*., synthesized copper (II), nickel(II) and cobalt(II) complexes having an imino benzene moiety bridging between the two metal ions [78]. The ligand (I) was obtained by the condensation of salicylaldehyde with m- or p-phenylenediamine. The copper and nickel complexes showed antiferromagnetic interaction and cobalt complex showed weak antiferromagnetic exchange interactions.



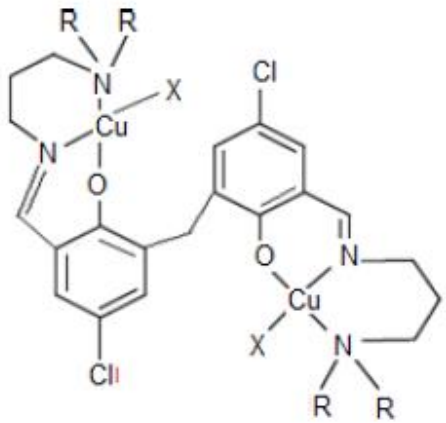
Condensation of 2,2′,6,6′-tetraaminobiphenyl with salicylaldehyde gives a binucleating ligand (II) which was used to prepare Cu_2 (sal-tabp), Ni_2(sal-tabp).H_2O and Co_2(sal-tabp).½ H_2O.



Karaböcek *et al*., synthesised and characterised mono- and di- nuclear copper (II) complexes (III) with a tetradentate Schiff base, 4′,5′-bis(salicylideneimino)benzo-15-crown-5 [(79)]. This ligating system provides an additional active site besides conferring on the copper(II) 15 ion in a square planarN_2O_2 environment which not only mimics the active site in galactose oxidase but also has a role in molecular magnetism.



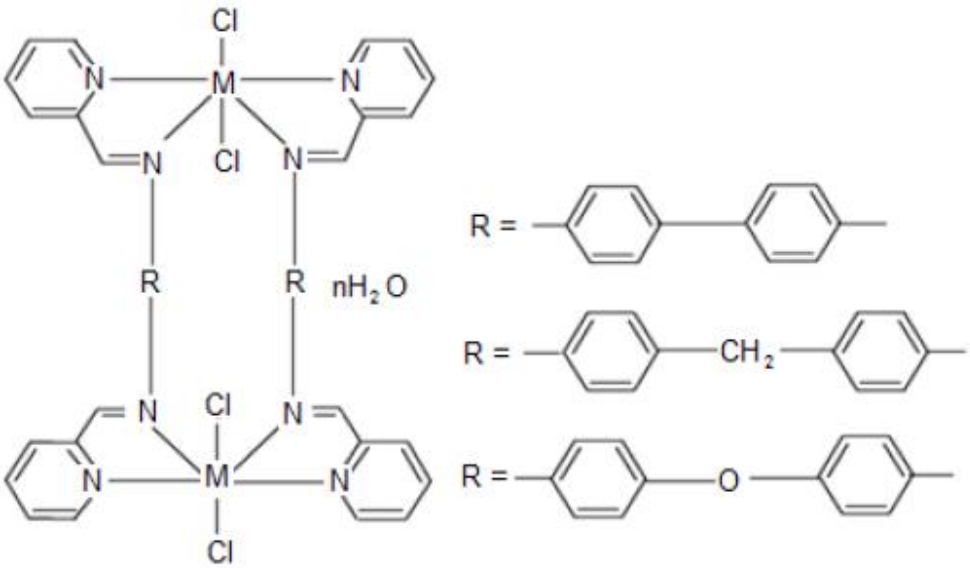
Kanadaswamy *et al.,* synthesised and studied remote donor set of complexes (IV) derived from methylene bridged bis (tridentate) ligands with the aim to study the influence of remote donor set of ligands on complex properties [(80)]. The EPR spectra is similar to mononuclear Cu (II) complex with nuclear spin 3/2. Variable temperature magnetic susceptibility measurements show no exchange interation between Cu (II) centre.



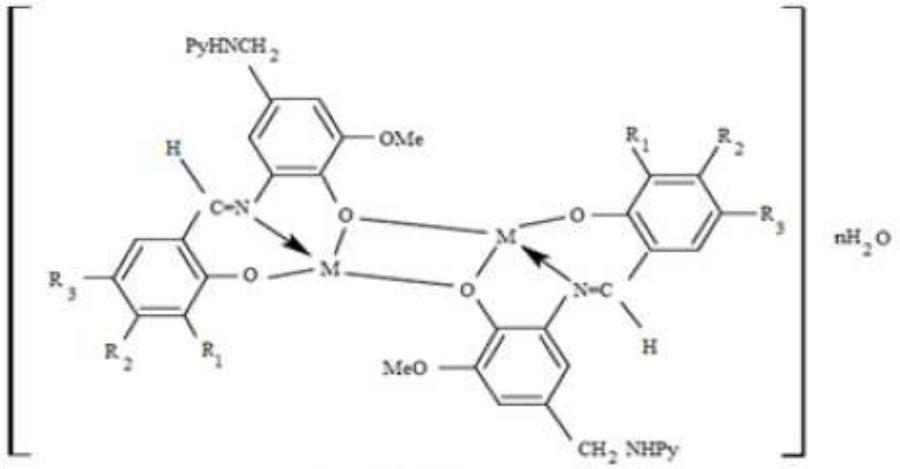
R = C_2H_5, CH_3

X = ClO_4^- , AcO^-, Cl^-, Br^-

Sureshan *et al*., prepared Mn(II) complexes (**V**) of Schiff base obtained by the condensation of pyridine-2-carboxaldehyde and longer aromatic diamines like 4,4′-diaminodiphenyl, 4,4’-diaminodiphenylmethane and 4,4′-diaminodiphenylether respectively [81]. The complexes have been characterized by elemental analysis, spectral, magnetic, electrochemical and FAB mass spectral studies. The complexes have been used as catalyst for the epoxidation of olefin using iodosyl benzene as oxidant.



Tumer *et al*., prepared, characterised and studied the antibacterial activity of binuclear Cu(II), Co(II), Ni(II), VO(II) and Zn(II) complexes (VI) derived from 3-hydroxysalicylaldehyde, 4-hydroxysalicylaldehyde and 5-bromosalicylaldehyde with N-(pyridyl)-2-hydroxy-3-methoxy-aminobenzylamine [82]. Antimicrobial activities of the ligands and their complexes have been tested against the strains of *Bacillus subtilis*, *Micrococcus luteus*, *Saccharamyes cerevisiae* and *Candida albicans*. Thermal properties of the complexes have been studied by thermogravimetric and differential analysis techniques which showed the presence of hydrated or coordinated water molecules.

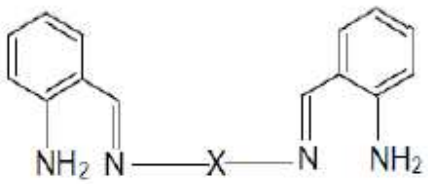


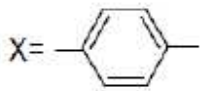
$R_1 = R_2 = H$

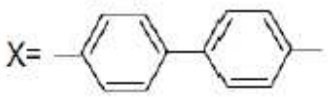
$R_3 = Br$

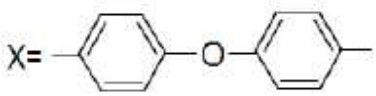
n=0, 1 or 2

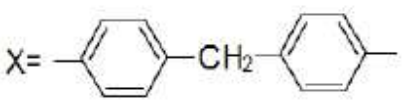
Rajavel *et al.,* synthesised and characterised binuclear Schiff base metal complexes derived from 2-aminobenzaldehyde (VII) [83]. The synthesised complexes were characterised by physicochemical methods. Low temperature magnetic moment shows the presence of weak antiferromagnetic interactions between the metal ions in benzidine type complexes.



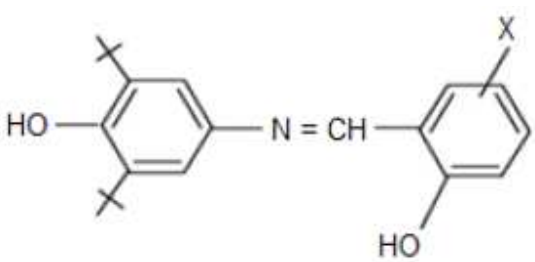






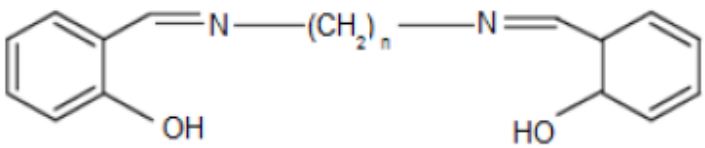


Kasumov synthesised bis-[N-(2,6-di-t-butyl-1-hydroxylphenyl) salicylideneminato] copper(II) complexes bearing OH and CH_3O substituents on the salicylaldehyde moiety (VIII) [84]. Their spectroscopicproperties as well as redox reactivity towards PbO_2 and PPh_3 were examined by EPR and UV spectroscopy.

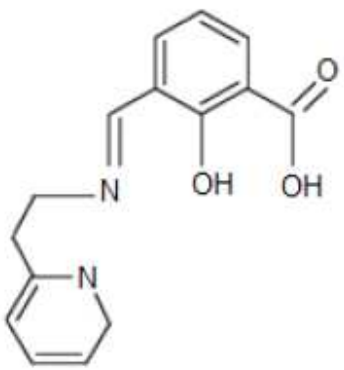


X = H, Cl, Br, NO_2

Nathan *et al.,* have synthesised N,N'-polymethylene-bis(salicylaldiminato) copper(II) complexes with alkyl back bones ranging from two to eight carbons (**IX**) [85]. The complexes are monomeric when the alkyl chain length is relatively short (two, three and four CH_2 groups) but are dimers when the chain length becomes longer (five, six and eight CH_2 groups).

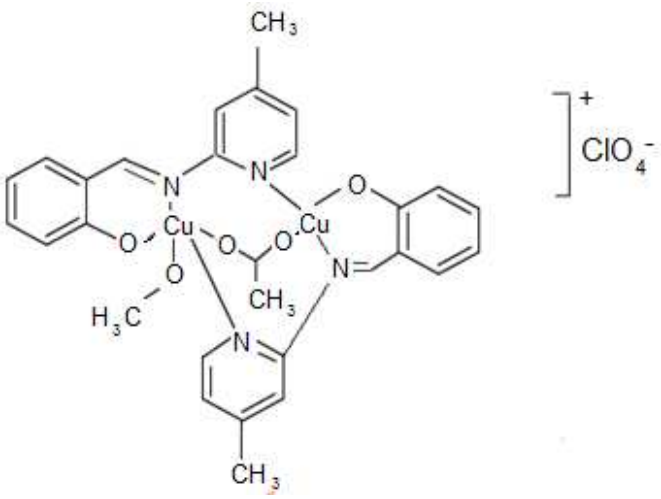


Tuna *et al.,* have reported synthesis of ligand (**X**) derived from 3-formyl-salicylic acid to form the complex 3-[N-2-(pyridylethyl)formimodoyl]salicylic acid [86]. The synthesised ligand and its metal complexes were characterised by elemental analysis, molar conductance, UV, IR, NMR and magnetic studies. The interactions between two metal centers were proved by magnetic studies.



Srinivasan *et al*., synthesised a dicopper complex (XI) of a Schiff base, 2-[(4-methyl-pyridin-2ylimino)-methyl]-phenol with a bridging acetato ligand characterised by single crystal XRD, EPR, magnetic susceptibility, IR, UV-Vis, CV and elemental analysis. One of the copper atoms in the binuclear complex adopts a square-pyramidal geometry, while the other copper assumes a square planar geometry [87]. EPR spectrum in frozen solution confirms the interaction

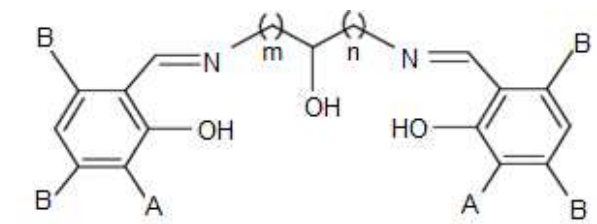
between the two copper ions. The molar conductance for the complex indicates that the complex is a 1:1 electrolyte.



Shu-Fei Huang *et al*., synthesised, characterised and studied the magnetic properties of μ-alkoxo-μ-pyrazolato bridged dicopper(II) complexes (XII) [88]. The variable-temperature magnetic susceptibitity measurements revealed that the metal centers in both the compounds are anti ferromagnetically coupled with J = -200 cm-1and J = -175 cm-1 for the complexes. The magnetic behaviours have been explained on the basis of two opposing factors, complementarity and counter complimentarity of magnetic orbitals.

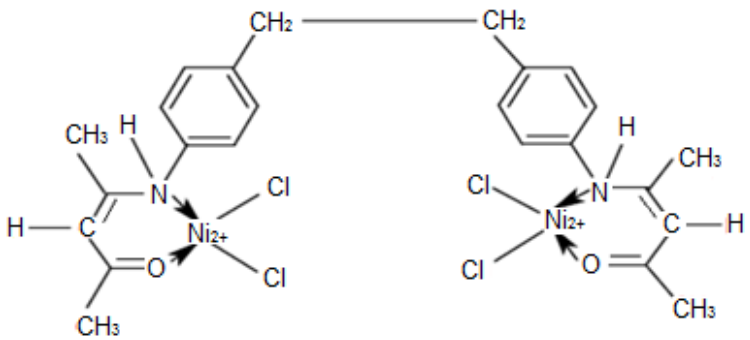
[Cu_2II (L1-F) (μ-prz)] and [Cu_2II (L1-2OMe) (μ-prz)] 0.5CH3CN (prz = pyrazolato;

- H2L1- F = 1,3-bis-(3-fluorosalicylideneamino)-2-propanol;
- H_2L1-2OMe = 1, 3-bis-(4,6-dimethoxysalicylideneamino)-2-proponal.



A = H, F B = H, OMe m = n = 1, 2

Ghames prepared, the structural and electrochemical studies of Co(II), Ni(II), Cu(II) and Cd (II) complexes with a new symmetrical N_2O_2 Schiff base and crystal structure of the ligand 1,2-di[4-(2-imino-4-oxopentane)phenyl]ethane was also studied [89]. The coordination occurs through the N_2O_2 system.

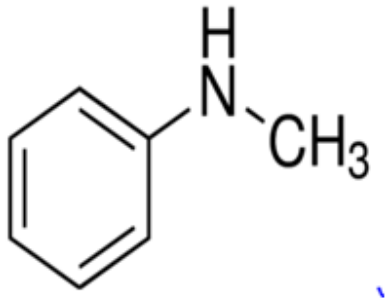


The binuclear nickel (II) complex (XIII) in which each Ni (II) ion presents a square planar arrangement and the Schiff base acts as a symmetrical tetradentate ligand through the keto- amino tautomer.

Sallam prepared binuclear copper, nickel and cobalt complexes (XIV) of the Schiff bases obtained by the condensation of glycylglycine with acetyl acetone, benzoyl acetone, dibenzoylmethane and thenoyltrifluoroacetone. The complexes were characterised by elemental analysis, conductivity measurements, magnetic moments, IR, UV-Visible spectra, EPR, X-ray diffraction, TGA, DTA and DSC thermal analysis. All the complexes were non-electrolytes with low magnetic moments that indicate spin-spin or antiferro magnetic exchange interactions. Spectral properties support square planar and square pyramidal or trigonal bipyramidal structure provided by the N_2O_2 chromophores. A mechanism for thermal decomposition is proposed for complexes.

N-Methyl aniline

Structure



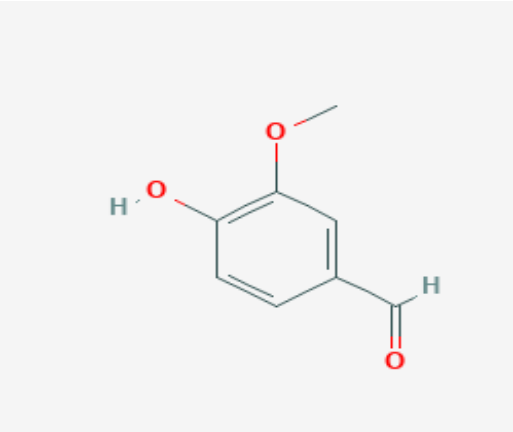
Molecular weight	107.156 g/mol
Solubility	Soluble in ethanol, ether and carbon tetra chloride
Boiling point	385.3 ° F at 760 mm Hg (NTP, 1992)
Melting point	-57°C (−71 °F; 216 K)
Density	0.99 g/ml
Appearance	Colorless to light viscous liquid with a characteristic odor. Turns brown on exposure to air
Stability	Turns reddish brown on standing

Uses

It is used as a latent and coupling solvent and is also used as an intermediate for dyes, agrochemicals and other organic products manufacturing. NMA is toxic and exposure can cause damage to the central nervous system and can also cause liver and kidney failure.

VANILLIN

Structure



Molecular weight	117.148 g/mol
Solubility	Cold ether, diethyl ether, acetone and hot benzene, and petroleum ether, chloroform, carbon disulfide, glacial acetic acid, pyridine, oils and in aqueous solutions of alkali hydroxides.
Boiling point	285°C
Melting point	81.83°C
Appearance	White crystals
Density	1.056 at 68°F

Uses

Vanillin is a vanilla extract alternative made from wood pulp. It is commonly used to reduce production costs. And, unlike real vanilla extract which is produced from real vanilla beans, vanillin is synthetic and may be produced using petrochemicals and byproducts from the paper industry.

The largest use of Vanillin is as a food flavoring, normally is desserts and sweet foods. Ice cream and chocolate industries use about 75% of the market for vanillin. It is used to increase the milk flavor in products such as cakes, chocolate, biscuits, and instant noodles.

Vanillin normally comes in two forms: liquid (refer to the picture above) and a powder (lower right hand corner). The both forms can be used to make vanillin sugar (refer to picture below), which is a popular substitute for vanilla and sugar. Vanillin is also used in perfumes, to mask unpleasant odors, or tastes in medicine. It is also used in cleaning products, tobacco, and toothpaste.

PRINCIPLES OF SPECTROSCOPY:

All organic compounds interact with electromagnetic radiation, that is, they absorb energy. When a molecule absorbs energy, a transformation occurs that may be either temporary or permanent. Lower energy radiation may cause the promotion of electrons to higher energy levels or bond cleavage.

Whether the transformation involves molecular rotation, bond vibration or electronic transition, the molecule absorbs only the wavelength of radiation with exactly the energy necessary for the transition.

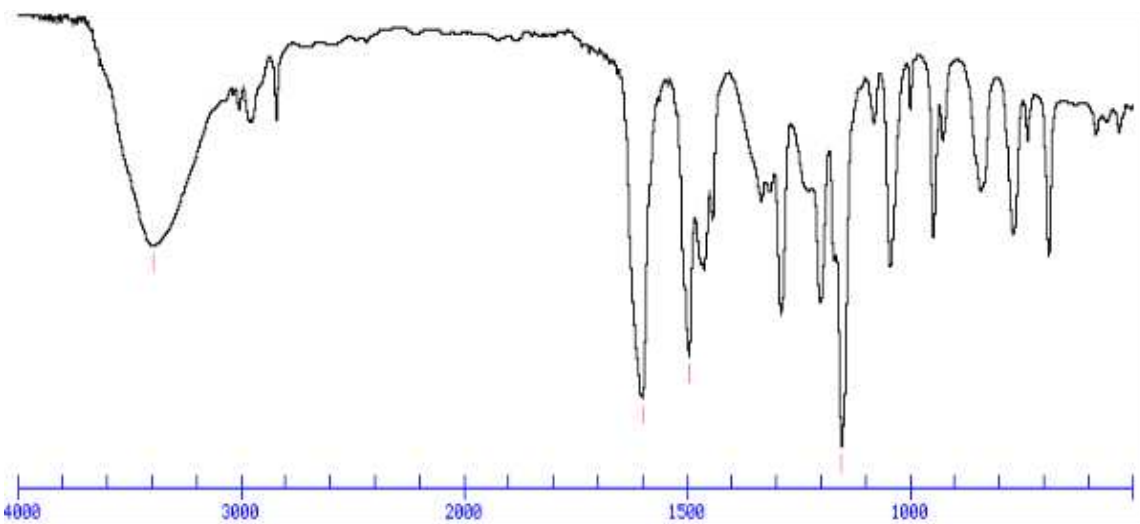
The absorption of wavelengths of radiation is selective for a particular transition which depends on the structure of the molecule. By measuring the absorption spectra of known compounds, we can correlate the wavelengths of energy absorbed with characteristic structural features. This information is then used to determine the structure of unknown compounds.

Infrared spectroscopy:

Theory:

Infrared spectroscopy is an absorption method in the wavelength region of 1 to 100 μm in that extends the region of the visible light to longer wavelengths and smaller frequencies/energies. The energy of infrared light is no longer sufficient to induce transitions of valence electrons. Instead, infrared radiation excites vibration and rotational motions in molecules.

However, infrared spectra are usually presented by a plot of the percentage of transmission is the wave number in cm^{-1} (as opposed to a plot of absorbance VS the wavelength in nm in UV/VIS spectroscopy). A typical IR spectrum is therefore recorded from about 4 000 to 10 000 cm^{-1}(upper limit) to about 100-800 cm^{-1} (lower limit).



An Example of IR Spectrum

Because each inter atomic bond may vibrate in several different motions (stretching or bending), individual bonds may absorb at more than one IR

frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar types of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibrations do not cause absorption of IR radiation. For example, neither of the carbon-carbon bonds in ethane or ethylene absorbs IR radiation.

Regions of the IR Spectrum:

Over time organic chemists have recorded and catalogued the types and locations of IR absorptions produced by a wide variety of chemical bonds in various chemical environments. These data can be quickly referenced through tables of IR absorption ranges and compared to the spectrum under consideration. As a general rule, the most important factors determining where a chemical bond will absorb are the bond order and the types of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore the same or similar functional groups in different molecules will typically absorb within the same, specific frequency ranges. Consequently tables of IR absorptions are arranged by functional group.

In IR absorption tables, signal intensities (height) are usually denoted by the following abbreviations: w = weak, m = medium, s = strong, v = variable. A broad signal shape is sometimes indicated by br. occasionally absorption frequency is given as a single approximation denoted with an approximetely rather than a range.

A Table of IR Absorptions:

These trends in absorption can be further summarized into the following categories

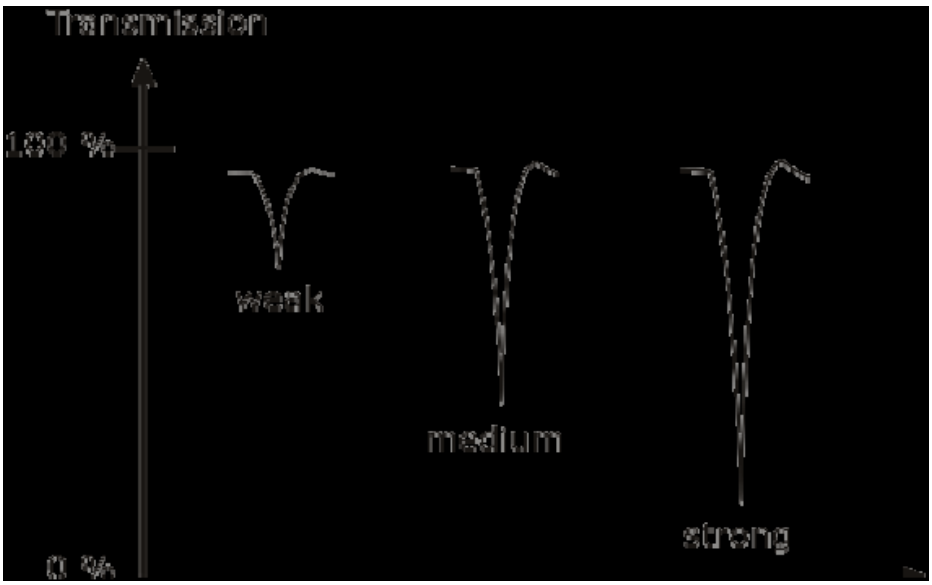
3600 - 2700 cm^{-1}	X-H
2700 - 1900 cm^{-1}	X=Y
1900 - 1500 cm^{-1}	X=Y
1500 - 500 cm^{-1}	X-Y

Upon first inspection, a typical infrared spectrum can be visually divided into two regions. The left half, above 2000 cm^{-1}, usually contains relatively few peaks, but some very diagnostic information can be found here. First, alkane C-H stretching absorptions just below 3000 cm^{-1} demonstrate the presence of saturated carbons, and signals just above 3000 cm^{-1} demonstrate unsaturation. A very broad peak in the region between 3100 and 3600 cm^{-1} indicates the presence of exchangeable protons, typically from alcohol, amine, amide or carboxylic acid groups. The frequencies from 2800 to 2000 cm^{-1} are normally void of other absorptions, so the presence of alkynes or nitrile groups can be easily seen here.

In contrast, the right half of the spectrum, below 2000 cm^{-1}, normally contains many peaks of varying intensities, many of which are not readily identifiable. Two signals which can be seen clearly in this area is the carbonyl group, which is a very strong peak around 1700 cm^{-1}, and the C-O bond with can be one or two strong peaks around 1200 cm^{-1}. This complex lower region is also known as the "fingerprint region" because almost every organic compound produces a unique pattern in this area. Therefore identity can often be confirmed by comparison of this region to a known spectrum.

Classification of IR bands

IR bands can be classified as strong (s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the *y*-axis. A medium band falls to about half of the *y*-axis, and a weak band falls to about one third or less of the *y*-axis.



Infrared active bonds

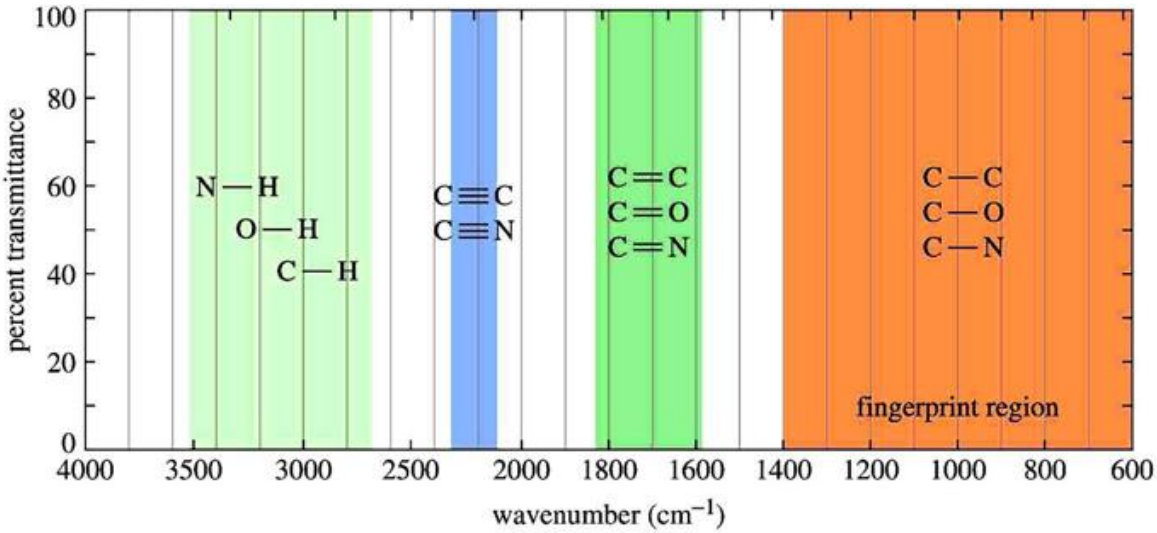
Not all covalent bonds display bands in the IR spectrum. Only polar bonds do so. These are referred to as IR active. The intensity of the bands depends on the magnitude of the dipole moment associated with the bond in question:

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.

IR absorption range

The typical IR absorption range for covalent bonds is 600 - 4000 cm^{-1}. The graph shows the regions of the spectrum where the following types of bonds

normally absorb. For example a sharp band around 2200-2400 cm^{-1} would indicate the possible presence of a C-N or a C-C triple bond.



Nuclear Magnetic Resonance (NMR)

Excitation of the nucleus of atoms through radiofrequency irradiation provides extensive information about molecular structure and atom connectivity.

^{1}H NMR Spectroscopy:

This important and well established application of nuclear magnetic resonance spectroscopy will serve to illustrate some of the novel aspects of this method. To begin with the NMR Spectrometer must be inturn to a specific nucleus, in this case the proton. The nucleus of hydrogen atom (proton) behaves as a spinning bar magnet. Because it posses both electric and magnetic spin. Like any other charged body, the nucleus of a hydrogen atom also generates a magnetic field. The actual procedure for obtaining the spectrum varied but the simplest is referred to as the continuous wave (cw) method.

The number of signals in an NMR spectrum tells the number of sets of equivalent protons in a molecule. The positions of signals in the spectrum help us to know the nature of protons via., aromatic, aliphatic, acetylenic, vinylic adjacent to some electron attracting or electron releasing group etc. shift in the position of

NMR absorptions which arises due to the shielding (or deshielding) of protons by the electrons are called chemical shifts.

For measuring the chemical shift of various protons in a molecule, the signal of tetramethylsilane (TMS) is taken as a reference. This difference in the absorption position of the proton with respect to TMS signal is called chemical shift (δ-value).

TLC:

TLC is a simple, quick and inexpensive procedure to confirm the formation of the product. TLC is also used to analyze the purity of the compound. To prepare the TLC plate, slurry of silica gel prepared by adding chloroform and methanol in the ratio 1:9 to silica powder was uniformly coated on a thin glass plate.

AIM AND SCOPE OF THE WORK

- The aim of this project is to synthesize, characterize and to establish the structure through the IR, ^{1}H NMR, and ^{13}C NMR spectral study of the newly synthesized Schiff base.

- The compounds containing nitrogen and sulphur are present in the ring and chloro group are found to be biologically important and also behave as potential donor. On account of this, compound containing hetero atom such as N-methyl aniline and vanaline are used for synthesis of Schiff base.

- The synthesized compounds are taken and characterized by analytical and spectral methods.

- To analyse antibacterial activity of the synthesised compound.

EXPERIMENTAL METHODS

The melting point was determined in open capillary and was uncorrected. The purity of the compound was checked by TLC on silica gel "G" coated glass plates. IR spectra were recorded in KBr on shimadzu FT-IR 8300 spectrophotometer, ^{1}H NMR spectra on a Bruker DRX-400 MHZ. Many experimental techniques are briefly discussed below:

1. IR spectra were recorded in St. Joseph College, Trichy-20.
2. ^{1}H NMR and ^{13}C NMR spectra were recorded in Alagappa University, Karaikudi.
3. The biological activity has been studied in Department of Biotechnology, Mohamed Sathak College of Arts and Science College, Sholinganallur, Chennai.

ANALYTICAL METHODS:

1. Lassaigne's test:

A small piece of sodium metal is fused in fusion tube and some portions of the sample are added. The tube is heated to red hot and quickly plunged into 5 ml of water. The solution is boiled and filtered. Then this filtrate is divided into two portions and tested. One portion is mixed with few ml of freshly prepared $FeSO_4$ solution and then acidified with dilute sulphuric acid. The appearance of the blue colour indicates the presence of nitrogen in the compound.

2. Dye test for primary amines:

0.1g of the compound was dissolved in 3ml of dilute HCL and cooled in tap water and 1ml sodium nitrite solution was added. Then it is added to β-naphthol and sodium hydroxide solution. A scarlet red was appeared indicating presence of primary amine.

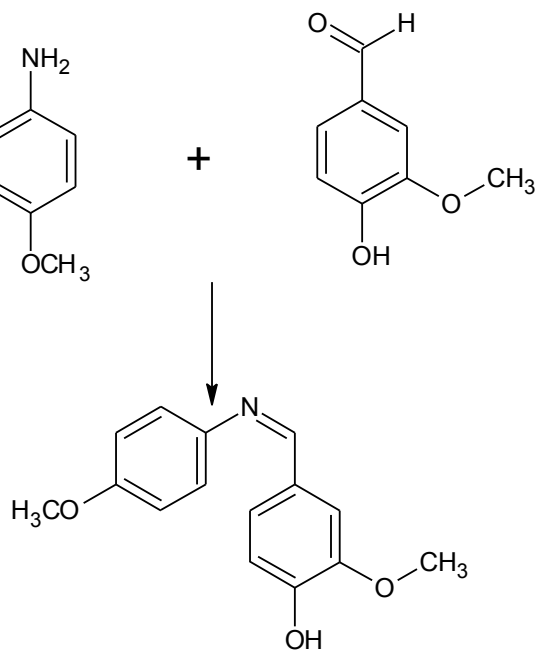
EXPERIMENTAL PROCEDURE:

Synthesis and characterization of (1*E*)-*N*-(1,3-benzothiazol-2-yl)-1-(5-chloropyridin-2-yl)ethan-1-imine

Chemicals Required:

Methyl aniline	(0.01m)	: 1.5 g
Vanillin	(0.01m)	: 1.5 g

Methyl aniline and vanillin are taken in 1:1 ratio. N-methyl aniline and vanillin were dissolved in ethanol and taken in round bottom flask with constant stirring for three hours, using a magnetic stirrer under ice cold condition. Then the yellow solid substance is separated out. It is washed several times with cold distilled water. The crude sample is recrystallized from ethanol. The scheme of the reaction is given below.



2-methoxy-4-{(*Z*)-[(4-methoxyphenyl)imino]methyl}phenol

RESULTS AND DISCUSSION

The compound of 2-methoxy-4-{(*Z*)-[(4-methoxyphenyl)imino]methyl}phenol was prepared from Schiff base.

- The structure of the compound was confirmed by IR, ^{1}H and ^{13}C NMR.

- The physical characterization of the synthesized compound is given in the table-I.

PHYSICAL CHARACTERIZATION

Physical characterization of the compound 2-methoxy-4-{(*Z*)-[(4-methoxyphenyl) imino] methyl}phenol

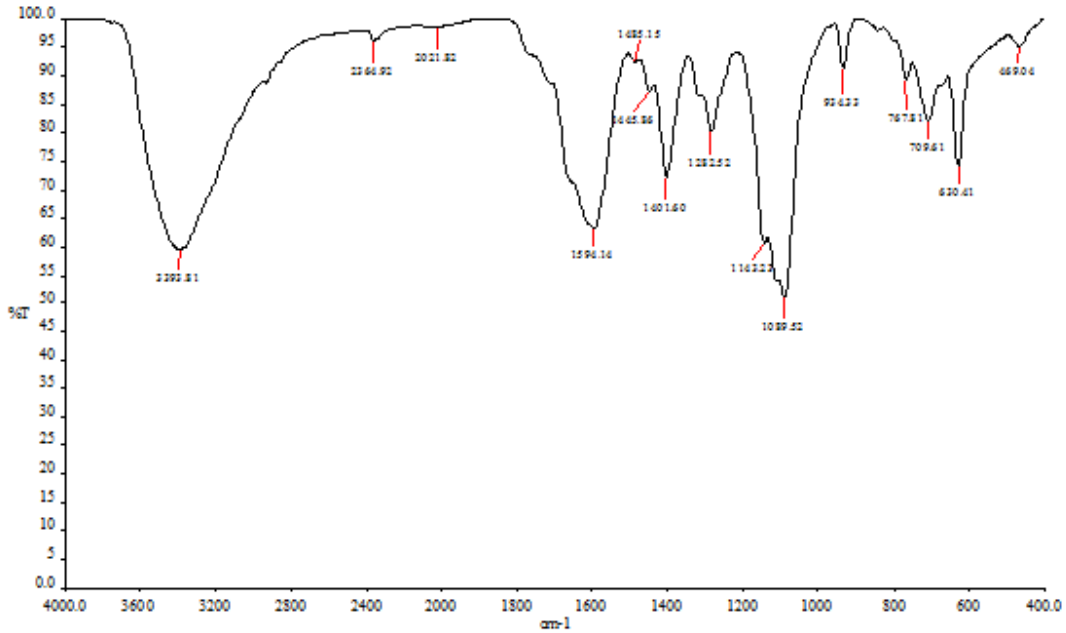
Molecular Formula	**Molecular Weight**	**Melting Point(^{0}C)**	**Elemental analysis (%) Found (calculated)**				**Solubility**
			C	H	**N**	**O**	
$C_{15}H_{15}NO_3$	257.2845		70.02	5.88	5.44	18.6	

IR SPECTRAL DATA

IR spectral data of the compound 2-methoxy-4-{(*Z*)-[(4-methoxyphenyl) imino]methyl}phenol.

Table-II

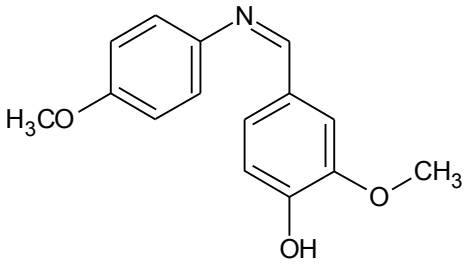
Frequency (cm^{-1})	**Functional group**
3393	O-H
2364	Aromatic C-H
2021	Aliphatic C-H
1282	C-N



IR spectral data of the compound 2methoxy -4-{(z)-[(4) methoxyphenyl)imino methyl } phenol

IR spectral data of the compound 2-methoxy-4-{(z)-[(4)methoxyphenyl)imino methyl } phenol was recorded to find out the functional groups present in the compound.

- The sharp band at 3393 cm^{-1} indicates that the presence of aromatic O-H.
- The medium banded attributed at 1282 cm^{-1} indicates the presence of C-N of benzothiozole ring
- The band at 2364 cm^{-1} shows the presence of aromatic C-H.
- The band at 2021 cm^{-1} indicates that the presence of aliphatic C-H.



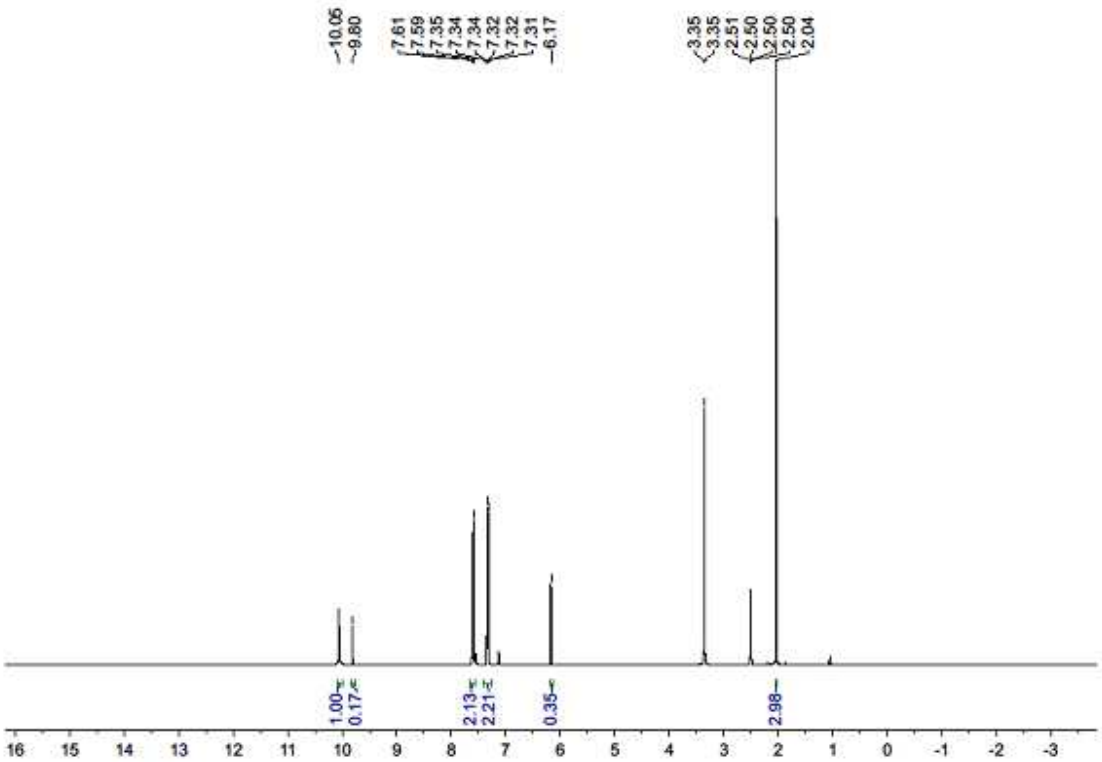
2methoxy-4-{(z)-[(4)methoxyphenyl)iminomethyl}phenol

^{1}H NMR SPECTRAL DATA

^{1}H NMR spectral data of the compound 2methoxy-4-{(z)-[(4)-methoxyphenyl) iminomethyl}phenol

TABLE-III

Chemical shift (ppm)	Assignment
3.35	Methoxy proton
6.17-7.61	Aromatic protons
9.30	Methine proton



^{1}H NMR spectral data of the compound 2-methoxy-4-{(z)-[(4)methoxyphenyl)iminomethyl}phenol

^{1}H NMR spectral data of the compound 2-methoxy-4-{(z)-[(4)methoxyphenyl)iminomethyl}phenol.

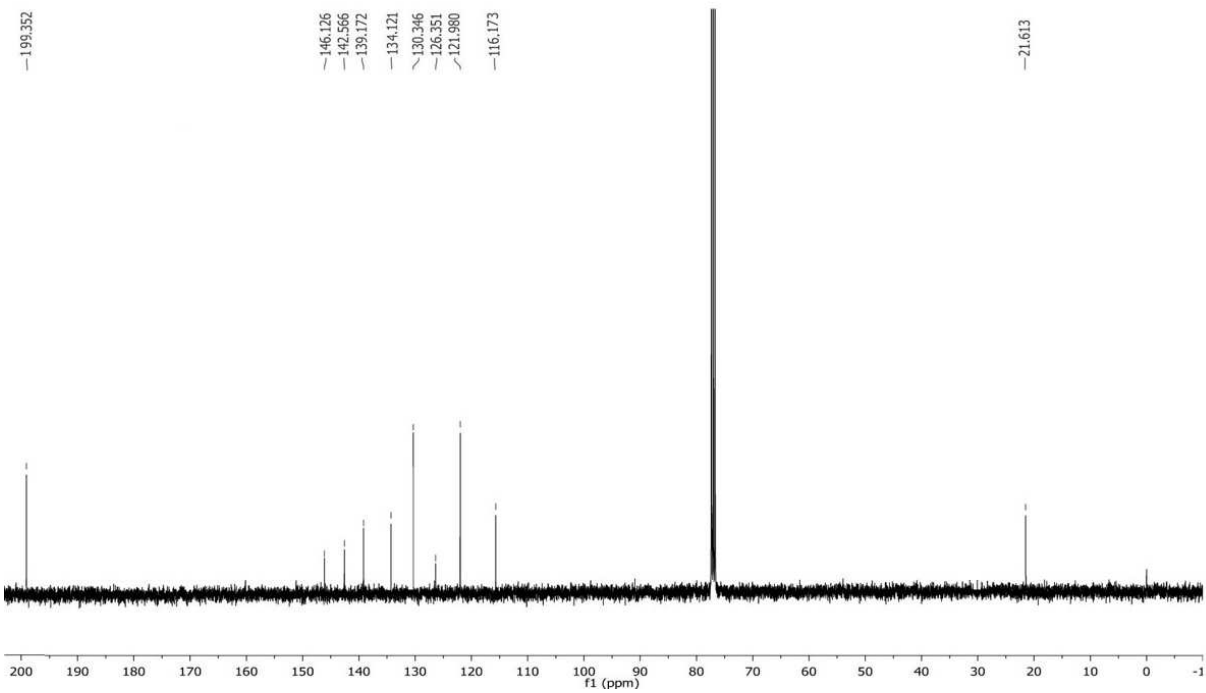
- The aromatic proton shows chemical shits value at 6.17-7.61 δ.
- The methoxy proton shows chemical shifts value at 3.35 δ.
- The methane proton shows chemical shifts value at 9.30.

^{13}C-NMR SPECTRAL DATA

^{13}C-NMR spectral data of the compound 2-methoxy-4-{(*Z*)-[(4-methoxyphenyl) imino]methyl}phenol.

TABLE-IV

Chemical shift (ppm)	Assignment
116.17	Methyl carbon
126.3-139.1	Aromatic carbons
146.12	Methoxy carbon
199.35	imine carbon



^{13}C-NMR spectral data of the compound 2-methoxy-4-{(*Z*)-[(4-methoxyphenyl)imino]methyl}phenol

^{13}C-NMR spectral data of the compound 2-methoxy-4-{(*Z*)-[(4-methoxyphenyl)imino]methyl}phenol

The chemical shift value at 126.3-139.1 ppm corresponds to aromatic carbon

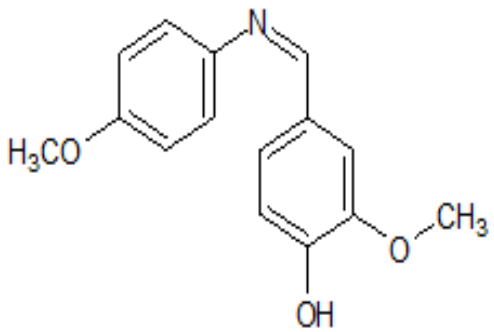
The peaks at 116.7 ppm are methyl carbons.

The peak at 146.12 shows the presence of the methoxy carbon.

The imine carbon is assigned to the chemical shift value of 199.35 ppm.

Structure of compound

Based on the above spectral studies, the following structure has been proposed for the compound.



2-methoxy-4-{(Z)-[(4-methoxyphenyl)imino]methyl}phenol

BIOLOGICAL ACTIVITY

Biological assay depends upon a comparison of the inhibition of growth of microorganism. For the antimicrobial study the in vitro disc diffusion method has been employed. In this study the compound is tested for their effect on certain human pathogenic bacteria, both Gram positive (Staphylococcus aureus) and Gram negative (Escherichia coli).

PROCEDURE:

Nutrient agar was used as a medium for studying the antimicrobial activity. The following reagents were required for the preparation of nutrient and agar medium.

Yeast extract	=	5 g
Meat extract	=	10 g
Peptone	=	5 g
Sodium Chloride	=	5 g
Agar	=	20 g

All the above reagents were dissolved in 1000 ml of distilled water in clean conical flask and the pH was maintained at 7. The solution was boiled to dissolve the medium completely and sterilized by autoclaving at 7 kg pressure (121˚C) for 15 minutes.

After sterilization, 20 ml media was poured into the sterilized Petri plates. These Petri plates were kept at room temperature for some time.

After few minutes, the medium gets solidified in plates. Then it was incubated for 12hrs. After the incubation this was inoculated with microorganisms using sterile swabs. All these manipulations were carried out with utmost care under aseptic conditions.

The antibacterial activity of the compound was done by the disc diffusion method using $CHCl_3$ as solvent. The test solutions are prepared by dissolving the compounds in $CHCl_3$. In a typical procedure, a well made on the agar medium is inoculated with microorganisms and it is filled with the test solution using micropipette at the plate is incubated at 35˚C for 24 to 48 h. During this period, the test solution diffuses and the growth of the inoculated microorganisms such as Staphylococcus aureus, and Escherichia coli are found to be affected. The activity developed on the plate is measured by measuring the diameter of the inhibited zone in millimeters.

BIOLOGICAL ACTIVITY

In Vitro Antibacterial Screening

The synthesis and characterization of biological activity compound were evaluated for their in vitro antibacterial activity against staphylococcus aurous and Escherichia coli by agar dilution method were performed using Mueller-Hinton agar (hi-media) each compounds and standard were tested at a concentration of 100µ/mg in DMSO, the zone of inhibition as measured after 24hr incubation at 37^{o}c. After the incubation period the diameter of clear zone around each well were measured in mm, clearing zone of variable size are visible the well of each compound. Ciprofloxacin was chosen as a standard antibacterial measurement.

The potato dextrose agar PDA is used as a medium for antifungal activity, the nutrient agar is prepared by dissolving 20g of potato extract 20g of agar and 20g of dextrose in one litre of dissolving distilling water in a clean conical flask. The solution is boiled to dissolve the media completely and sterilized by autoclaving with 7kg pressure (121^{o}c) for the 30 minutes after the sterilization 20 ml media poured in to the sterilized Petri plate. These Petri plate are kept at room temperature for some time. After a few minutes, the medium get solidifies in plate. DMSO (0.5µL) is used as solvent and clotrimazole (10µg/disc) as control in a typical procedure, a well made on the agar medium is inoculated with microorganism and it is filled with test solution using a micro pipette (50µL) and the plate is incubated at 35oc for 72 h. During this period the test solution diffuses and affects the growth of the inoculated microorganism. A zone is developed on the plate and the inhibition zones are measured by measuring the diameter of inhibited zone in mm. The zone of inhibition value is given in the table- 4.

Table-V

Antibacterial Activity of Compounds

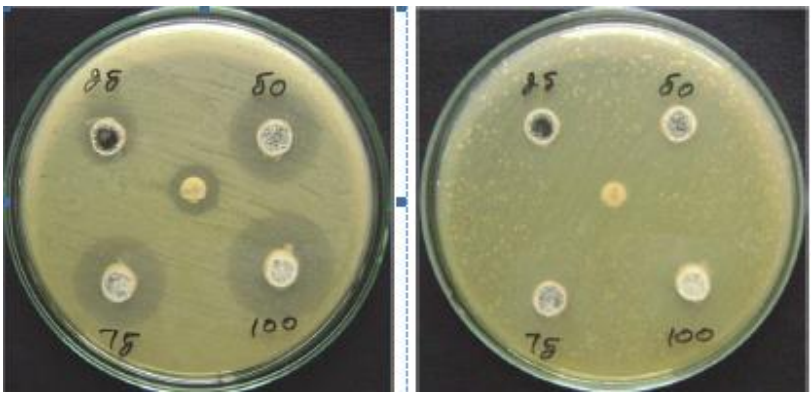
ORGANISM	**Concentration of DMSO extract added and Zone of inhibition (mm/ml)**				
	25 µl	50 µl	75 µl	100 µl	Control
Staphylococcus aurous	9	11	12	14	11
A.nigers	11	13	15	18	14

Result and discussion for antibacterial activity:

Antibacterial activity of the compound has activity against Staphylococcus aurous and A. nigers at various concentrations.

Photo Graphical Evidence

The zone inhibition of the compound is shown below:



Staphylococcus **aureus** **A.nigers**

CONCLUSION

The compound of 2-methoxy-4-{(*Z*)-[(4methoxyphenyl)imino]methyl}phenol was synthesized from Schiff method.

- The synthesized compound was characterized using IR, ^{1}H and ^{13}C NMR.
- The synthesized compound was screened for antibacterial activity.
- The compound is highly active against both Staphylococcus aureus and A. nigers in anti bacterial activity.

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Post Graduate Project – 11

Corrosion Inhibition Effect of Aqueous Leaves Extract of *Artabotrys Hexapetalus* on Mild Steel in 1.0 M H_2SO_4

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Name of the Candidate: L. Kavitha

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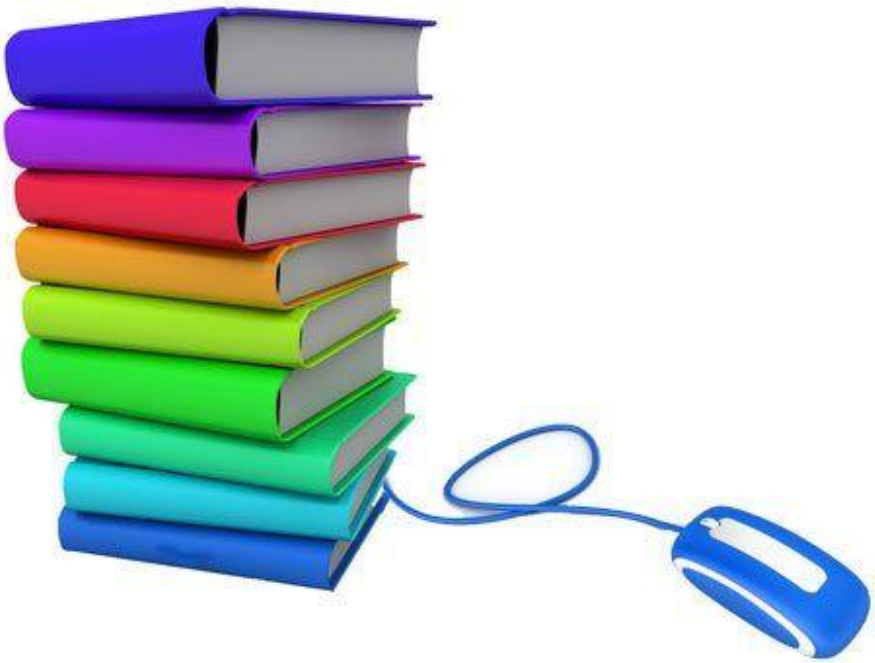

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CHAPTER-1

INTRODUCTION

CORROSION

Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Both the type of metal and the environmental conditions, particularly gasses that are in contact with the metal, determine the form and rate of deterioration.

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment.

Figure -1: Deterioration on metal surface

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media.

Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its location. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media. The present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

DEFINITION OF CORROSION

- Corrosion is the irreversible damage or destruction of living tissue or material due to a chemical or electrochemical reaction. A prime example of corrosion is rusting of iron or steel.
- Corrosion is a natural process, which converts refined metal to a more chemically stable form, such as its oxide, hydroxide or sulfide. It is the gradual destruction of materials (usually metals) by chemical or electro chemical reaction with their environment.
- Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species.
- Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymers) with its environment which results in its consumption or dissolution into the material of a component of the environment. Corrosion is the destructive attack on a metal through interaction.

THEORIES OF CORROSION

- **Homogeneous Theory**

A corroding metal irrespective of the presence or absence on its surface of any micro heterogeneity can be regarded as single electrode on which reactions take place. Metal becomes unstable due to the charge transfer reaction taking place at the interface. Hence, it is necessary that the potential difference across the interface be more negative than the equilibrium potential for the metal dissolution (anodic) reaction or more positive than the equilibrium potential for the electronation (cathodic) reaction.

- **Heterogeneous Theory**

According to this theory, corrosion is caused by local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity. Corroding metal consists of an electron sink area, where de-electronation reaction occurs. b. an electron source area, where electronation reaction occurs in an ionic conductor to keep the current flowing.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I_{corr}. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding, on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

The most common and important electrochemical reactions in the corrosion of iron are

Anodic reaction (corrosion)

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Cathodic reactions (simplified)

$$2H^+ + 2\,e^- \longrightarrow H_2$$

$$H_2O + 1/2O_2 + 2e^- \longrightarrow 2\,OH^-$$

This reaction is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

MECHANISM OF CORROSION

Although several mechanisms have been proposed for the corrosion process, corrosion is mainly electrochemical in nature and hence in this chapter, the electrochemical mechanistic aspects have been discussed. According to this approach, the corrosion reaction can be considered as taking place by two simultaneous reactions; the oxidation of a metal at an anode (a corroded end releasing electrons) and the reduction of a substance at a cathode (a protected end receiving electrons). In order for the reaction to occur, the following conditions must exist:

- A chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition).
- An electrolyte must be present to provide solution conductivity and act as a source of material to be reduced at the cathode.
- An electrical path through the metal or between metals must be available to permit electron flow.

The below diagram illustrates the typical electrochemical corrosion of iron in contact with water.

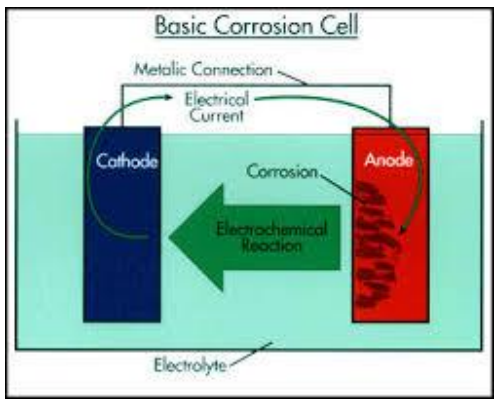

Figure -2: Electrolyte corrosion cell

In a nearly neutral or slightly acid environment, the water is dissociated into hydrogen ions (H^+) and hydroxyl ions (OH^-) as

$$H_2O \rightleftharpoons H^+ + OH^-$$

When metal is placed in contact with a liquid, surface ionization occurs, because of the electric charge difference at the solid-liquid interface. For example, iron dissolves in water in the form of positively charged ferrous ions (Fe^{++})

$$Fe \rightleftharpoons Fe^{++} + 2e^-$$

Electrochemically, a chemical substance is "oxidized", when it loses electrons to a second substance. The electrode at which the oxidation takes place is called as the "anode". A chemical substance is "reduced", when it acquires electrons. The electrode at which reduction takes place is called the "cathode". Hence, oxidation reaction results in the formation of positive charge ferrous ions at the anode. Ferrous ions moving away from the metal surface are further oxidized to ferric ions (Fe^{++}) as follows

$$Fe^{++} \rightleftharpoons Fe^{+++} + e^-$$

The positively charged ferric ions are attracted to the negatively charged hydroxyl ions and form the corrosion product $Fe(OH)_3$

$$Fe^{+++} + 3(OH)^{-} \rightleftarrows Fe(OH)_3$$

The rust consists of iron hydroxide or iron oxide hydrates in various states, depending on the degree of oxidation and dehydration.

The reduction reaction at the cathode must take place concurrently in order to continue the corrosion process. Several reactions are possible and the one that occurs is determined by the environment. Without the presence of air or oxygen, hydrogen ions can be reduced by the excess of electrons at the cathode surface and evolve as molecular hydrogen by

$$2H^{+} + 2e^{-} \rightleftarrows H_2$$

If hydrogen is not removed from the surface, the cathodic reaction decreases and the corrosion rate is reduced. With the presence of air, the more likely reaction is the reduction of oxygen. Two possible reactions occur:

$$O_2 + 4H^{+} + 4e^{-} \rightleftarrows 2H_2O$$

$$O_2 + 2H_2O + 4e^{-} \rightleftarrows 4(OH)^{-}$$

Hydrogen evolution or oxygen reduction with the formation of water is likely to occur in acid media. On the other hand, oxygen reduction with the formation of hydroxyl ions is more dominant in a neutral or alkaline environment. In either case, there is an increase in the alkalinity of the solution at the cathode.

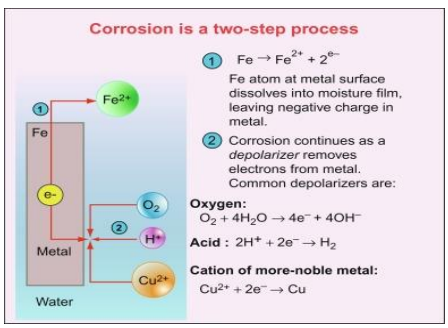

Figure -3: Two step process of corrosion

In summary, corrosion occurs when metal atoms detach themselves from the metal surface at the anode and enter the solution as ions, leaving behind electrons in the metal. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen ions that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In

solutions, where hydrogen tends to evolve too slowly, oxygen is reduced and combines with hydrogen ions or water to form hydroxyl ions.

TYPES OF CORROSION

They are many different types of corrosion, each of which can be classified by the cause of the metals chemical deterioration.

The metal corrodes at the same rate over the entire surface for the former and only small areas are affected in localized corrosion. Classification by appearance is manifested by the morphology of the corrosion attack and this can be visualized either by naked eye or magnification. The schematic in the given below diagram illustrates some of the most common forms of corrosion.

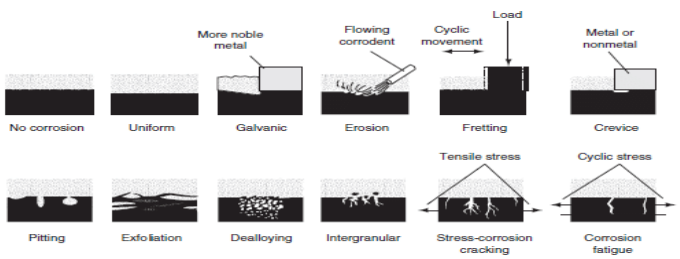

Figure -4: Schematics of the common forms of corrosion

General Attack Corrosion

It is also known as uniform attack corrosion. General attack corrosion is the most common type of corrosion and is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal. Ultimately, the metal deteriorates to the point of failure.

Figure -5: Uniform corrosion

General attack corrosion accounts for the greatest amount of metal destruction by corrosion but is considered as a safe form of corrosion, due to the fact that it is predictable, manageable and often preventable.

Localized Corrosion

Unlike general attack corrosion, localized corrosion specifically targets one area of the metal structure. Localized corrosion is classified as one of three types:

Pitting

Pitting results when a small hole, or cavity, forms in the metal, usually as a result of de-passivation of a small area. This area becomes anodic, while part of the remaining metal becomes cathodic, producing a localized galvanic reaction. The deterioration of this small area penetrates Crevice corrosion: Similar to pitting, crevice corrosion occurs at a specific location. This type of corrosion is often associated with a stagnant micro-environment, like those found under gaskets and washers and clamps. Acidic conditions or a depletion of oxygen in a crevice can lead to crevice corrosion.

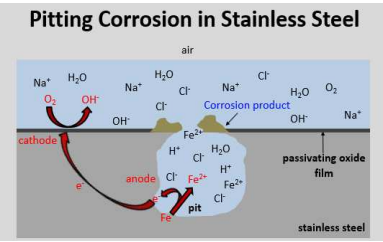

Figure -6: Pitting corrosion

Filiform Corrosion

Occurring under painted or plated surfaces when water breaches the coating, filiform corrosion begins at small defects in the coating and spreads to cause structure. This form of corrosion is often difficult to detect due to the fact that it is usually relatively small and may be covered and hidden by corrosion-produced compounds.

Galvanic Corrosion

Galvanic corrosion or dissimilar metal corrosion occurs when two different metals are located together in a corrosive electrolyte. A galvanic couple forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly.

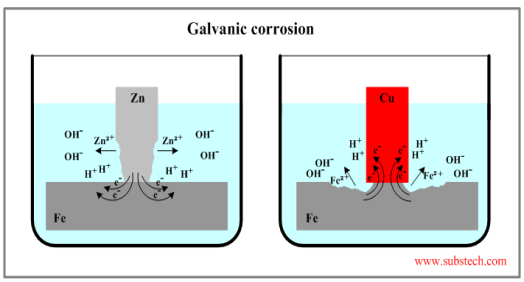

Figure -7: Galvanic corrosion

Three conditions must exist for galvanic corrosion to occur:

- Electrochemically dissimilar metals must be present
- The metals must be in electrical contact
- The metals must be exposed to an electrolyte

Environmental Cracking

Environmental cracking is a corrosion process that can result from a combination of environmental conditions affecting the metal. Chemical, temperature and stress-related conditions can result in the following types of environmental corrosion:

Figure -8: Environmental cracking

- Corrosion cracking
- Corrosion fatigue
- Hydrogen-induced racking
- Liquid metal embrittlement

Flow-Assisted Corrosion (FAC)

Figure -9: Flow-assisted corrosion

- Flow-assisted corrosion, or flow-accelerated corrosion, results when a protective layer of oxide on a metal surface is dissolved or removed by wind or water, exposing the underlying metal to further corroding and deteriorate
- Erosion-assisted corrosion
- Impingement
- Cavitation

Intergranular Corrosion

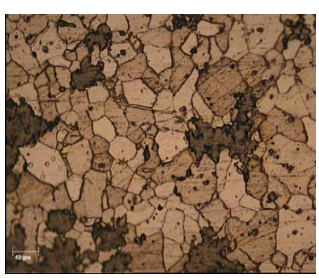

Figure -10: Intergranular corrosion

Intergranular corrosion is a chemical or electrochemical attack on the grain boundaries of a metal. It often occurs due to impurities in the metal, which tend to be present in higher contents near grain boundaries. These boundaries can be more vulnerable to corrosion than the bulk of the metal.

De-Alloying

De-alloying, or selective leaching, is the selective corrosion of a specific element in an alloy. The most common type of de-alloying is de-zincification of unstabilized brass. The result of corrosion in such cases is a deteriorated and porous copper.

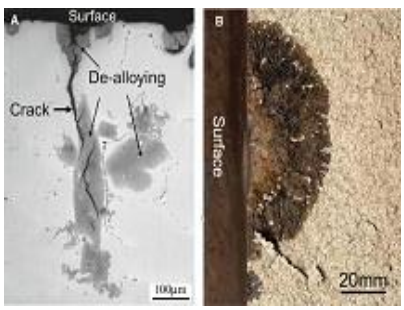

Figure -11: De-alloying corrosion

It is the removal of one solid element from alloy by corrosion processes. De alloying corrosion is also called de-zincification.

The most common example is de-zincification which is selecting removal of zinc in brass alloy. Similar processes occur in other alloy systems in which aluminium, Iron, Cobalt, Chromium and other elements are removed**.**

Fretting Corrosion

Fretting corrosion occurs as a result of repeated wearing, weight and/or vibration on an uneven, rough surface. Corrosion, resulting in pits and grooves, occurs on the surface.

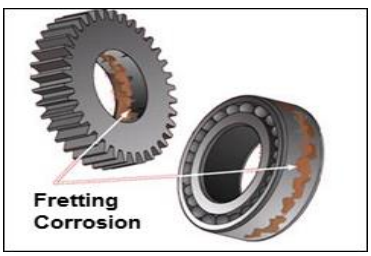

Figure -12: Fretting corrosion

Fretting corrosion is often found in rotation and impact machinery, bolted assemblies and bearings, as well as to surfaces exposed to vibration during transportation.

High-Temperature Corrosion

Figure -13: High-temperature corrosion

High-temperature corrosion is a mechanism of corrosion that takes place in gasturbines, diesel engines, furnaces or other machinery coming in contact with hot gas containing certain contaminants. Fuel sometimes contains vanadium compounds or sulfates which can form compounds during combustion having a low melting point. These liquid melted salts are strongly corrosive for stainless steel and other alloys normally inert against the corrosion and high temperatures. Other high-temperature corrosions include high-temperature oxidation, sulfidation and carbonization**.**

Crevice Corrosion

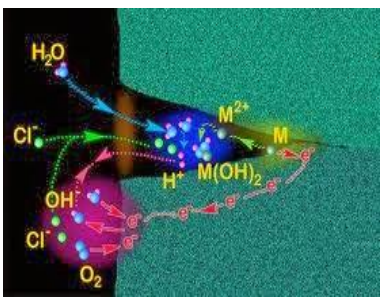

Figure -14: Crevice corrosion

Crevice corrosion is also a localized form of corrosion and usually results from a stagnant microenvironment in which there is a difference in the concentration of ions between two areas of a metal.

Crevice corrosion occurs in shielded areas such as those under washers, bolt heads, gaskets, etc. where oxygen is restricted. These smaller areas allow for a corrosive agent to enter but do not allow enough circulation within, depleting the oxygen content, which prevents re-passivation. As a stagnant solution builds, pH shifts away from neutral. This growing imbalance between the crevice (micro environment) and the external surface (bulk environment) contributes to higher rates of corrosion. Crevice corrosion can often occur at lower temperatures than pitting. Proper joint design helps to minimize crevice corrosion.

Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is a result of the combination of tensile stress and a corrosive environment, often at elevated temperatures. Stress corrosion may result from external stress such as actual tensile loads on the metal or expansion/contraction due to rapid temperature changes.

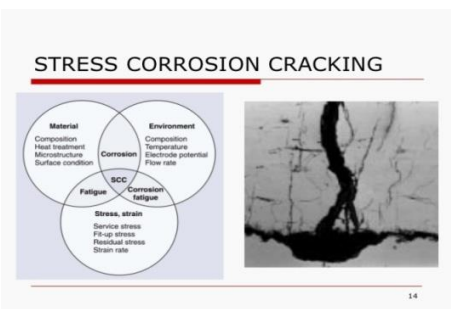

Figure -15: Stress corrosion cracking

It may also result from residual stress imparted during the manufacturing process such as from cold forming, welding, machining, grinding, etc. In stress corrosion, the majority of the surface usually remains intact; however, fine cracks appear in the microstructure, making the corrosion hard to detect. The cracks typically have a brittle appearance and form and spread in a direction perpendicular to the location of the stress. Selecting proper materials for a given environment (including temperature and management of external loads) can mitigate the potential for catastrophic failure due to SCC.

Caustic Agent Corrosion

Figure -16: Caustic agent corrosion

Caustic agent corrosion occurs when impure gas, liquids, or solids wear a material down. Although most impure gases do not damage metal in dry form, when exposed to moisture they dissolve to form harmful corrosive droplets. Hydrogen sulfide is an example of one such caustic agent.

Microbial Corrosion

Figure -17: Microbial corrosion

Microbial corrosion, commonly referred to as microbiologically influenced corrosion (MIC) is caused by microorganisms. It applies to both metallic and non-metallic materials with or without oxygen. When oxygen is absent, sulfate-reducing bacteria are active and produce hydrogen sulfide causing sulfide stress cracking. When oxygen is present, some bacteria may directly oxidize iron to iron oxides and hydroxides. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

Filiform Corrosion

Filiform corrosion: It is basically a special type of crevice corrosion, sometimes termed as “under film” corrosion. This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating.

Figure -18: Filiform corrosion

Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided unless absence of an adverse effect has been proven by field experience.

Cavitation Damage

Figure -19: Cavitation damage

Cavitation damage is a special form of erosion corrosion caused by the formation of vapour bubbles and their collapse in the liquid near a metal surface. This form of damage occurs in hydraulic turbines, pump impellers, and other surfaces that are in contact with high-velocity liquid flow along with high pressures.

Erosion Corrosion

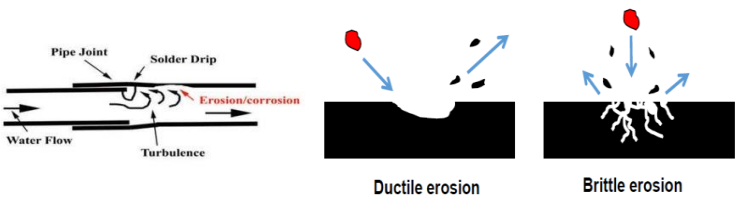

Figure -20: Erosion corrosion

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities. Erosion corrosion can be controlled by the use of harder alloys (including flame-sprayed or welded hard facings) or by using a more corrosion resistant alloy

Concentration Cell Corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. Concentration cell corrosion is associated with gaskets, joints, scale, debris, loose protective films, etc.

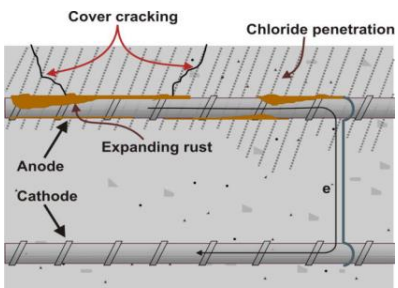

Figure -21: Concentration cell corrosion

Corrosion attack is accelerated, where the oxygen concentration is least. Metal at the area of low oxygen availability becomes anodic to other areas. As the cathodic area is large compared to the anodic area, the intensity of attack is usually more severe on surrounding areas of the same surface. This condition can be eliminated by sealing the faying surfaces in a manner to exclude moisture. Proper protective coating application with inorganic zinc primers is also effective in reducing faying surface corrosion.

Corrosion Fatigue

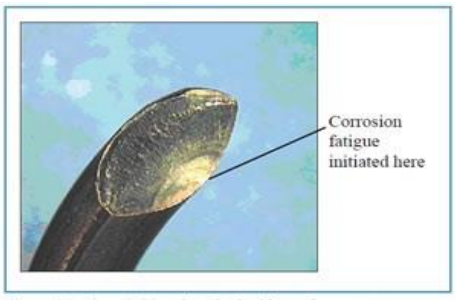

Figure -22: Corrosion fatigue

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment. Control of corrosion fatigue can be accomplished by either lowering the cyclic stresses or by corrosion control by using protection methods.

Direct Chemical Corrosion (or) Dry Corrosion

This type of corrosion occurs mainly through the direct chemical action of environment/atmospheric gases such as oxygen, halogens, hydrogen sulphide, nitrogen or anhydrous liquid sulphur dioxide with metal surface in immediate proximity

- . The extent of corrosion depends upon the following factors: Chemical affinity between the corrosive environment and solid metals.
- Ability of reaction product on metal surface to form a protective film.

FACTORS AFFECTING RATE OF CORROSION

Nature of the metal

Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum and silver. Whereas metal with lower electrode potentials, readily undergo corrosion. e.g., metals like zinc, magnesium, aluminium. When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion. For e.g.,the potential difference between the iron and copper is 0.78V which is more than that between iron and tin is 0.30V. Therefore, iron corrodes faster when in contact with copper than that with tin. On this account, the use of dissimilar metals should be avoided wherever possible. For example, bolt and nut or screw and washer should made by the same metal (or alloy) to avoid galvanic corrosion.

Ratio of cathodic to anodic region

The rate of corrosion is influenced by relative size of cathodic to anodic area. If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio decreases corrosion rate further increases. This is because at anode electrons are liberated. Which are consumed at cathodic region. If cathodic region is larger the liberated electrons are rapidly consumed at cathode. This further enhances, the anodic reactions leading to increase in overall rate of corrosion. When two dissimilar metals are in contact, Corrosion is more rapid and severe, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank), If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode. An intense localized corrosion occurs at the exposed small anodic surface. On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas.

Nature of the corrosion product

The corrosion product formed like metal oxide may act as protective film, if it is stable, insoluble, and non-porous. If it acts as protective film it prevents further corrosion by acting as barrier between metal surface and corrosion medium. On the other hand if corrosion product is

Unstable, porous, and soluble, it further enhances corrosion in oxidizing environments, metals like aluminium, chromium, titanium, etc., are highly passive as their oxides as corrosion products form protective films on the metal surface, preventing further corrosion. Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments

pH of the medium

In general rate of corrosion is higher in acidic pH than in neutral and alkaline pH.In case of iron, at very high pH protective coating of iron oxide is formed which prevents corrosion. Whereas at low pH, severe corrosion takes place. But for metals like aluminium, corrosion rate is high even at high pH.

Temperature

The rate of corrosion increases with increasing temperature. This is due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

Effect of oxygen

Oxygen plays an important corroding medium. If the metal is exposed to different concentration of oxygen, differential aeration corrosion takes place. The region which is less 0exposed to oxygen acts as anode hence undergoes corrosion and region exposed to high oxygen Concentration acts cathode hence doesn‟t undergo corrosion.

Hydrogen over voltage

The metal with lower hydrogen over voltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. Since at lower hydrogen over voltage, the liberation of hydrogen gas is easy. Therefore cathodic reaction is very fast, which in turn makes anodic reaction very fast. Thus increasing the rate of corrosion. Higher the over voltage lesser is the corrosion.

PREVENTION OF CORROSION

Rust and other corrosion forms can lead to safety issues and ruin the integrity of your equipment and supplies. Even routine maintenance to remove and repair corrosion can drive up costs. Fortunately, there are a variety of measures you can take to minimize corrosion. Herewe‟ll highlight four of these methods based on cost and effectiveness

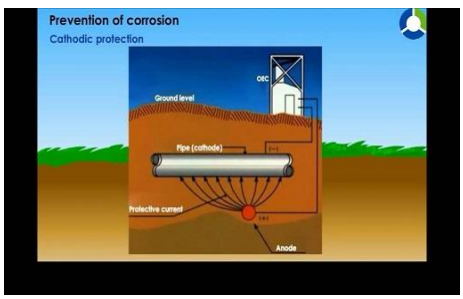

Figure -23: Prevention of corrosion

Barrier Coatings

One of the easiest and cheapest ways to prevent corrosion is to use barrier coatings likepaint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film. Plastic and waxes are often sprayed onto metal surfaces. Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds. Today‟s paint systems are actually a combination of different paint layers that serve different functions. The primer coat acts as an inhibitor, the intermediate coat adds to the paint‟s overall thickness, and the finish coat provides resistance to the environmental factors.

The biggest drawback with coatings is that they often need to be stripped and reapplied. Coatings that aren‟t applied properly can quickly fail and lead to increased levels of corrosion. Coatings may also contain volatile organic compounds, which can make them vulnerable to corrosion.

Hot-Dip Galvanization

This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly-bonded alloy coating which serves as protection.

The process has been around for more than 250 years and has been used for corrosion protection of things like artistic sculptures and playground equipment. Compared to other corrosion prevention methods, galvanization is known for lower initial costs, sustainability, and versatility. Unfortunately, galvanization can‟t be done on-site, meaning companies have to pull equipment out of work to be treated. Some equipment may simply be too large for the process,

forcing companies to abandon the idea altogether. In addition, if the process isn‟t done properly,

the zinc can chip or peel. And high exposure to environmental elements can speed up the process of zinc wear, leading to increased maintenance check-ups. Lastly, the zinc fumes that release from the galvanizing process are toxic.

Alloyed Steel (Stainless)

Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product. Corrosion-resistant nickel, for example, combined with oxidation-resistant chromium results in an alloy that can be used in oxidized and reduced chemical environments. Different alloys provide resistance to different conditions, giving companies greater flexibility.

Despite its effectiveness, alloyed steel is very expensive. Companies with limited financial resources will likely have to turn to other methods. Monitoring surface conditions arecritical, as cracks or scratches can result in an increase of corrosion. Companies also need to

make sure the agents used in maintenance don‟t include corrosion properties.

Cathodic Protection

Cathodic protection protects against galvanic corrosion, which occurs when two different metals are put together and exposed to a corrosive electrolyte. To prevent this, the active sites on the metal surface need to be converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

While cathodic protection is highly effective, anodes need to be checked often which can drive up costs of maintenance. They also increase the weight on the attached structure and aren‟t always effective in high-resistivity environments. Finally, anodes lead to increased water flow on ships and other underwater equipment.

Coatings

Coatings provide physical barriers that do not allow corrosive materials to come in contact with the structure that is being protected. Mainly, coatings are used on the exterior of pipelines to protect from external factors and are not used to directly protect the pipeline from CO_2 corrosion. The most common type of coatings are painting and platting which both provide effective corrosion protection and aesthetic appearance. Painting: Painting is an effective way to protect pipelines from external environmental factors. Although when looking at CO_2 corrosion on the interior of the pipeline, it is not ideal because painting the inside of a pipeline is impractical. The paint will breakdown over time, either through chemical reactions with the flowing fluid or the erosion due to turbulent or transient flow. Once the coating has broken down it leaves unprotected sections of the pipe when fluid induced localized corrosion occurs.

Plating

Plating involves using electric currents to coat a metal with a thin layer of another metal that acts as a protective barrier. Plating an entire pipeline is very uncommon as it is expensive; however, it can be done when dealing with high pressures and high amounts of H_2S and CO_2. One draw back of plating is if the plating fails in a small section (either an imperfection or a scratch) then highly localized corrosion occurs. Another factor to consider is if the plating is more noble than the pipeline (for example, chromium on steel), the steel will act as a sacrificial anode for the chromium. This causes the exposed area to corrode much more rapidly than an un-plated surface would.

CORROSION INHIBITORS

An inhibitor is a chemical substance or combination of substances which when added in very low concentrations in a corrosive environment effectively prevents or reduces corrosion without significant reaction with the components of the environment. Concentrations of

corrosion inhibitors can vary from 1 to 15,000 ppm (0.0001 to 1.5 wt %). Corrosion inhibitors can be solids, liquids and gases, and can be used in solid, liquid and gaseous media. Solid media can be concrete, coal slurries or organic coatings (paints). Liquids may be water, aqueous solutions or organic solvents. A gaseous medium is an atmosphere or water vapor. Corrosion inhibitors are selected on the basis of solubility or dispersibility in fluids which are to be inhibited. For instance, in a hydrocarbon system, a corrosion inhibitor soluble in hydrocarbon is used. Two phase system composed of both hydrocarbons and water is utilized as oil soluble water- dispersible inhibitor.

Corrosion inhibitors have been found to be effective and flexible means of corrosion mitigation. The use of chemical inhibitors to decrease the rate of corrosion processes is quite variable. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment and product additive industries. In the oil extraction, processing and chemical industries, corrosion inhibitors have always been considered to be the first line of defense. A great number of scientific studies have been devoted to the subject of corrosion inhibitors.

Inhibitors find major use in closed environmental systems that have good circulation so that an adequate and controlled concentration of inhibitor is ensured. Such conditions can be met, for instance in cooling water recirculation systems, oil production, oil refining, and acid pickling of steel components. One of the more recognizable applications for inhibitors is in antifreeze for automobile radiators. The application of inhibitors must be viewed with caution by the user because inhibitors may afford excellent protection for one metal in a specific system but can aggravate corrosion for other metals in the same system. Inhibitors can be organic or inorganic compounds and they are usually dissolved in aqueous environments. Some of the most effective inorganic inhibitors are chromates, nitrites, silicates, carbonates, phosphates and arsenates. The organic inhibitors include amines, heterocyclic nitrogen compounds, sulfur compounds such as thioethers, thioalcohols, thioamides, thiourea and hydrazine. Chromates and zinc salts are used increasingly less due to their toxicity and are nowadays largely replaced by organic inhibitors. Thus practical criteria for the selection of corrosion inhibitors from the great variety of inorganic and organic substances with inhibiting properties are not only their inhibition efficiency but also safety of use, economic constraints and compatibility with other chemicals in the system, and environmental concerns.

In order to avoid or reduce the corrosion of metallic materials, inhibitors used in cooling system must satisfy the following criteria.

- ❖ It must give good corrosion protection at a very low concentration of inhibitor. It must protect all efficient exposed materials from the attack of corrosion.
- ❖ It must remain in extreme operating conditions (higher temperature and velocity. In case of an under or over dosage of inhibitor, corrosion rate should not increase drastically.
- ❖ The inhibitor or reaction products of the inhibitor should not form any deposits on the metal surface particularly at locations where heat transfertakes place.
- ❖ It should suppress both uniform and localized corrosion. It should have long range effectiveness. It should not cause toxicity and pollution problems.

CLASSIFICATION OF CORROSION INHIBITORS

A common classification of inhibitors is based on their effects on the electrochemical reactions involved in the corrosion process.

Passivating Inhibitors

Passivating inhibitors cause a large anodic shift of the corrosion potential forcing the metallic surface into the passivation range. There are two types of passivating inhibitors.

- ❖ The oxidizing anions such as chromates, nitrites and nitrates that can passivate steel in the absence of oxygen.
- ❖ The non-oxidizing ions such as phosphates, tungstates and molybdates that require the presence of oxygen to passivate steel.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential to monitor the inhibitor concentration.

Volatile Inhibitors

Volatile corrosion inhibitors (VCIs) also called vapor phase inhibitors (VPIs) are compounds transferred in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing the acidic carbon dioxide or by shifting the surface pH towards less acidic. If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors.

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Liquid Phase Inhibitors (LPIs)

LPIs are in wide scale use to combat CO_2 corrosion in pipelines. The inhibitor is that is injected into the pipeline is transported in low concentrations and adsorbs onto the surface of the steel. Because the inhibitor is in the liquid phase only the interior of the pipeline needs to be in contact with the liquid either continuously or semi-continuously. One of the main benefits in using inhibitors to protect from CO_2 corrosion is that it can continuously be added to the flow to provide continuous protection.

Cathodic Inhibitors

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. For example, calcium, magnesium and zinc ions will precipitate as hydroxides on cathodic sites as the local environment becomes more alkaline due to the reduction reaction at these sites. cathodic inhibitors are effective when they slow down the cathodic reaction rate. Arsenic, bismuth and antimony which are referred to as cathodic poisons reduce the hydrogen reduction reaction rate and thus lower the overall corrosion rate. Other cathodic inhibitors remove reducible species from the environment. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through.

- The use of oxygen scavengers such as sodium sulfite and hydrazine which react with the oxygen and remove it from the solution.
- Vacuum de-aeration or boiling to lower the dissolved oxygen concentrations.

Anodic Inhibitors

Anodic inhibitors such as chromates, phosphates, tungstates and other ions of transition elements with high oxygen content are those that stifle the corrosion reaction occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface forming a protective film or barrier, thereby reducing the corrosion rate. Anodic inhibitors build a thin protective film along the anode and increasing their potential and thus slow down the corrosion reaction. Chromates, nitrates, tungstate and molybdates are some examples of anodic inhibitors. Although, this type of control is affected, yet it may be dangerous since severe local attack can occur, if certain areas are left unprotected by depletion of the inhibitors.

Mixed Inhibitors

Some substances inhibit corrosion by reducing simultaneously the rate of anodic and cathodic reactions involved in the corrosion process and are therefore called mixed inhibitors. They are typically film forming compounds that cause the formation of precipitates on the

surface blocking both anodic and cathodic sites indirectly. Anodic inhibitors are, for the most part, dangerous inhibitors, especially if their concentrations are too less. But cathodic inhibitors are generally safe. Mixed inhibitors are less dangerous than pure anodic inhibitors, and in number of cases they may not increase the corrosion intensity. The most common inhibitors of this category are the silicates and the phosphates.

Synergistic Inhibitors

It is very rare that a single inhibitor is used in systems such as cooling water systems. More often, a combination of inhibitors (anodic and cathodic) is used to obtain better corrosion protection properties. The blends which are produced by mixing of multi-inhibitors are called synergistic blends. Examples include chromate-phosphates, polyphosphate-silicate, zinc-tannins, and zinc-phosphates.

Precipitation Inhibitors

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust. In aerated hot water systems, sodium silicate protects steel, copper and brass.

GREEN CORROSION INHIBITORS

Extracts of plant materials contain a wide variety of organic compounds. Most of them contain hetero atoms such as P, N, S, O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented.

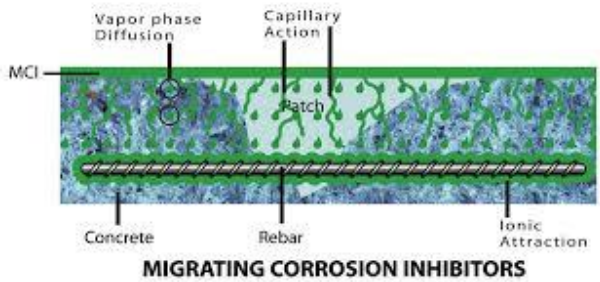


Figure -24: Migrating corrosion inhibitors

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties. The term "green inhibitor" or "eco-friendly inhibitor" refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of "inhibitors", "green inhibitors" can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

Organic Green Inhibitors

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from natural sources like plants. It also includes synthetic compounds with negligible toxicity. Some of the notable developments on organic green inhibitors especially plant extracts are discussed here.

Plant Extracts

The authors have so far investigated the application of plant extracts, as well as other organic inhibitors against corrosion of steel in acidic fluids. Loto had reported the application of the extract of Mangifera indica (Common name: mango, indigenous area: India and other tropical regions) leaves and bark for corrosion of mild steel in diluted sulphuric acid (H_2SO_4) medium. The weight loss measurements and electrochemical impedance spectroscopic studies were used to determine the inhibition efficiency of the inhibitors. Though the extract of leaves

and bark showed a significant effect on the corrosion rate separately, the combination of these two extracts exhibited rather higher efficiency.

The inhibitive effect of Zenthoxylum alatum (Winged Prickly Ash, East and South Asian Countries) fruit extract was reported for corrosion of mild steel in phosphoric acid medium at temperatures ranging from 50–80^{0}C. The surface analysis using X-ray photoelectron spectroscopy (XPS) revealed the layer formation of the plant extract on the surface of mild steel. And the results were indicated the possible formation of iron phosphate that was catalyzed by the formation of the iron-plant extract organo-metallic complex.

Satapathy et al studied the methanol extract of Justicia gendarussa (Willow-leaved justicia, India, Indonesia) leaves for corrosion inhibition of mild steel in hydrochloric acid medium (HCl). The authors have made an attempt to characterize the organic compounds present in the methanol extract by means of gas chromatography- mass spectrometric technique. The results showed that the compounds present in the methanol extract were difficult to separate, since the retention times of majority of the compounds were close to each other. The electron spectroscopy for chemical analysis and atomic force microscopywere employed to obtain the information about the film formation on the surface of the mild steel specimen.

Inorganic Green Inhibitor

A number of inorganic elements (minerals) are essential for the growth of living things. Mineral elements in wide variety are present in trace amounts in almost all foodstuffs. The higher concentrations of many metals cause toxicity to all forms of lives. Chromates are among the most common substances used as inhibitors or incorporated in anticorrosive pretreatments of aluminums alloys. The corrosion of galvanized steel was inhibited by the formation of cerium-rich film. The film contains Ce^{4+}which was formed by the cerium oxides and hydroxide

IMPORTANCE OF GREEN INHIBITOR

- Inhibitors are a great method of preventing corrosion and are easy to apply. Has application in a wide range of sectors. The knowledge of the method of the action,facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects

- ❖ It is important in the choice of inhibitor; ascertain the subsequent effects of this towards the environment.

- ❖ The search for environmental friendly inhibitors has shown excellent results, outperforming conventional inhibitors. Reference organic inhibitors newly developed. Inhibitors play a vital role in providing protection against corrosion.

- ❖ The selection of the inhibitor is important for environmental protection not all inhibitors are eco-friendly.

- ❖ There is a growing trend to use plant extracts and pharmaceutical compounds as corrosion inhibitors. Most of these compounds are environmentally-friendly.

ECO-FRIENDLY INHIBITORS FOR CORROSION CONTROL OF MILD STEEL (MS)

In recent years several researchers have indicated the use of eco-friendly corrosion inhibitors for mild steel in different media. They forms complexes with metal ion onto the metal surface and thus forming a protective coating on the metal surface and protecting them from corrosive agents in different media. Inhibition efficiency of these inhibitors in different media have been evaluated by employing different investigational techniques like weight loss method, electrochemical studies, Raman spectroscopy, gasometric techniques, potentiodynamic polarization, electrochemical impedance, polarization method, SEM, FTIR etc. are being used.

CHAPTER-II

AIM AND SCOPE OF THE PRESENT WORK

Green compounds represent a potential class of corrosion inhibitors. There is a wide range of studies regarding corrosion inhibition by hetero atoms containing green compounds. Green compounds containing lot of hetero atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or sulfur. The corrosion-inhibiting property of these compounds is attributed to their molecular structure.

Acid solutions are widely used in industries for pickling, acid cleaning of boilers, rescaling and oil well as acidizing. Corrosion inhibitors are widely used in order to control the corrosion of metallic materials by cleaning acids. 1.0 M H_2SO_4 is employed in such purposes. Most of the earlier studies on inhibition of corrosion of metals in acids have been related to the performance of organic compounds containing hetero groups.

Recently, environmental friendly inhibitors have attracted several researchers. Natural products are non-toxic, biodegradable and readily available. They have been widely used as inhibitors. Corrosion inhibition of mild steel by various types of plant extracts has been studied.

Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly, and acceptable and possess no threat to the environment. The present work in undertaken:

1. To evaluate the inhibition efficiency of an aqueous leaves extract of *Artabotrys hexapetalus* in controlling the corrosion of mild steel in 1.0 M H_2SO_4 medium.
2. To analyse the best fit isotherm for corrosion inhibition.
3. To understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization and impedance analysis.
4. To propose a suitable mechanism for corrosion inhibition.

CHAPTER-III

EXPERIMENTAL METHOD

The experimental studies related to the inhibition action of *Artabotrys hexapetalus* leaves extract on mild steel in 1.0 M H_2SO_4 have been present here. Such studies include weight loss, polarization and impedance studies.

Artabotrys hexapetalus

Artabotrys hexapetalus is a genus of plants in the *Annonaceae* family. There are over 100 species in the old world tropics, with 31 species in Africa. It is part of the clustered apple family (Annonaceae). All species are small trees or shrubs with a tendency to climb. Leaves are simple and alternate, without hairs. Bisexual flowers are borne singly or in clusters opposite the leaves. The 6-pettalled flowers are scented, and the plant bears fleshy fruits.

Artabotrys hexapetalus is indigenous in southern India and Sri Lanka but later introduced throughout the Old World tropics. It is commonly cultivated in southern China, Indo-China, and the Philippines and also in Java.

Figure -25: ***Artabotrys hexapetalus***

Properties

Botanical name : *Artabotrys hexapetalus*

Family : Annonaceae

Kingdome : Plantae

Order : Magnoliales

Genus : Artabotrys

Division : Magnoliphyta

Tamil name : Manoranjitham

Therapeutic uses: The flowers of *Artabotrys hexapetalus* are tonic and stimulant. The fruits and the bark are used to treat fever, diarrhea, skin diseases, wounds, ulcers, inflammation, cough, asthma and bronchitis. The leaves extract has antibacterial, antifertility and antifungal activities.

Pharmacological action: Anti-inflammatory, anti-oxidant, anti-osteoporatic, and anti -bacterial activity.

Collection of the plant material: The leaves were collected from the area Elur, Namakkal (DT), Tamilnadu. Fresh leaves were authenticated and identified by Dr. John Britto, The Rapient Herbarium and centre for Module systematics, St, Joseph's College, Trichirappalli, Tamil nadu, India.

Preparation of extract

The leaves were collected, shade dried and powdered. An aqueous extract was prepared by refluxing 100 gm of powdered *Artabotrys hexapetalus* leaves in double distilled H_2O. The extract was cooled, filtered and made up to 1000 ml with distilled water. From that, various distributions were prepared.

Preparation of the specimens

Mild steel specimen (0.026%-S, 0.06%-P, 0.4%-Mn, 0.1%-C and the rest iron) of the dimensions 1x5x0.2 cm were polished to mirror finished. They are decreased with acetone and used for the weight loss method, polarization and impedance studies.

Materials and chemicals used

For polarization, cylindrical mild steel rod embedded in Teflon with an exposed area of 1 cm^2 was used. The electrodes were polished with emery papers of 0/0, 2/0, 3/0, and 4/0 grades and degreased with acetone, dried and used.

Acid

H_2SO_4 was used of G.R. Grade (MERCK CHEMICALS)

TABLE-1

Phytochemical screening of aqueous extract of *Artabotrys hexapetalus* leaves extract

Phyto-constituents	Chemical Test	Aqueous extract
Alkaloids	Wagners	-
Coumarin	Anthraquinone	+
Tannins	$FeCl_3$	+
Flavonoids	Lead acetate	+
Sterols	Libermann	-
Saponins	Sodium hydroxide	+
Phenols	$FeCl_3$	+
Quinones	Alcoholic KOH	-
xanthoproteins	HNO_3	+

(Note: + : Presence; - : Absence)

Weight loss method

Weight loss measurements were performed in 1.0 M H_2SO_4 medium with and without the presence of different volumes of inhibitor by using the formula, inhibition efficiency were calculated.

Inhibition efficiency (%) = W_0-W_i/W_0*100

Where

W_0= Weight loss in plain acid

W_i = Weight loss in inhibited acid

Potentiodynamic polarization studies:

Potentiodynamic polarization studies were performed for mild steel specimen in the presence and the absence of the inhibitors. Polarization measurements were performed to evaluate the corrosion current, corrosion potential and the Tafel‟s slope.

The electrode used was a mild steel rod of the same composition embedded in araldite and with an exposed area of $1cm^2$. The polarization cells contain a three electrode assembly. A rectangular foil was used as the counter or auxiliary electrode. The area of the counter electrode is much larger compared to the area of the working electrode. This will exert a uniform potential field on the working electrode. The reference electrode is Hg/$HgCl_2$/1N H_2SO_4 for HCl solution.

A solution quantity of 100 ml of the test solution was taken in a polarization cell. The working electrode was polished with 0/0, 1/0, 2/0, 3/0, and 4/0 emery papers successively and degreased with acetone. The working electrode, reference and auxiliary platinum electrodes were assembled and connections were made.

Stirring was provided to the test solutions to avoid for the system the volume polarization before start of experiment. A time interval of about 15 minutes was given for the system to attain steady state and open circuit potential was recorded. Polarization measurements were made carried out from 800mV to 250mV at a constant identical to weight loss measurements.

Polarization measurements were made from mild steel specimens in 1.0 M H_2SO_4 in the presence and absence of the inhibitor. Current in mA and potential in mV were plotted. From the graph, the Tafel slope (in mV/decade) and the corrosion potential (in mV/decade) were calculated.

Impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell setup was the same as that used for polarization measurements.

The real part and imaginary part of the cell impedance were measured in ohms at varies frequencies. The value of charge transfer resistance, R_t , and the double layer capacitance, C_{dl} were calculated.

CHAPTER-IV

RESULTS AND DISCUSSION

It is a well known fact that research activities leading to the development of corrosion inhibitors based on natural products have immense scope in several industries, because of their non-toxicity, biodegradable nature and are also easily available. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly and possess no threat to the environment.

The efficiency of an extract as a corrosion inhibitor can be attributed to the number of mobile electron pairs present, π-orbital character of free electrons and the electron density around the hetero atoms. In the present study, inhibition efficiency of *Artabotrys hexapetalus* leaves extract in 1.0 M H_2SO_4 medium has been evaluated using weight loss measurements and its potentiodynamic polarization and impedance studies. The effect of this extract on the extent of inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by this extract can be explained in terms of its adsorption on the metal surface. This extract gets adsorbed on the metal surface by means of, when mild steel is immersed in the acid solution the phyto-components diffuses from the bulk of solution towards the metal surface.

The inhibitive influence of *Artabotrys hexapetalus* on the corrosion of mild steel in 1.0 M H_2SO_4 leaves was studied by weight loss method, polarization and impedance measurements. The inhibition efficiency values determined by these techniques showed closed agreement. The maximum inhibition efficiency was found to be 91.2%.

The corrosion decreased with increase in addition of *Artabotrys hexapetalus* probably due to the progressive adsorption of the inhibitor on the metal surface.

The percentage of inhibition efficiency increases with increase in the inhibitor volume. The corrosion inhibition by *Artabotrys hexapetalus* leaves extract is attributed to the adsorption of the additive onto the mild steel surface.

The values obtained from the weight loss technique for the studied inhibitor fit well into the Temkin and El-awady adsorption isotherm. The values of free adsorption process indicate that both physisorption and chemisorption studied for the mild steel surface.

The leaves of *Artabotrys hexapetalus* prevent the corrosion due to the presence of any of the phytochemical components shifting the corroded metal into the noble. The polarization study also shown an agreement with inhibitor efficiency obtained from weight loss studies.

Weight loss studies

Table-2 gives the inhibition efficiency of different volume of *Artabotrys hexapetalus* 1.0 M H_2SO_4 medium. The inhibition depends upon the nature and mode of adsorption of the metal surface. The adsorption is assumed to be quasi-substitution process between the water molecules on the surface and any of the natural components present in the inhibitor.

The inhibition of heterocyclic compound present in the plant extract with the metal surface may occur through any of the phyto-components present in the inhibitor and also to the interaction of π-electrons of ring with metal surface, thereby enabling the compound to get adsorbed on the metal surface.

Adsorption isotherm

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Temkin, Flory-Huggins, Frumkin, and the recently formulated thermodynamic/kinetic model of El-awady et al. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clue to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs as the interaction energy between molecules and metal surface is higher than that between the H_2O molecules and the metal surface.

Langmuir adsorption isotherm

Adsorption isotherms are very important to determine the mechanism of phyto-electrochemical reaction. The adsorption isotherm values are shown in **table-3**.

Langmuir adsorption isotherm is

$$\Theta = K_{ads}.\ C/1 + K_{ads}\ .C$$

$$\Theta\ (1+K_{ads}.C) = K_{ads}\ .C$$

$$\Theta = K_{ads}.\ C - K_{ads}\ .C\Theta$$

$$\Theta = (1-\Theta)\ K_{ads}\ .C$$

$$\Theta/1-\Theta = K_{ads}\ .C$$

The plot of $3+ \log s\ (\Theta/1-\Theta)$ against $3+\log C$ is a straight line as shown in **figure-26**. Thus the Langmuir isotherm is valid for the inhibitor.

Temkin adsorption isotherm

It is given by the expression;

$$\Theta = -2.303 \log K/2a.-2.303 \log C/2a$$

Where "K" is the adsorption equilibrium constant, "a" is the lateral interaction parameter. The plot of Θ against log V is shown in **figure-27**. The linear plot indicates that Temkin adsorption isotherm was obeyed and negative, value of "a" indicated repulsion exist in the adsorption layer. The results are shown in **table -4.**

Florry-Huggins adsorption isotherm

It is given by the expression

$$\log \Theta/C = \log K + x \log (1-\Theta)$$

Where "x" is the size parameter and it is a measure of the number of adsorbed water molecules substituted by an inhibitor molecule. The adsorption parameter is shown, in **table-5.** The plot of log Θ/C against log (1-Θ) is linear as shown in **figure-28.**

El-awady isotherm

It is given by the expression:

$$\log (\Theta/1-\Theta) = \log K + y \log C$$

Here K_{ads} the equilibrium constant of adsorption process is calculated by the relationship, K_{ads} = 1/k. A plot of 2 + log (1-Θ) Vs. 2+ logC is linear as shown in **figure-29**. The calculated K_{ads} and 1/y values are given. The adsorption isotherm values are shown in **table-6.**

Frumkin isotherm

$$K_{ads}\, C = (\ /1-\Theta)e^{-2a}$$

Take logarithm on both sides of the equation, it can be rearranged as given below.

$$\log K_{ads} + 2a = \log(\ /(1-\Theta)C)$$

where, K_{ads} is the adsorption desorption equilibrium constant, V is the inhibition volume and "a" is the interaction parameter describing the lateral interaction among inhibitor molecular in the absorbed layer on the metal surface. Linear plots of **log(/(1- Θ)C)** Vs. Θ is shown in **figure-30** obtained. The values for the Frumkin adsorption parameters are shown in **table-7.**

Free energy change

The (ads) of inhibitor on mild steel surfaces related to the constant of the adsorption according to equation.

$$\Delta G^{0}_{ads} = -2.303RT\log (K_{ads} \times 55.5)$$

From the results, shown in **table-8**, most of the values of ΔG^{0}_{ads} were found to be negative and were below the threshold value of -40 kJ/mole indicating that the adsorption of *Artabotrys hexapetalus* leaves extract, on mild steel susrface is spontaneous and thatmechanism of physical adsorption is applicable.

Potentiodynamic polarization studies

Table-9 and **figure**s **31, 32, 33, & 34** gives the values of potentiodynamic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}) and the cathodic Tafel slopes (b_c and b_a) for the different volume shown in the green inhibitor understudy. It can be seen that the phyto-components diffuse from the bulk of the solution and gets absorbed on metal surface.

AC impedance study:

Table-10 and **figures 35, 36, 37 & 38** shows the AC impedance value for different volume of the inhibitor. The R_t value increases and C_{dl} value decreases with inhibitor volume. This implies the formation of protective film on the metal surface. It can be also seen from **table-11** that there is a close agreement between the values of inhibition efficiencies obtained from weight loss measurements, polarization and impedance studies.

TABLE-2

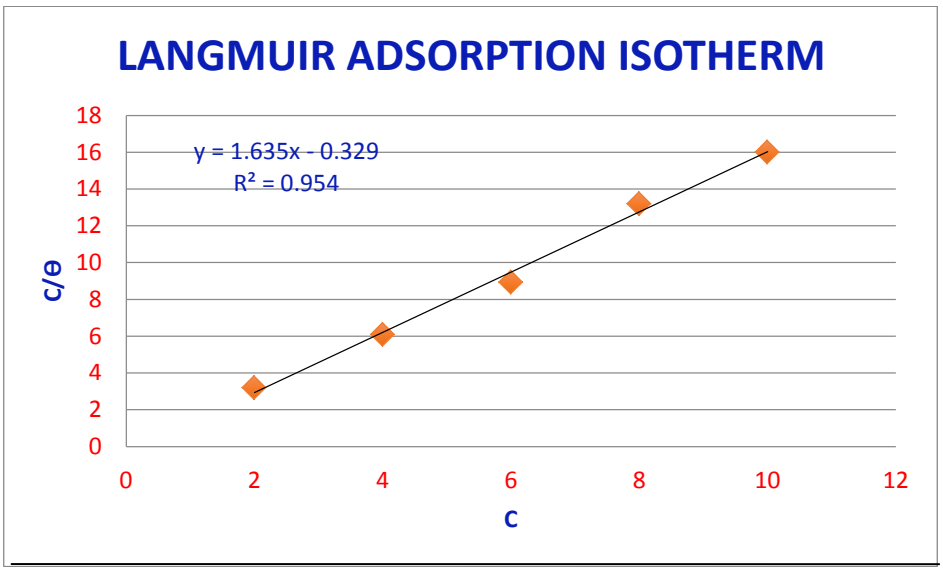
Inhibition effect on corrosion of mild steel in 1.0 M H_2SO_4 medium by *Artabotrys hexapetalus* leaves extract using weight loss method

Concentration, (%)	Weight loss	Inhibition Effect (%)	Rate of corrossion
2	0.012	11.5	5×10^{-4}
4	0.011	28.2	4.583×10^{-4}
6	0.010	43.7	4.166×10^{-4}
8	0.018	63.7	7.5×10^{-4}
10	0.006	91.2	2.5×10^{-4}

TABLE-3

Langmuir adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Artabotrys hexapetalus* leaves extract

Concentration, (%)	Θ	1-Θ	Θ/1-Θ	logΘ/1-Θ	3+log Θ/1-Θ	3+logC
2	0.115	0.375	1.6666	0.2218	0.2218	3.301
4	0.282	0.314	1.9069	0.2803	0.2803	3.6020
6	0.437	0.313	2.1948	0.3413	0.3413	3.7781
8	0.637	0.563	0.7761	0.1100	2.89	3.9030
10	0.912	0.188	4.3191	0.6353	3.6353	4.000



Fifure-26: Langmuir adsorption isotherm for the inhibition of corrosion mild steel in 1.0 M H_2SO_4 medium using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = -0.329

K_{ads} = -3.0395

ΔG^0_{ads} = -12.9224

Slope = 1.635

R^2 = 0.954

1/y = 0.611

TABLE-4

Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0M H_2SO_4 medium by *Artabotrys hexapetalus* leaves extract

Concentration (%)	log C	2+log C	θ
2	0.3010	2.301	0.115
4	0.6020	2.602	0.282
6	0.7781	2.778	0.437
8	0.9030	2.903	0.637
10	1.00	3.00	0.912

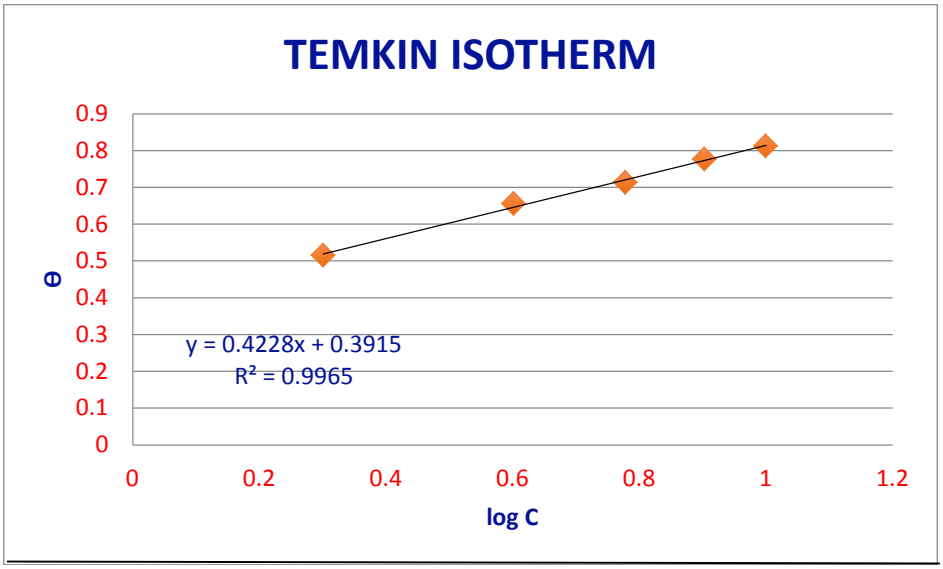


Figure -27: Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0M H_2SO_4 medium using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = 0.391

K_{ads} = 8.4411

ΔG^0_{ads} = -15.4960

Slope = 0.422

R^2 = 0.996

1/y = 2.369

A = -2.7286

TABLE-5

Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Artabotrys hexapetalus* leaves extract

Θ	**Concentration (%)**	**Θ/C**	**log Θ/C**	**4+logΘ/C**	**1-Θ**	**log (1-Θ)**	**4+log(1-Θ)**
0.115	2	0.3125	-0.5051	3.4949	0.375	-0.4259	3.5741
0.282	4	0.164	-0.7851	3.2149	0.344	-0.4634	3.5366
0.437	6	0.1145	-0.9411	3.0589	0.313	-0.5044	3.4956
0.637	8	0.0546	-1.2623	2.7372	0.563	-0.2494	3.7506
0.912	10	0.0812	-1.0904	2.9096	0.188	-0.7258	3.2742

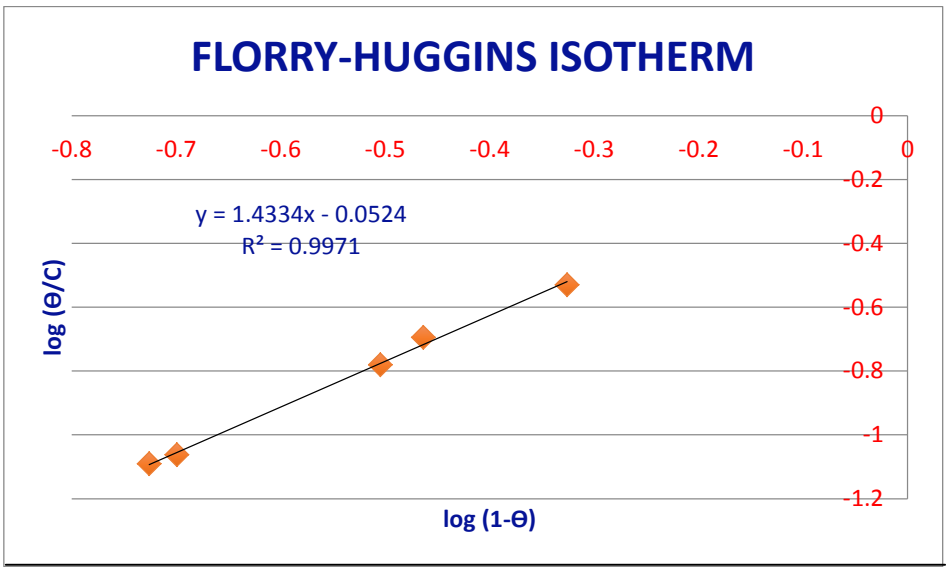


Figure -28: Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = -0.052

K_{ads} = 0.8871

ΔG^0_{ads} = -9.8197

Slope = 1.433

R^2 = 0.997

1/y = 0.697

TABLE – 6

El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 medium by *Artabotrys hexapetalus* leaves extracts

Concentration (%)	2+log C	Θ	1-Θ	Θ/1-Θ	2+log (Θ/1-Θ)
2	2.301	0.115	0.375	1.6666	3.6666
4	2.602	0.282	0.344	1.9069	3.9069
6	2.778	0.437	0.313	2.1948	4.1948
8	2.903	0.637	0.563	0.7761	2.7761
10	3.00	0.912	0.188	4.3191	6.3191

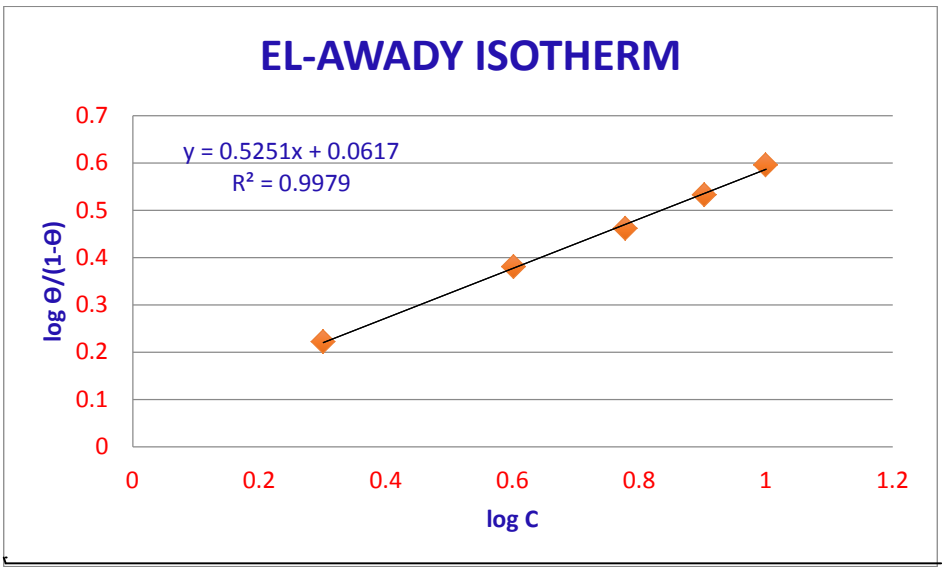


Figure 29: El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 M H_2SO_4 using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = 0.061

K_{ads} = 1.3080

ΔG^0_{ads} = -10.797

Slope = 0.523

R^2 = 0.997

1/y = 1.9120

TABLE – 7

Frumkin adsorption isotherm for the inhibition of mild steel in 1.0 M H_2SO_4 medium by *Artabotrys hexapetalus* leaves extract

Concentration (%)	**Θ**	**(1-Θ) C**	**logΘ/(1-Θ)C**
2	0.115	1.15	-0.3393
4	0.282	1.776	-0.3917
6	0.437	1.878	-0.4367
8	0.637	1.784	-0.4632
10	0.912	1.88	-0.4946

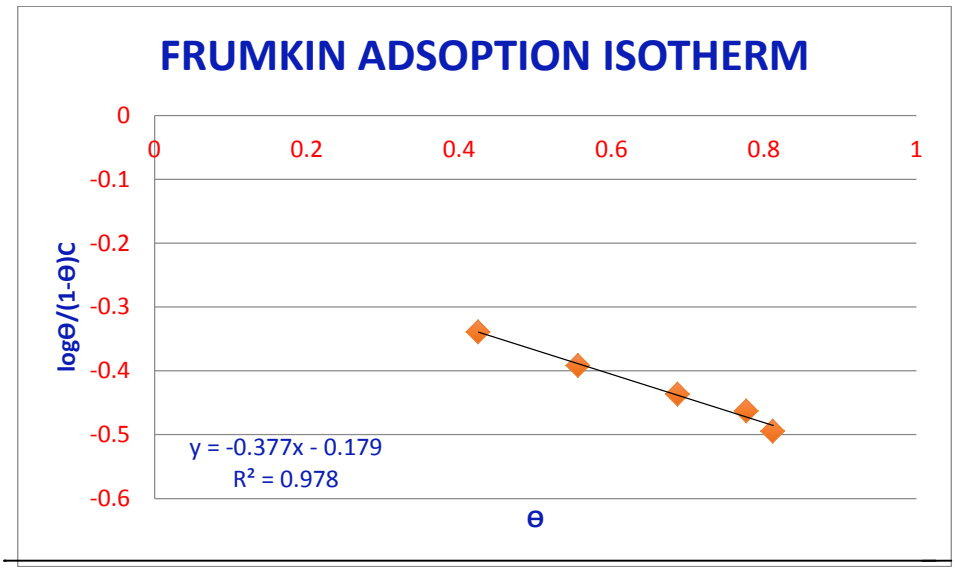


Figure 30: Frumkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0M H_2SO_4 using *Artabotrys hexapetalus* leaves extract.

Calculation:

Intercept = -0.179

K_{ads} = 0.6622

ΔG^0_{ads} = -9.0829

Slope = -0.377

R^2 = 0.978

1/y = -2.652

A = -0.1885

TABLE – 8

Adsorption isotherm parameters for the inhibition of the corrosion of mild steel in 1.0M H_2SO_4 by *Artabotrys hexapetalus* leave extract

Isotherm	$-\Delta G^0_{ads}$	Slope	R^2	a	1/y
Langmuir Isotherm	-12.922	1.635	0.954	-	0.611
Temkin Isotherm	-15.496	0.422	0.996	-2.728	2.369
Florry-Huggins Isotherm	-9.819	1.433	0.997	-	0.697
El-awady Isotherm	-10.797	0.523	0.997	-	1.912
Frumkin Isotherm	-9.0829	-0.377	0.978	-0.1885	-2.652

The R^2 value shows that **Temkin, Florry-Huggins & El-awady** are the best fit isotherms.

TABLE – 9

Corrosion parameters obtained from polarization curves for mild steel in 1.0 M H_2SO_4 medium in the presence and absence of inhibitor

SYSTEM	[Inhibitor], (%)	$I_{corr.}$, mV	$-E_{corr.}$, mV	b_a, mV dec^{-1}	b_c, mV dec^{-1}	Inhibition Efficiency (%)
Blank	-	870.004	491.966	90.836	180.905	-
Artabotrys hexapetalus leaves extract	2	779.975	466.145	54.242	658.794	10.37
	6	448.849	459.944	52.740	512.807	43.85
	10	4.153	470.181	59.929	545.356	95.22

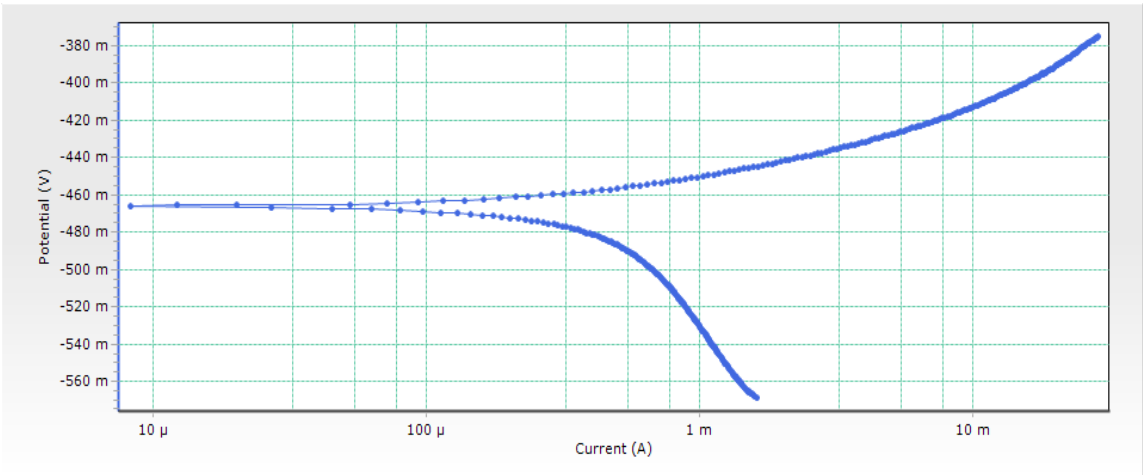


Figure -31: Potentiodynamic polarization curve for mild steel in 1.0 M H_2SO_4

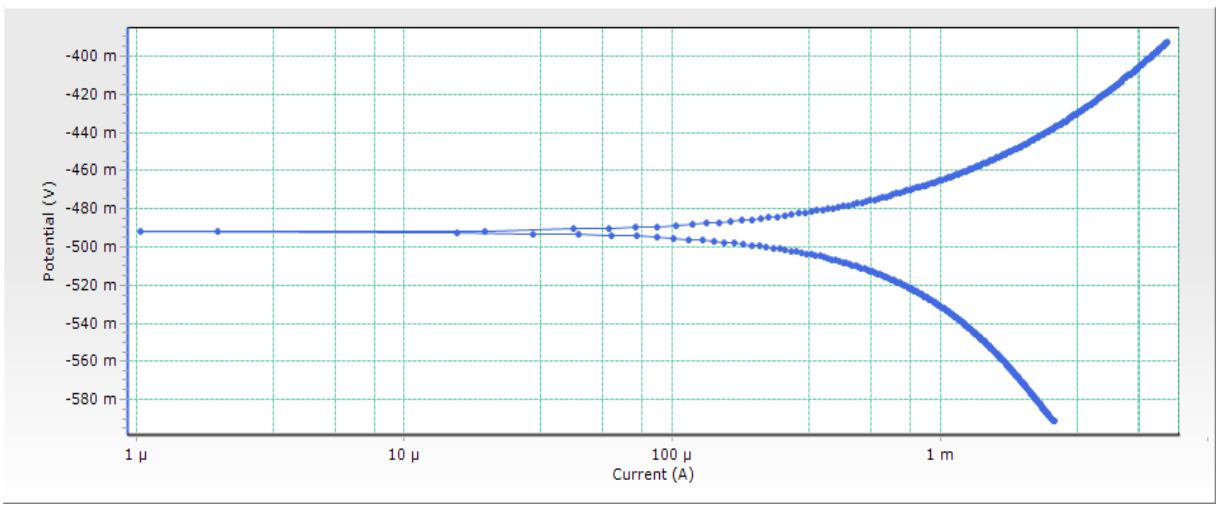


Figure-32: Potentiodynamic polarisation curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 2 % of *Artabotrys hexapetalus* leaves extract

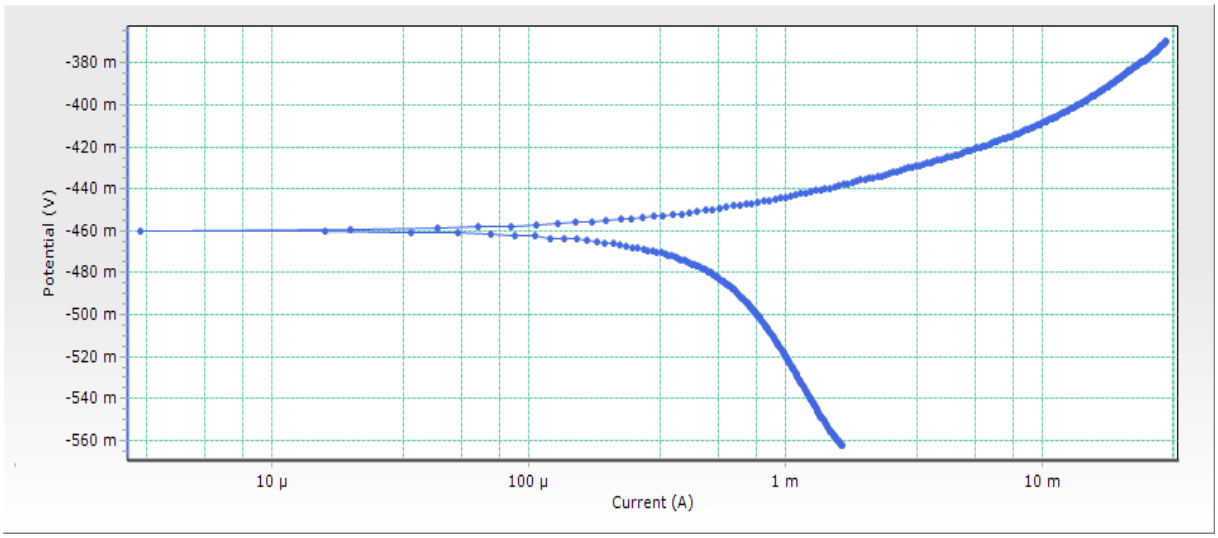


Figure-33: Potentiodynamic polarisation curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 6 % of *Artabotrys hexapetalus* leaves extract

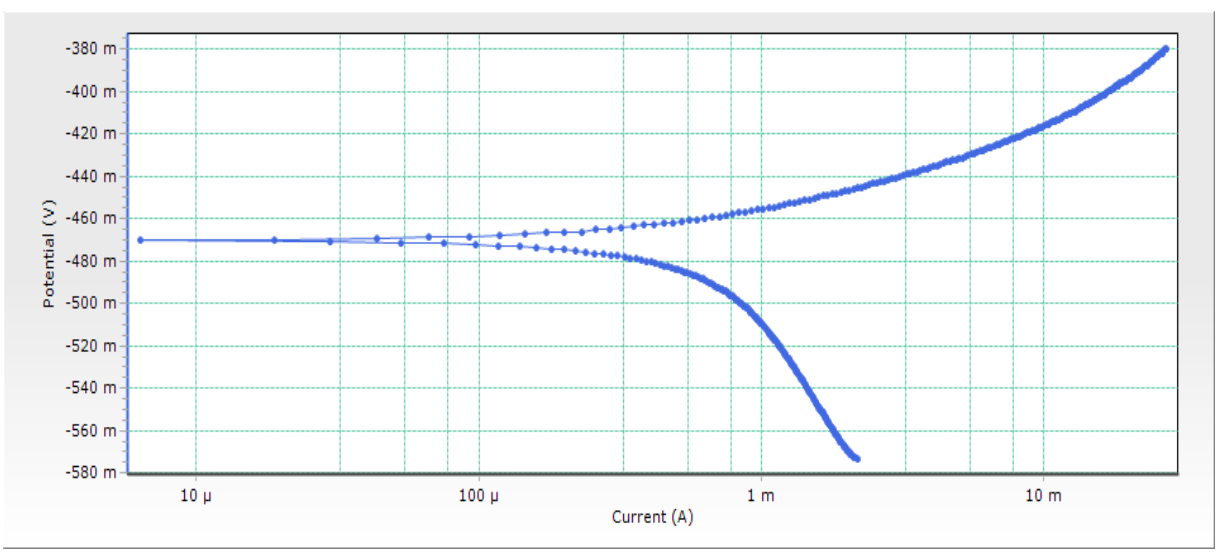


Figure-34: Potentiodynamic polarisation curve for mild steel in 1.0 M H_2SO_4 solution in the presence of 10 % of *Artabotrys hexapetalus* leaves extract

TABLE – 10

Corrosion parameters obtained from impedance curve for mild steel in the presence and absence of inhibitor in 1.0 M H_2SO_4 medium

[Inhibitor], (%)	R_t , Ohm.cm^2	C_{dl}, F/cm^2	Inhibition Efficiency (%)
Blank	31	5.3130	-
2	34	4.6442	12.59
4	42	2.9215	45.02
6	67	0.4582	91.30

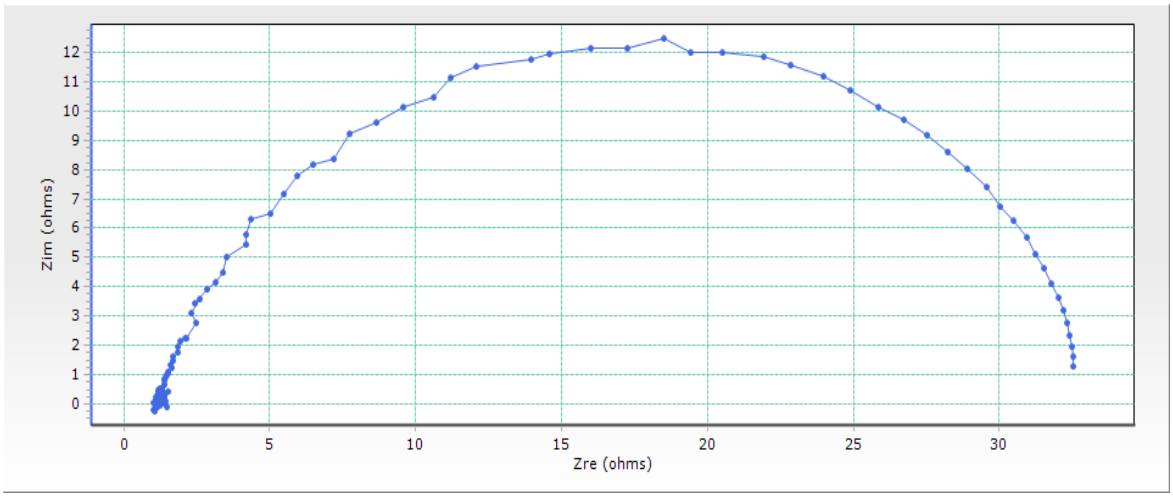


Figure -35: Impedance diagram for mild steel in 1.0 M H_2SO_4

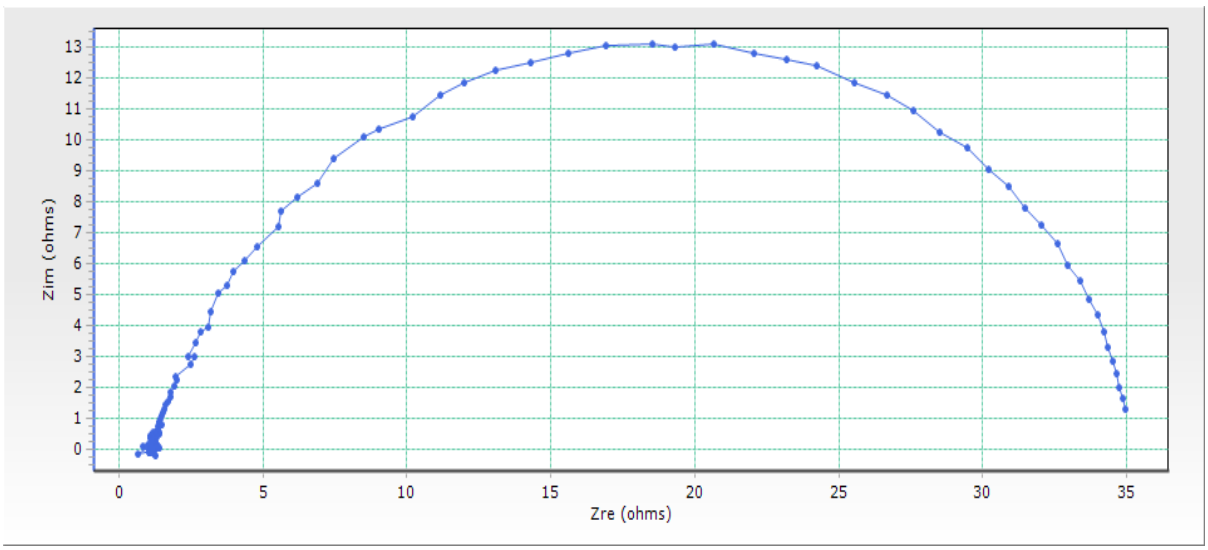


Figure -36: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 2% concentration of *Artabotrys hexapetalus* leaves extract

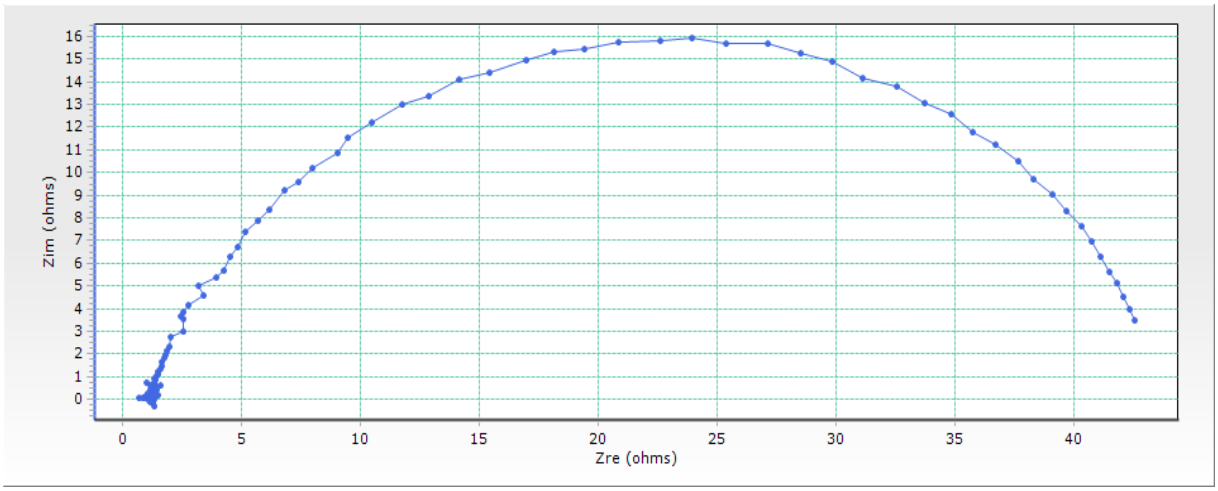


Figure -37: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 6 % concentration of *Artabotrys hexapetalus* leaves extract

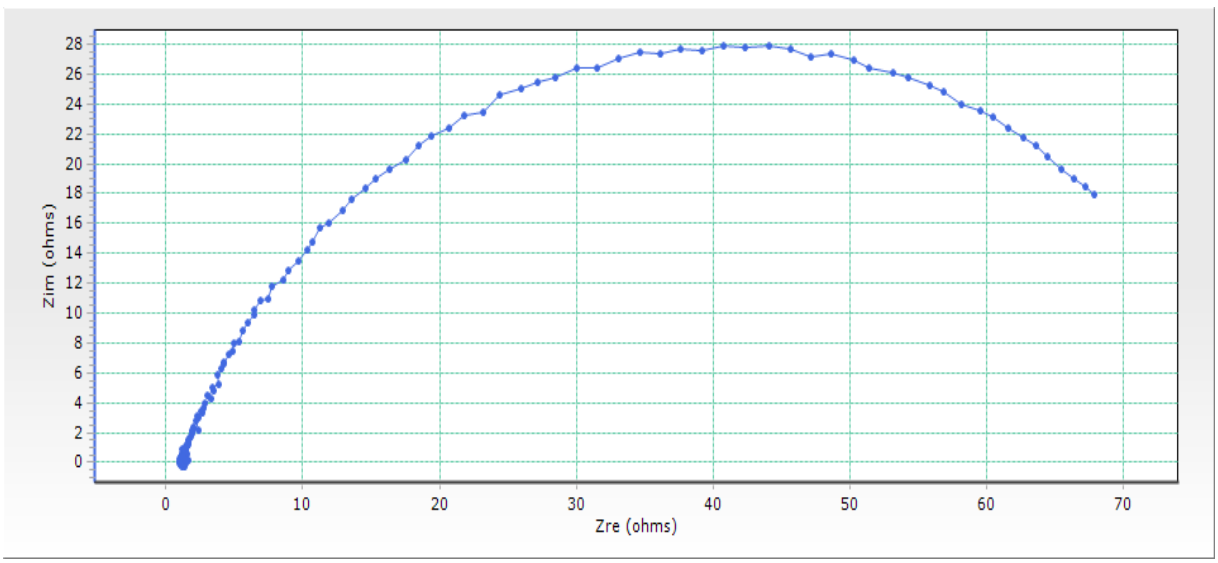


Figure -38: Impedance diagram for mild steel in 1.0 M H_2SO_4 solution in the presence of 10% of *Artabotrys hexapetalus* leaves extract

TABLE-11

Comparison of inhibition efficiency measured by Weight loss, Polarization method and Impedance method

[Inhibitor], (%)	Inhibition efficiency		
	Weight loss studies	**Polarization studies**	**Impedance studies**
Blank	-	-	-
2	11.5	10.37	12.59
6	43.7	43.85	45.02
10	91.2	95.22	91.30

CHAPTER-V

SUMMARY AND CONCLUSION

The inhibitive influence of leaves of *Artabotrys hexapetalus* on the corrosion of mild steel in 1.0 M H_2SO_4 medium was studied by weight loss method, polarization and impedance measurements. The corrosion is decreased with increase in the addition of *Artabotrys hexapetalus* leaves extract probably due to the progressive adsorption of the inhibitor on the metal surface. The maximum inhibition efficiency was found to be 91.2%.

- The corrosion of mild steel in 1.0 M H_2SO_4 solution is inhibited by the addition of leaves extract of *Artabotrys hexapetalus*.
- The percentage of inhibition efficiency increases with increase of the inhibitor concentration.
- The corrosion of mild steel inhibited by leaves extract of *Artabotrys hexapetalus* is attributed to the adsorption of phytochemical components present in the inhibitor onto the mild steel surface.
- The values obtained from the weight loss technique for the studied inhibitor fit well into the Temkin, Florry-Huggins and El-awady adsorption isotherm.
- The values of free energy for the adsorption process indicate that the adsorption of the inhibitor on the mild steel surface occurs spontaneously.
- The leaves of *Artabotrys hexapetalus* prevent the corrosion of mild steel due to the presence of phytochemical components shifting the corrosion into the noble.
- The polarization and impedance study also shows an agreement with inhibitor efficiency obtained from weight loss studies.
- The results obtained suggest that the *Artabotrys hexapetalus* leaves extract is a good corrosion inhibitor for mild steel in 1.0 M H_2SO_4 medium and it can be preferentially use to replace toxic and non-biodegradable inhibitor.

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Post Graduate Project – 12

Synthesis, Spectroscopic Characterization and Antibacterial Screening of Mixed Ligand Cadmium Complex Derived from Nicotinamide and 4-Aminotriazole

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Name of the Candidate: D. Hemalatha

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INTRODUCTION

Chapter -I

1 INTRODUCTION

1.1 COORDINATION COMPLEXES

Coordination complexes are so important in chemistry and biochemistry that some of their basic features are worth knowing and they play an especially crucial role in physiology and biochemistry. Coordination compounds have always been a challenge to inorganic chemists. Today, they comprise a large body of current inorganic research. The rapidly developing field of bioinorganic chemistry is the centre in the presence of coordination with living systems. The vast number of organic ligands and their complexes has been established as an integral part of the general field of coordination chemistry. Metal complexes of biologically important ligands are sometimes more effective than free ligands [1]. Coordination compounds have found application in medicine in the treatment and diagnosis of diseases. Transition metal complexes possess special features like structural arrangements and beneficent applications in the field of catalysis, molecular electronics and medicines. Enormous studies have been reported in the literature in the field of transition metal chemistry mainly due to the development of crystal field theory, molecular orbital theory and various physical, characterization techniques. Metal complexes play a vital role in agriculture, biological, industrial, pharmaceutical and analytical chemistry. Various metal complexes used in these areas are mainly derived from the reactions of Mannich bases, Schiff bases or Mixed ligand complexes [2,3,4].

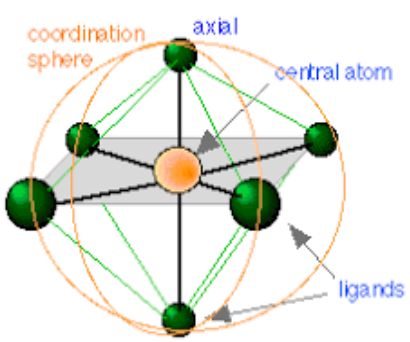


Figure 1.1 Coordination sphere

The fact that coordination compounds have been a great challenge to the Inorganic chemists because of their structure and wide range of application from materials to medicine was identified in the nineteenth century. More recent researches on coordination compounds have been concerned with nearly all the metals in the periodic table, with all coordination numbers from two to twelve and in many oxidation states. The growth of interest in coordination chemistry has been greatly stimulated by developments in catalysis, especially for hydrogenation, activation of carbon-hydrogen bonds and also by the effective role of metals in biochemistry. It has also attracted interest chiefly because of its role in biological processes. One can think, of course iron and magnesium, but there are many others (e.g. copper, zinc, cobalt, molybdenum and manganese). It is known that all metals in the periodic table from vanadium to zinc are essential to human life. Complexes of even the alkali and alkaline earth metals with crown ethers and other cyclic ligands play important biological roles. Other coordinated metals have found their use in the of treatment of disease, e.g. gold compounds for arthritis and platinum compounds for some cancers still others are injected inadvertently and cause disease, e.g. cadmium. Metal complexes of biologically important ligands such 4 – amino pyridine (4AP) are mostly known for their anti-inflammatory, anti-tumor and anti-bacterial activities [5,6].

Coordination compounds have been extensively studied during the past decade due to their attractive structures and topologies as well as their potential applications as multifunctional materials in magnetism, conductivity, luminescence, gas adsorption and storage, catalysis and so on. Although numerous metal-organic complexes have been synthesized, rational control in the synthesis of coordination compounds have been synthesized, rational control in the synthesis of coordination compounds has been a great challenge even now. The study of mixed complexes is becoming increasingly more important in equilibrium chemistry. Using stability constants, the chemical behaviour , coordination ability ,coordination mode and the relation regarding the structure and stability of the complexes can be obtained , and its basis of enzyme-mimicking investigation[7,8].

1.2 METAL COMPLEXES

Chiral metal complexes are well known for their use as catalysts especially in asymmetric synthesis, asymetric epoxidation or shapeless epoxidations and resolutions of racemes compounds. Light catalyzed inversion and diastereoisomeric equilibration in chiral metal

complexes have been studied extensively. Some metal ligand complexes are found to catalyze reaction such as oxidation, oxidative cleavage, hydroformylation etc., and have shown catalyzes like activity in decomposition of hydrogen peroxide. Phthalocyanines have found wide application in diverse areas .It is well established that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances. The binary and ternary transition metal complexes of transition metals are commonly found in biological activity [9, 10]. Metal complexes of transition metals are commonly found in biological systems. During recent years metal complexes of some nitrogen donor ligands have attracted considerable attention because of their greater antifungal and antibacterial activities than those of the parent ligands. Ternary complexes containing amino acids as a secondary ligands are of significance as they are potential models for enzyme- metal ion substrate complexes. There are many reports on the transition metal malonates with structural and magneto structural characterization [11].

Metal ions can be introduced into a biological system either for therapeutic effect or as diagnostic aids. It has been found that metals like copper, zinc, cobalt and iron bound to ligand containing oxygen, nitrogen or sulphur show enhanced property of antihypertensive drugs, antimalarial, antimicrobial, electron transfer or any type of oxygen transport reaction[12]. On the industrial side, metal complexes of copper, nickel, cobalt and chromium have a wide range of applications such as dyes and pigments.

The first row transition metal like chromium, nickel and copper generally give colored complexes and the IIB group elements zinc, cadmium and mercury give colorless complexes as their d-orbitals are completely filled. The chemistry of these metals is discussed brief in the following section [13].

The pyridine complexes show different thermal behavior from the other amine complexes. The amines form complexes through the donation of a single pair of nitrogen electrons to the metal, whereas in the case of pyridine the nitrogen atom is incorporated into a conjugated ring system, and therefore, acts as a π-acceptor (through a delocalized orbital) as well as a donor ligand, indicating a higher interaction of pyridine moiety, and thereby, decomposing in different ways from the other amine members.

1.3 MIXED LIGAND COMPLEXES

Mixed ligands are significant interest not only for their pharmacological properties as antibacterial, antifungal and anticancer agents but also for their capacity for chemical recognition of anions and metals of biochemical and environmental importance. The coordination chemistry of are current interest because they can provide new materials with useful properties such as magnetic exchange, electrical conductivity, photoluminescence, nonlinear optical property and antimicrobial activity. The biological importance of mixed ligands complexes is that they are sometimes more effective than the free ligands. Mixed ligands complexes containing nitrogen and oxygen donors are important owing to their antifungal, antibacterial and anticancer activities [14].

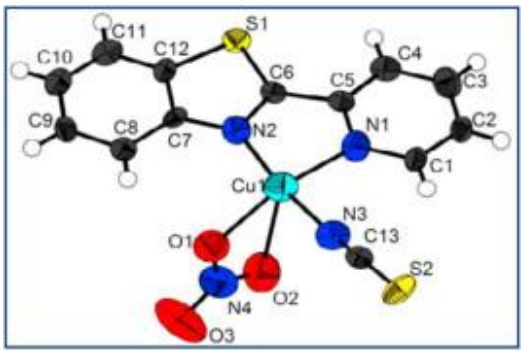


Fig 1.3 Mixed ligand complex

Mixed ligands complexes differ from traditional complexes in the sense that they are having at least two different kinds of ligands associated with the same metal ion in a complex. The presence of more than one type of ligands in a complex increases chances of variation in properties expected for the complex. This makes the researcher interest in the synthesis of mixed ligand complexes is gaining importance day to day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publications are devoted to synthesis and characterization of mixed ligand complexes [15,16].

1.4 ANTI MICROBIAL STUDIES

Antibacterial resistance is becoming an important and challenging problem with the rapid increase in number of the multidrug resistant microbial pathogens. Some previously treatable pathogens are now becoming untreatable, like methicillin-resistant staphylococcus aurous and vanomycin –resistant entercoccus, isoniazid resistant M.tuberculosis and klebsiell pneumonia [17, 18, 19]. In spite of a large number of antibiotics and chemotherapeutics available for medical use, at the same time the emergence of old and new antibiotics resistance created in the last decades revealed a substantial medical need for new classes of antimicrobial agents. Due to the outbreak of infectious diseases caused by different pathogenic bacteria and the development of antibiotic resistance, researchers are searching for new antibacterial agents.

The treatment of infectious diseases still remains an important and challenging problem because of a combination of factors including emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens. In spite of a large number of antibiotics and chemotherapeutics available for medical use, at the same time emergence of old and new antibiotic resistance created in the last decades revealed a substantial medical need for new classes of antimicrobial agents. There is a real perceived need for the discovery of new compounds endowed with antimicrobial activity, possibly acting through mechanism of action, which is distinct from those of well-known classes of antimicrobial agents to which many clinically relevant pathogens are now resistant.

Due to outbreak of infectious diseases caused by different pathogenic bacteria and the development of antibiotic resistance, researchers are searching for new antibacterial agents. Therefore, new antimicrobial agents and nanotechnological materials have to be synthesized for the treatment of resistant bacterial diseases. The field of bioinorganic chemistry, which deals with the study of role of metal complexes in biological systems, has opened a new horizon for scientific research in coordination compounds. A large number of compounds are important from the biological point of view.

Biologically relevant metal complexes have several requirements in terms of their synthetic design. First, a biologically active metal complex should have a sufficiently high thermodynamic stability to deliver the metal to the active site. The metal-ligand binding should

be hydrolytically stable. The kinetics with which the metal ion undergoes ligation or deligation reactions is of great importance. The molecular weight of the metal complex is also critical. The compounds of low molecular weight with neutral charge and some water solubility are soluble in almost any medium and may slip through biological membranes by passive diffusion.

Generally, drug combinations have proven to be an essential feature of antimicrobial treatment due to a number of important considerations; (1) they increase activity through the use of compounds with synergistic or additive activity; (2) they thwart drug resistance; (3) they decrease required doses, reducing both cost and the chances of toxic side effects; (4) they increase the spectrum of activity.

1.5 APPLICATIONS

The importance and role of coordination compounds in living systems are well established. The coordination complexes which are found in plants, minerals and animals are of great significance because they exhibit important functions in the environment. The synthesis of newer organic chelating agents that can coordinate with transition metal ions have tempted the researchers to synthesize more and more coordinate compounds as a great challenge to the present day chemist. The application of coordination chemistry to medicine is a rapidly developing field. Some pharmaceutical agents contain examples of coordination metal compounds which are of current clinical use [20, 21] and new areas of applications are rapidly emerging. The important applications of coordination compounds find use in qualitative and quantitative chemical analysis. Many familiar color reactions are given by metal ions with a number of ligands. The importance of metal complexes in coordination chemistry gives various applications in biological processes such as photosynthesis and dioxygen transport.

Haemoglobin, the red pigment of blood which acts as an oxygen carrier is a coordination compound. The coordination compounds are used as dyes and pigments [22]. They are used as catalyst for many industrial processes [23] and other transformations of organic and inorganic chemistry. Thus coordination compounds find its applications in the area of biological function system, industry and medicine. It is also used as radiotherapeutic agents[24].These complexes also have applications in analytical, industrial, biological, clinical, biochemical, antimicrobial,

anticancer, antifungal and antitumor activity[25-29]. In addition, it also play a important roles in ranging from anticorrosion, soil treatment agents and medicinal agents.

Numerous transition metal complexes are of special interest in industry, medicine in biology, e.g. the electrical and thermo chromic properties, anti oxidation, vulcanization acceleration, protecting paintings, catalyses and antibacterial properties. So for a number of solid-state reactions of coordination compounds (such as thermal isomerization, conformational changes, polymorphic transformations, thermal phase transition, thermochromism) have been studied and they have readily entered into the scientific basis of co-ordination chemistry [30,31,32].

Presently transition metal complexes have attracted the attentions of inorganic, metallo-organic as well as bio-inorganic chemists because of their extensive application in wide ranging area from material to biological sciences[33], for e.g., as vulcanization agents, protector for painting, catalyst, antioxidants and in pharmaceuticals[34]. Several metal complexes are known to accelerate the drug action and they are also therapeutically important viz., platinum (anticancer), gold (antiarthritic), bismuth (antiulcer), antimony (antiprotozoal), vanadium and chromium (antidiabetic), iron (antimalarial), nickel and copper (antitumor), sliver, cadmium and mercury (antibacterial). Metal ions are electro deficient, whereas most biological molecules (proteins and DNA) are electron rich. Consequently, there is a general tendency for metal ions to bind and interact with many important biological molecules. The efficacy of the various organic therapeutic agents cans often the enhanced [35] when they are in coordination with a suitable metal ion. The pharmacological activity of metal complexes is highly dependent on the nature of the metal ions and the donor sequences of the ligands because different ligands exhibit different biological properties [36]. Metal complexes containing oxygen donor ligands as a primary ligands and heteroaromatic N-bases as an auxiliary ligand have been of special interest as they can display exceptionally high stability [37]. Metal complexes of pyridine derivatives have also been successfully used as model systems for the design of new metallo-pharmaceutical compounds [38].

1.6 NICOTINAMIDE

Nicotinamide, also known as niacinamide is the amide of nicotinic acid (vitamin B3/niacin). Nicotinamide is a water soluble vitamin and is a part of vitamin B group. Niacin is converted to nicotinamide in vivo [38]. Nicotinamide as a neutral ligand is a part of the pyridine nucleotides as NADC and NADPC, which takes part in redox reactions [39]. The deficiency of the vitamin niacin causes pellagra, a human disease characterized by weakness, diarrhea, dermatitis and nervous disorders. The interaction of nicotinamide with transition metal elements is important for understanding the effect of it on vital organs, thus a number of nicotinamide complexes have been investigated both structurally and spectroscopically [40,41]. Nicotinamide is one of the essential compounds for growth cells and its excess in human body causes increase of lipid peroxidation and its shortage decreasing level of antioxidants such as Vitamin E, or glutathione [42]. Moreover, nicotinamide is known as substance helping against cell apoptosis caused by free radical presence, it is frequently used in treatment of different skin diseases or in prevention against some neurodegenerative diseases as Alzheimer one.

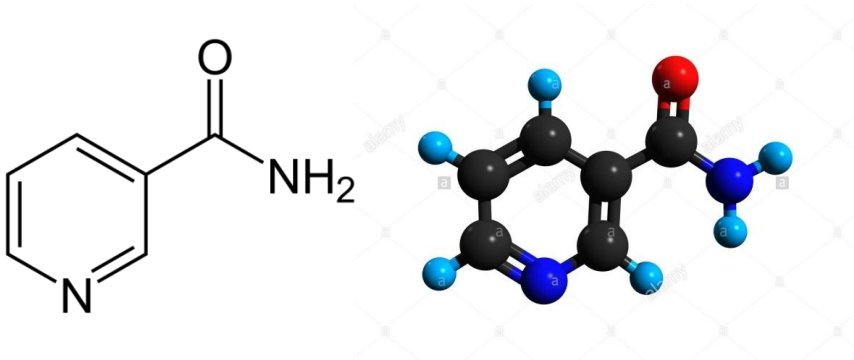


Figure 1.6 Structure of Nicotinamide

1.7 Chemistry of cadmium

Cadmium is almost invariably found in small amounts in the zinc ores. It is obtained as a by- product in the metallurgy of zinc. Cadmium is electropositive as zinc. Hence in many of its chemical properties it resembles zinc, but it is less reactive. It is very slowly affected by moistened air and it does not react with cold water. Cadmium rods are used in atomic reactors to

slow down the nuclear reactions as it is a good absorber of neutrons. It is also used in western standard cell. The $d^{10}s^2$ configuration of cadmium has a tendency to lose the s electron to form stable +2 cations and $cd^{2}{}_{2}{}^{+}$ [43]. There is no ligand field stabilization effect in cd^{2+} ions because of the completed d-shell; the stereochemistry is determined by considering the size, electrostatic force and covalent bonding forces. Organo cadmium compounds are of great interest due to their mild reactivities toward certain organic functional groups, which imparts them unique synthetic potentialities.

Cadmium appears to be one of the most important metals in biology. More than twenty five cadmium containing proteins have been identified, most of them are enzymes. The cd^{2+} ion is present in several dehydrogenises, aldolases, peptidases, phosphatases, transphophorylase and phospholipase attesting to its importance in carbohydrate, lipid and protein metabolism and virtually in all organisms [44]. Among the enzymes, the most thoroughly studied are aldol dehydrogenises, alkaline phosphatases of bacteria, carboxyl peptidases and metallo thioneins.

Metallothioneins are found in kidneys, liver and the gut of horses, rabbits and human beings. They have the molecular weight of 10,000 Dalton units and Cd contains 9% of weight of the metal and nearly one third of their amino acid residues are cysteines. The metal content is mainly zinc but an appreciable fraction is cadmium. The same factors that favor the formation of certain complexes in the laboratory probably are also important in biological systems [45].

LITERATURE SURVEY

REVIEW OF THE LITERATURE

The aim of the present work is to synthesis and characterize the Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) mixed ligand metal complexes with primary ligands derived from benzofuran-2-carbohydrazide and 3,4,5-trimethoxybenzaldehyde (TMeOBFC) and secondary ligand as malonydihydrazide (mdhz).

Rajasekar et.al have synthesized mixed ligand complexes with bioactive phenacemide and thiocyanate ion and reported the antibacterial and anti-fungal activity by Kirby Bauer disc diffusion method. He also reported the antimicrobial activity of the mixed ligand complexes from microwave assisted synthesis with 4- aminopyridine and Thiocyanate [46].

Dilip et.al reported that Cr(III), Co(II), Ni(II), Cu(II) and Cd(II) metals coordinate with pyridine nitrogen of nicotinic acid ligands which acts as a monodentate ligand and the proposed geometry of the complexes are distorted octahedral with Cr, Co and Ni, pseudotetrahedral with Cd and Tetragonal with Cu [47].

The mixed ligand complexes have been characterized on the basic of elemental analysis, electrical conductance, room temperature, magnetic susceptibility measurements, spectral and thermal studies. Probable structures have been suggested for the mixed ligand complexes on the basic of the results of elemental analysis and various physic-chemical studies.

Mixed ligand nickel (II), copper(II) and zinc(II) complexes of nicotinanilide and thiocyanate were prepared and their electrochemical and biological properties were discussed [48]. Balan et.al have studied the structure of nicotinanilide and thiocyanate metal complexes. He performed cyclic voltammetric studies for all the complexes and differentiated the oxidation and reduction processes and indicated that the CV studies exhibit one electron irreversible process.

Microwave-associated synthesis of mixed ligand complexes of Zn(II), Cd(II) and Hg(II) derived from 4- aminopyridine and nitrite ion were reported by Dhaveethu et.al [49]. Microwave assisted synthesis and structural characterization of nicotinic acid and nitrito-ko mixed ligand complexes were reported and their geometry was interpreted by various characterization techniques.

Foziah et.al have reported the thermal studies of the alkaline earth metal nicotinamide complexes. She proposed that the complexes are non electrolytic in nature and the anions are coordinated to the central metal ion [50].

Guang et.al have reported the synthesis and crystal structure of non-interpenetrating metal organic coordination networks constructed from Cd(II) with thiocyanate and nicotinic acid. By using bridging ligands instead of monodentate ligands, they are successfully extended the one dimensional chain structure into two dimensional networks through covalent or the hydrogen bonds.

Bio potential efficiency and DNA cleavage applications have been reported for mixed ligand complexes using nicotinamide and nitrite as primary and secondary ligands respectively. Dilip et.al have proposed the probable structure for metal complexes with metal ions such as Ni, Co, Cu, Zn, Hg and also stated that chromium complex alone have bridged ligands and confirmed by IR spectroscopy[51].

Marijina et.al reported the thiocyanate complexes of group 12 metals with pyridine-2- carboxamide and the crystal structure of the complexes have been elucidated by X-ray diffractometer. Here the thiocyanate shows a number of bonding modes with group 12 metals as terminal and bridging ligand. In the structure investigation of Zn and Hg complexes with thiocyanate, the authors proposed that both the N-donor and S-donor thiocyanate ligands can act as a bridged and terminal which are coordinated to mercury in a nonlinear fashion whereas the coordination sphere along the zinc ions are distorted tetrahedral in structure [52].

It was proposed that the nicotinamide complexes are six coordinate with a metal ion through nitrogen atom. Chandrasekaran et.al have reported the synthesis and characterization of metal complexes with FCNH ligand. He proposed that the ligand coordinate to the metal as a neutral bidentate ligand and possess octahedral geometry [53].

Angela et.al have reported the synthesis and structural studies of mixed ligand coordinate through both the N and O atoms. Cu complex behaves as a dimer with four bridges between acetate ions and Cu(II).

Novel mixed complexes of isoniazid and ascorbic acid have been synthesized and revealed the bi-dentate coordination of isoniazid ligand to the metal through the oxygen of the carbonyl and nitrogen of the amine group and ascorbic acid coordinating through the carbonyl and C-2 enolic hydroxyl groups. The antimicrobial studies of the synthesized compounds on micro-organisms such as: Escherichia coli, Staphylococcus aureus, Pseudomonas aureginosa and Salmonella typhi have good antimicrobial activities [54].

El-masry et.al have reported the synthesis and antimicrobial activity of some benzimidazole derivatives incorporated into a triozole moiety. A number of arylidine hydrazones incorporated into the parent benzimidazole were also synthesized [55]. Ishar et.al have proposed that the copper halide complexes with nicotinamide, nicotinic acid exhibit significant antimicrobial activities [56]. Isonicotimide zinc complexes have more stability due to intra and inter molecular hydrogen bonding formed between the aromatic rings [57].

Sabbir et.al have prepared the nicotinamide complexes in aqueous medium in the ratio 2:1. They conclude that the compounds do not contain any chemically coordinated water molecules [58].

Lawal et.al have confirmed that the nicotinamide co-ordinate to the metals ions through the pyridine ring nitrogen atom. Nicotinamide act as a chelating ligand and it possesses good antimicrobial and antifungal activity [59].

Khawla have proposed the structure of the mixed ligand complexes with isoniazid and aminoacids to be distorted octahedral. These complexes show positive activity against tuberculosis bacteria [60].

Mariana et.al have proposed the copper and cobalt complexes with isoniazid perform as a very good anti tuberculosis agent. Here the copper complex acts as a polymeric complex where the cobalt complex exhibits octahedral geometry [61].

Pooja singh et.al have described the synthesis and characterization of hydrazone derivative with different metal ions. Here the O-hydroxy acetophenone, 2- thiophenoyl hydrazone acts as a tridentate ligand. The ligand and its metal complexes act as a corrosion inhibitor [62].

Ramadevi et.al have reported the synthesis of isoniazid complexes with different aldehydes and revealed the cytotoxic studies of the compounds are less than the clinically used cis platin drug [63]. The recrudescence of tuberculosis (TB) coincident with the spread of AIDS is nowadays a challenging health problem all over the world.

The search for new anti-mycobacterial agents is justified by many important reasons, mainly: (a) the emergence of multidrug resistant (MRD) strains of Mycobacterium tuberculosis; (b) the spreading of opportunistic infections due to non- tubercular mycobacterium (NTM), M. avium complex (MAC) in particular; (c) the poor effectiveness of the present treatment on immune depressed patients; (d) the complexity of the current therapeutic regimens.

Bottari et.al have discovered novel against TB and other AIDS-associated pathologies, by modifying the structure systematically and consequently the chemical-physical features of Isoniazid (INH). INH and its hydrazones have been reported as forming stable metal complexes behaving as mono-, bi-and sometimes poly-dentate ligands [64]. A number of these complexes possess ant tubercular activity. In particular some reports demonstrate that the capture of INH and ISNEs by both INH-resistant M.tuberculosis strains is enhanced by copper (II) ions [65, 66].

Sindhuja et.al have synthesized and characterized the mixed ligand metal complexes of nitrite and nicotinamide ligand for various metal ions. Here the Fe, Mn and Co complexes possess distorted octahedral geometry. The antimicrobial activities of these complexes were studied by growth curve method and mentioned that the Mn and Fe complex act as a supportive agent and Co complex acts as an inhibiting agent against the microbes [67].

In the search for novel vitamins-metal complexes, the modification of existing vitamin by coordination to a metal ion has attracted considerable attention in recent years. This has led to lots of study on vitamin-metal complexes, with the hope of improving and enriching the quality of existing vitamins, thereby serving as better substitute as chemotherapeutic agents (Obaleye and Orjiekwe (1933).

Despite the fact that some metal complexes of vitamins: ascorbic acid, thiamine hydrochloride, pyridoxine have been reported in literature (Franklin and Richrdson) (1989), Thompson (1980), Adeyemo(1981), Cramer et.al (1984), Hadjiliadis and Yannopoulous(1983).

Very few reports on the synthesis and characterization of nicotinamide have appeared in literature [69].

Werner who organized the subject by put forward in his coordination theory in (1893) on the basic of old history which was the invention of [Co $(NH_3)_6$] cl_3 by Tassaert in 1798 [70]. Mittal, et.al.,(2009) had synthesized and characterized metal complexes of analytical, physical and spectral data.

H. Ellison and A.E. Mattel [71] determined the equilibrium measurements of the interactions of the polyphosphate anion with Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) ions Potentiometrically and data was interpreted in terms of equilibrium constants for the formation of a chelate compound containing both a metal and a hydrogen ion together with the normal chelating agent from which all dissociable hydrogen‟s are displaced.

Joshi and Bhattacharya [72] determined the formation constants of Cd(II), Cu(II), Ni(II), Zn(II), Be(II) and Ag(l) by using the Irving-Rossotti titration method. They reported that above mentioned complexes are more stable than the corresponding hydroxyacid complexes, indicating there by a general preference of these metal ions for coordination with nitrogen in comparision to oxygen.

Von Euler [73], in addition to potentiometric method also used the solubility measurements to determine overall stability constants of complexes of Ag(I) with ammonia and several amines. He also studied ammonia and pyridine complexes of zinc, cadmium & nickel.

Albert [74] determined the stability constant of the complexes of divalent metal ions of Mg, Mn, Fe, Co, Ni, Cu and Zn with serine, -alanine, phenylalanine and methionine, using Bjerrum‟s method. The following order of stability of complex formation amongst the metal ions was found: Mg(II) Mn(II) Fe(II) Co(II) Zn(II) Ni(II) Cu(II).

Ahmed et.al [75-76] have conducted a detailed study of the amino acids complexes of certain metals in their unusual oxidation states by using pH-metric and Potentiometric methods. Stability constants were calculated by Bjerrum‟s method. They found that there seems to be no definite relationship between the nature of an amino acid and the stability constant of its resulting complex.

Barrio et.al [77] determined the stability constants of Zn(II) and Pb(II) complexes with several amino acids by Potentiometric method. This method gives not only the apparent stability constants of ML type complex but also the acid constants of MLHx type complex. A hanging drop Pb or Zn amalgam electrode was used as the indicator electrode of pPb and pZn respectively.

Rey and Co-worker [78] investigated the complexation equilibrium of L-Serine and L-Leucine with Ca(II), Mg(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) at 25ºC, I=0.1M KNO_3 in various ethanol-water media. The equilibrium constants of the complexes formed were discussed in terms of the acid-base characteristics of the amino acids and the properties of the cat ions concerned.

Ahmed Malik and Farooq [79-83] have investigated systematically the chelating behavior of a number of amino acids with various metal ions in unusual oxidation states. The stability constants of the complexes were evaluated by studying the formation curves obtained from pH-metric and Potentiometrically methods. No definite trend and correlation have been suggested as the resulting complexes were not isolated and characterized.

Tombeax et.al [84] carried out the Potentiometric study of Ag(I) complexes of sulphur containing amino acids in aqueous phase by simultaneous pH and pM measurements at 25ºC and 0.5 M KNO_3. Complexes, in the acid medium, are formed only through the thioether group and the carboxylate group is not involved. In alkaline medium, both the thioether and amino groups are bound in the tetrahedral chelates.

Perrin [85] calculated the stability constants of divalent and trivalent-Iron complexes with 20 amino acids by Potentiometric titration method. Molar electrode potentials for Fe^{3+}/Fe^{2+} amino acids complexes show a linear relationship with logarithm of dissociation constants of amino acids, as computed from these result.

Clarke and Martell [86] studied the Chelate systems resulting from the interactions of Ca(II), Mg(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with Ornithine, Citruline and arginine and reported the formation constants of chelates containing 1:1 and 1:2 molar ratios of metal ion to mono-protonated ligands.

Maley and Mellor [87] reported the stability constants for glycine, alanine, valine and leucine complexes of copper, zinc, cobalt and manganese. However the elaborate studies on the avidity of amino acids with trace metal ions was conducted by Albert [88] , wherein he computed the overall stability constant (Ks) for the complex formation between amino acids having only two ionizing groups like glycine, L-proline, DL-serine, DL-methionine, DL-tryptophan, DL-phenylalanine, DL-norleucine, DL-valine, L-asparagine, β-alanine and taurine with metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+} and $Fe2^{+}$.

Perkins [89] determined the stability constants by using Potentiometric method in which ratio of amino acid to metal was 2:1 for bivalent and 1:1 for univalent metals. Group II metal ions form complexes with very low stability constants as compared to group 12 metals which form complexes with very high stability constants.

Muenz [90] determined the stability constants of the 1:1 and 2:1 complexes of EDTA with Pb(ll), Mg(ll), Cd(ll), Cu(ll) and La(lll) by calculating the free energies of complex formation by a method based on a electrostatic model taking into account the covalent interactions. The results agreed well with known experimental data. The decrease in the stability with successive ligand addition and the chelate effects are only due to the action of repulsive forces and excess free energy changes.

Berezina and co-workers [91] reported the stability constants and thermodynamic parameters of complex formation for MA+ and MA2 complexes were M stands for Mn (II) and A stands for serine, methionine, norvaline, tryptophan, phenyl-β-alanine and α-alanine. The relative stabilities of the complexes were discussed. The 1:2 complexes were formed only in the presence of the large excess of amino acids in the solution.

Rangaraj and Ramanujan [92] determined the stability constants of Uranyl complexes with glycylglycine, DL-α-alanine, DL-valine, L-asparagine, αamino-butyric acid and DL-β-phenylalanine using pH titrations at 310ºC, 0.1M ($NaClO_4$) ionic strength and pH 1.7 to 3.5. Ionization constants were determined for the ligands under the same experimental conditions; 1:1 complexes were formed in all the cases.

T. Kiss and co-workers [93] studied the stability constants of the mixed ligand complexes of L-dopa, L-tyrosine, L-phenylalanine and dopamine with copper (ll) and nickel (ll)

ions and 2, 2‟-bipyridyl and 1,10-phenanthroline pHmetrically at 250ºC and an ionic strength of 0.2 mol/dm3 (KCl) . Spectral studies were made to establish the binding mode of the ambidentate L-dopa in the ternary complexes. In contrast with the aromatic (N, N) donar atoms, the (O, O) binding mode of L-dopa is particularly favoured in its ternary systems with copper (II) and nickel (II).

A. Corsini and E. J. BillO [94] studied the stability of metal chelates of the rigid ligands: 4-amino-5-hydroxyacridine and 4, 5-dihydroxyacridine and compared results with existing data for several 2-substituted 8- hydroxyquinoline. They have explained stability effects in terms of ring strain and substituent steric hindrance.

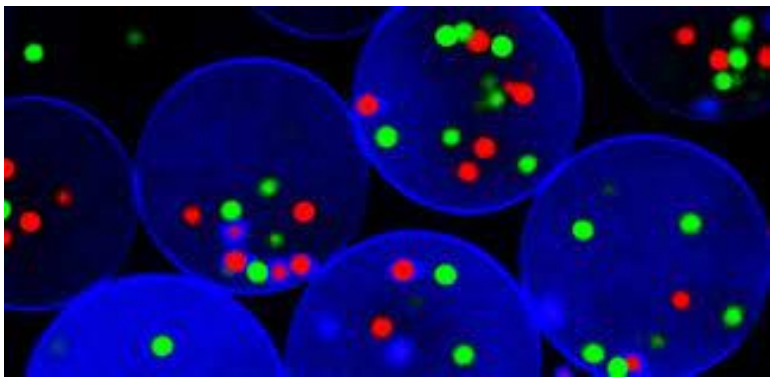
Flood and Loris [96] have reported the equilibrium constant of glycine with copper, nickel, cobalt, zinc, cadmium and mercury. The order of stability among various metal complexes has been found to be: Hg(II) > Cu(II) > Ni(II) > Zn(II) > Co(II) > Cd(II).

Karezynski and co-workers [97] have determined stability constants of Cu(II) complexes with some amino acids and peptides by Bjerrum‟s method. Computed values have been reported. Masood and co-workers [98] have investigated the complexing behavior of Co(II), Ni(II), and Cu(II) with S-containing amino acids by pH-metrictechnique in the temperature range of (25-40)ºC. The thermodynamic parameters have been evaluated and the effect of the transition metal ions on the mode of ionization of the ligands is discussed.

Kabiruddin and Zubaida [99] have used polarographic technique to study the complexing behavior of Cd(II) with some amino acids as the primary ligand and 2, 2-bipyridyl as the secondary ligand. Dissociation constants of the amino acids have been calculated and the stability constants of binary and ternary complexes have been determined.

Nair and co-workers [100] have determined the stability constants of heterobinuclear complexes, formed in aqueous solution with the biologically important ligands viz, L-dopa, dopamine and L-Histidine by Cu(II)-Ni(II), Cu(II)-Zn(II) and Ni(II)-Zn(II) and L-Cysteine and D-pencillamine with Ni(II)- Zn(II) by computation of pH titration data.

AIM AND SCOPE



Chapter - III

AIM AND SCOPE

The present work aims at the preparation of the coordination complex of cobalt using Nicotinamide and 4- amino triazole as ligands.

To arrive at the composition and structure of the complexes, it is proposed to

1. **Measure the electrical conductivity of complex solution in acetonitrile, to find whether the complex is ionic or neutral.**
2. **Compare the infrared spectra of complexes with those of parent ligand, to determine the coordination position of the ligands.**
3. **Record the electronic spectra of the complexes, which will throw light on the probable geometry of the complexes.**
4. **To test the antimicrobial activity of the complex and pure ligands.**

CHARACTERIZATION TECHNIQUES

4.1 CONDUCTANCE

Conductivity is a physical property with an inclusive range of applications in various chemical and biochemical approaches [1,2]. The notion of conductance has miscellaneous application in judging solvent purity, ionic strength of solutions, dissolution kinetics, critical micellar concentrations, enzymatic reactions and thermodynamic data. The molar conductivity is given by the following equation.

$$\Lambda m = k/C$$

Where k and C are specific conductivity and concentration in mol cm^{-3}, respectively. The unit of molar conductivity is $\Omega^{-1}cm^2\,mol^{-1}$. However, molar conductivity is a characteristic property of chemical substances independent of concentration. The studies of electrolytic behavior of metal complex solutions provide brief details about their nature and composition. The ionic species in solution carry more conductance value than that of the non electrolyte. Like other physicochemical methods, molar conductance has been used for structural elucidation of newly synthesized metal complexes [3 – 13]. The tentative structures of the metal complexes can be easily established by molar conductance data. Molar conductance data predict the electrolytic and non-electrolytic nature of metal complexes. It is also used to determine the Metal- Ligand stoichiometry. Moreover, ligand sizes of structurally relevant complexes, the amount of ligand forming part of a complex and the solution structures of metal complexes can be easily obtained from their molar conductance data [16].

The Molar conductance range for non-electrolytes and electrolytes in different solvents were predicted in the table given below

Molar conductance ranges for nonelectrolytes and electrolytes in different solvents

S. No.	Solvent	Non-electrolyte molar conductance range ($\Omega^{-1}cm^2mol^{-1}$)	Electrolyte molar conductance range ($\Omega^{-1}cm^2mol^{-1}$)
1	Nitromethane	<70	>75
2	Nitrobenzene	<20	>20
3	Acetonitrile	<120	>120
4	Acetone	<95	>100
5	DMF	<60	>65
6	Methanol	<80	>80
7	Ethanol	<30	>35
8	DMSO	<50	>50
9	Water	<80	>118

Table 4.1 Molar conductance ranges for nonelectrolytes and electrolytes in different solvents

Accordingly, the formula of the complex whether it is associated or dissociated or polymeric might be assigned.

4.2 INFRA RED SPECTRA

When Infrared light is passed through a sample, some of the frequencies of the sample are absorbed while other frequencies are transmitted through the sample without being absorbed. The resulting plot of percent transmittance or percent absorbance against frequency is an Infra red spectrum. The IR spectroscopy is widely used as a characterization technique for metal complexes. The basic theory involved is that the stretching modes of the ligand changes upon complexation due to weakening or strengthening of the bonds involved in the bond formation resulting in the subsequent change in the position of the bands appear in the IR spectrum. The changes in the structural features of the ligands are observed with the bands observed mainly in

the fingerprint region 4000-400 cm^{-1}. The bands due to the metal ligand bonds are observed in the far IR region 600-100 cm^{-1} [1].

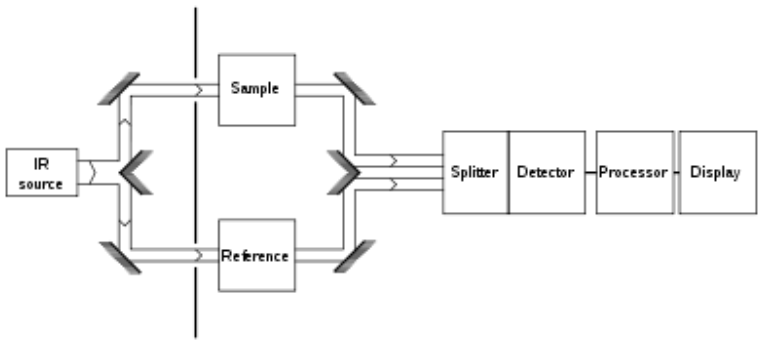


Figure 4.2 I R instrument

In contrast to UV spectroscopy, the IR spectrum provides a rich array of absorption bands which can provides a wealth of structural information about a molecule. It provides methods for studying materials in all three physical states i.e., gas, liquid or solid. Analytically useful IR spectrum covers the following range of the electromagnetic range.

Infrared spectroscopy gives valuable information on the mode of bonding between the metal ions and the coordinated ligands through various frequencies of peaks in the complex. Far-infrared spectroscopy provides metal-ligand vibrations in the metal complexes. The information contained in an IR spectrum originates from molecular vibrations. These are either fundamental modes that are associated with the vibration of specific functional groups, complex modes of the total molecule, vibrational overtones or summational modes of fundamental vibrations. IR analysis may simply involve the characterization of a material with respect to the presence or absence of a specific group frequency associated with one or more fundamental modes of vibration or by a complex pattern recognition or by a computer search-match algorithm when an unknown spectrum is compared to an existing reference database. The spectral data is also used to measure one or more compounds in a simple or complex mixture.

4.3 ELECTRONIC SPECTRA

The Electronic spectroscopy is a powerful tool for structural elucidation.The electronic transitions led to the absorption spectra in UV-Visible region. The ligands which are considered as the organic compounds shown their absorption bands in the UV region of 200-400 nm in the electromagnetic spectrum. Due to conjugation in some cases, these bands extend over to higher wavelength region. In the transition metal complex ion, the change in electronic properties of the system is due to the transition with the metal ion. Due to d-d absorption and charge transfer spectra from metal to ligand or ligand to metal, new features or bands in the visible region can be observed and this data can be processed to obtain information regarding the structure and geometry of the compounds [2]. We can get information about the possible distortions of symmetry environment, magnitude of the ligand field splitting, certain bonding characteristics, charge transfer bands etc. from the analysis of the spectrum of the complex.

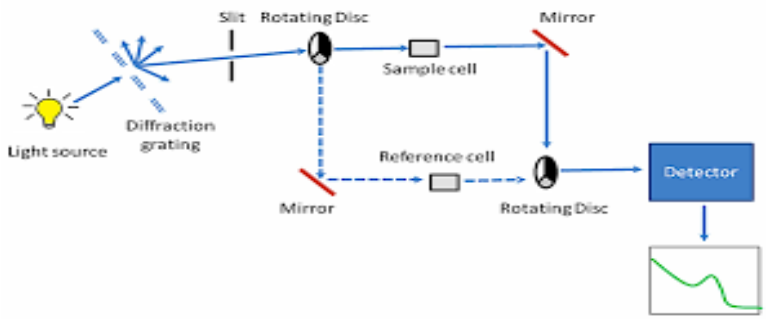


Fig 4.3 Electronic spectroscopy

The electronic spectra of molecular interactions between electron donors and acceptors have gained a great attention as one of the important topics of research in many fields of chemistry. These molecular interactions are often associated with the formation of intensely colored charge-transfer (CT) complexes accompanying with absorption of radiation in the UV region. Electronic spectra give information about geometry of the complexes. UV and visible spectrometers have been in general use for the last 35 years and over this period have become the most important analytical instrument in the modern day laboratory. In many applications other

techniques could be employed but none rival UV-Visible spectrometry for its simplicity, versatility, speed, accuracy and cost-effectiveness.

- Absorption of light in the UV/Visible part of the spectrum (210-900 nm).
- The transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels.
- Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest occupied molecular orbital (LOMO).
- UV light can be absorbed by molecules to excite higher energy (most loosely bound) electrons from lower energy states to higher state.
- Such transitions can be studied extensively to understand the binding energy of the corresponding electrons undergoing transition.
- Since π-electrons are most loosely bound in an organic molecule, UV spectroscopy yields a lot of information about the degree of unsaturation in a molecule.

When the wavelength of the transition exceeds the UV range, based on the same principle, even the colours of molecules can be explained on the basis of absorption of visible light.

4.4 NMR SPECTRA

NMR spectroscopy is a powerful and versatile technique that can provide site-specific information about chemical bonding, structure and dynamics in molecular systems. The most successful applications of NMR to biological systems have been typically carried out in aqueous solutions, and they have utilized spin I=1/2 nuclei, such as $H^{1,}$ $C^{13,}$ N^{15} and P^{31} whereas NMR spectroscopy has proved less powerful when applied to nuclei with spin quantum number I greater than ½, those having a non-spherical charge distribution and an electric quadrupole moment.

NMR is the most powerful technique for molecular characterization. It can provide three-dimensional information on any type of molecule as long as the compound in question possesses NMR active nuclei-almost all do. In this workshop you will learn about the basic physics behind NMR spectroscopy followed by an introduction to the kind of structural information that can be extracted from an NMR spectrum. The workshop is limited to nuclei that possess a nuclear spin of ½ and within that subgroup focusing on the most widely used nuclei H^1,C^{13},F^{19} and P^{31}. In a magnetic field it each of these nuclei possesses 2I+1 spin states i.e. 2,+1/2 and -1/2. Only in a magnetic field is this degeneracy lifted (Zeeman effect). Subatomic particles (electron, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as C^{12}) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as H^1 and C^{13}) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows.

- If the number of neutrons and the number of protons are both even, then the nucleus has no spin.
- If the number of neutron plus the number of protons is odd, then the nucleus has half-integer spin (i.e. 1/2, 3/2, 5/2).
- If the number of neutrons and the protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3).

4.5 ANTIBACTERIAL STUDY

The treatment of infectious diseases still remains an important and challenging problem because of a combination of factors including emerging infectious diseases and the increasing number of multi-drug resistant microbial pathogens. In spite of a large number of antibiotics and chemotherapeutics available for medical use, at the same time the emergence of old and new antibiotic resistance created in the last decades revealed a substantial medical need for new classes of antimicrobial agents. mechanism of action, which is distinct from those of well-known classes of antimicrobial agents to which many clinically relevant pathogens are now resistant The field of bioinorganic chemistry, which deals with the study of role of metal complexes in biological systems, has opened a new horizon for scientific research in coordination

compounds[51]. A large number of compounds are important from the biological point of view. The variation in the activity of different complexes against different organisms depends either on the impermeability of cells of the microbes or differences in the ribosomes of microbial cells.

Many researchers have studied characterization, antimicrobial and toxicological activity of mixed ligand complexes of transition metals. The role of mixed ligand complexes in biological process has been well recognized. Anti-tumor activity of some mixed ligand complexes has also been reported. The antibacterial and anti-fungal properties of a range of copper(II) complexes have been evaluated against several pathogenic bacteria and fungi (15ñ18). The metal complexes have been characterized by elemental analysis and various physico-chemical techniques such as molar conductance, magnetic susceptibility, electronic spectra, IR spectra and thermal studies.

4.5.1 Disc Diffusion method

The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of the test compounds is expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition.

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibilition by test compound (diamter)}}{\text{Zone of inhibilition by standard (diamter)}} \times 100$$

The nutrient medium was prepared by following composition like Yeast extract- 5 g, Meat extract-10 g, Peptone-5 g, Sodium Chloride-5 g, Agar-20 g. The antibacterial activity of the compound was done by the disc diffusion method using DMSO as solvent. The test solutions were prepared by dissolving the compounds in DMSO.

Figure 4.5.1 Disc diffusion method sample

In a typical procedure, agar medium was inoculated with microorganisms and it is filled with the test solution using micropipette and the plate is incubated at 35˚C for 24 to 48 hr. During this period, the test solution diffuses and the growth of the inoculated microorganism *E. Coli*, is found to be affected. The activity developed on the plate is measured by measuring the diameter of the inhibited zone in millimeters.

RESULTS AND DISCUSSION

5.1 PREPARATION OF MIXED LIGAND COMPLEX

CHEMICAL REQUIRED

i) Nicotinamide (0.61 g)

ii) Cadmium chloride (1 g)

iii) 4-aminotriazole (0.42 g)

PREPARATION

A solution of metal chlorides (5mM) [Cd(II) = 1 g] dissolved in ethanol was added gradually to a stirred ethanolic solution of Nicotinamide ligand (5mM) (0.61g). Further to this reaction mixture, 4-aminotraizole (0.42g) (5mM) dissolved in methanol solution was added in the molar ratio 1:2 (metal: ligand) with constant stirring. The precipitated solid complexes were filtered, washed several times with methanol to remove any traces of unreacted starting materials and dried and kept in air tight container.

5.2 Physicochemical properties

The physico chemical properties of the newly synthesized complex were analyzed conductance measurements were tabulated.

5.2.1 Electrical conductivity

The electrical conductivity of 10^{-3} M solution of each complex was found out. This observation reveals the neutral nature (non-electrolytic nature) of the complex. The mixed ligand complexes of nicotinamide have a molar conductivity values in the range from 21 – 28 $\Omega^{-1}mol^{-1}cm^2$.

S. No	Parameters	Observation
1.	Conductance (Ω^{-1} mol^{-1} cm^2)	23
2.	Colour	Dirty white
3.	Yield %	81
4.	Solubility	
5.	Molecular formula	C16H22CdN12O4
6.	Molecular Weight	558.8
7.	Elemental Analysis	
	C, 34.39; H, 3.97; Cd, 20.12; N, 30.08; O, 11.45	

Table 5.2 Physicochemical parameters for the complex $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$

5.3 IR Spectra

The structure of Isoniazid ligand and the metal complex has been confirmed by Infrared spectroscopy. The characteristics bonds in infrared spectrum of the ligand and its metal complex are reported in table 5.3.

S.NO	Compound	υ NH_2		υ C=O	υ M-N	υCN of triazole	N-N	OH of H_2O
		Asy	sy					
1	Nicotinamide	3366	3176	1680	----			
2	$[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$	3399	3195	1670	670	1619	1250	3564

Table 5.3 I R bands of Nicotinamide ligand and its complex (cm^{-1})

In IR spectra, the change in the band position or appearance of any new bands tells us that whether the ligands have entered the coordination sphere or not. The shifts in the IR vibrational bands of the ligands on complex formation provide useful information about the bonding characteristics of the complex.

The IR spectrum of the Nicotinamide ligand was compared with the other synthesized metal complexes. The absorption bands at 3361cm^{-1} due to N-H_2 vibration is seen in free Nicotinamide and same range of peaks 3399 were observed in the Cd complex mentioning that NH_2 groups are not involved in the coordination. The broadness of the peak may due to the hydrogen bonding by water molecules. The υ (C=O) vibrations at 1680 cm^{-1} in free Nicotinamide was also observed in Cd complex as 1690 complex without any noteworthy change. The υ (C=N) band of pyridine at 1613cm^{-1} in the Nicotinamide was shifted in the complex says that the coordination takes place at the Nitrogen of the pyridine ring.

The bands between 670 – 690cm^{-1} in the IR spectra of the metal complex were absent in the IR spectrum of free Nicotinamide predicting that the bands in these regions corresponds to the M-N stretching band.

The peak at 1619 corresponds to the NH_2 group of triazole which is involved in coordination. The peak at 1250 corresponds to N=N stretching frequency.

The bands at 3450 were attributed to the presence of water molecules inside the coordination sphere and the bending mode at 949cm-1 confirms the presence of water molecules.

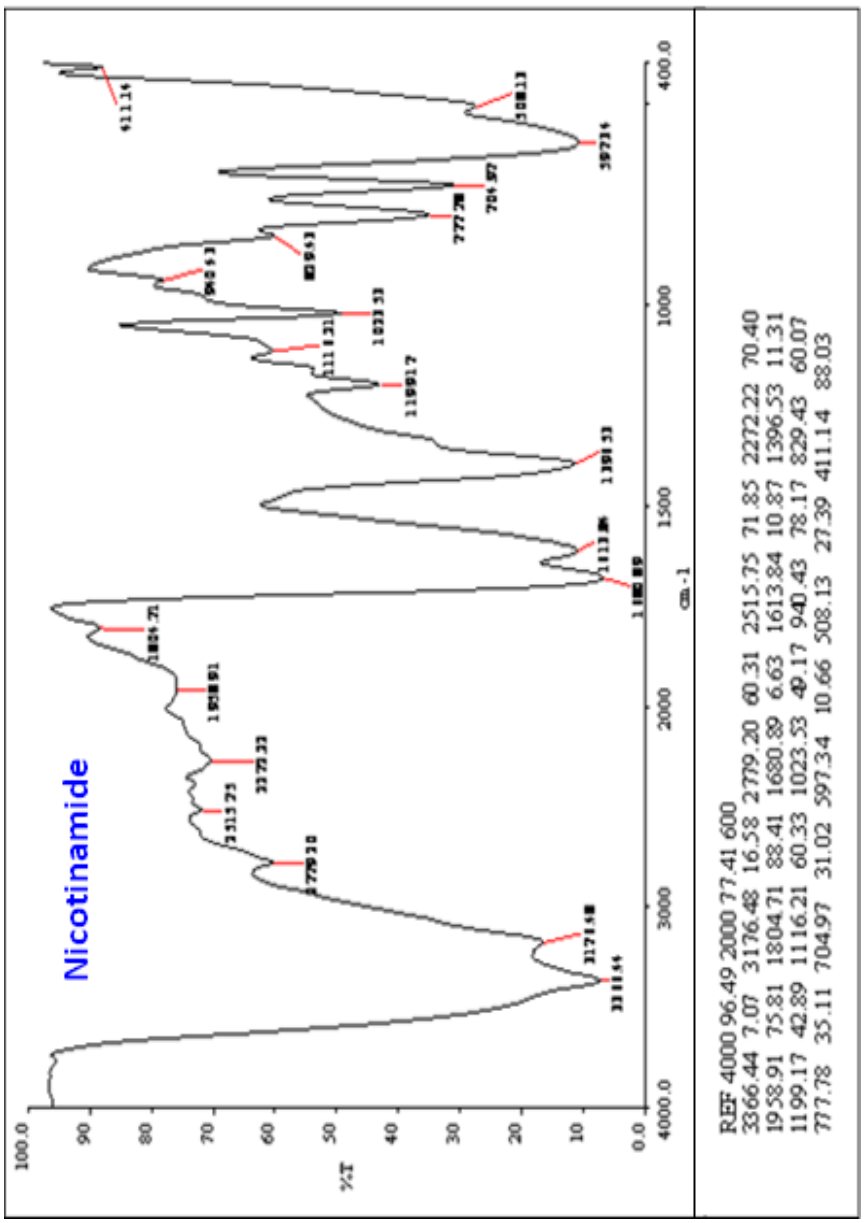


Fig 5.3 I R spectrum of pure Nicotinamide

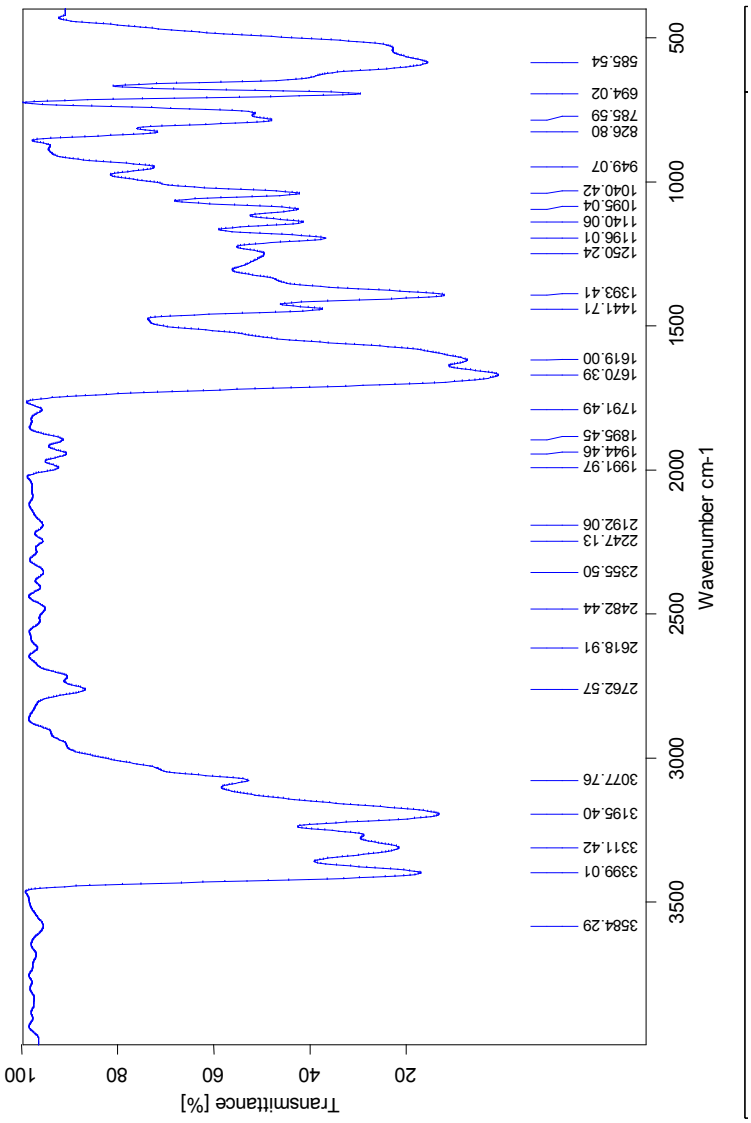


Fig 5.3.1 I R Spectrum of the complex $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$

5.4 Electronic Spectra

S. No	Complex	Absorption maxima		Transition Assignments	Probable geometry
		λ_{max} nm	cm^{-1}		
1	**$[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$**	228 260		$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Distorted Octahedral

Table 5.4 Electronic spectral data for the complex $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$

The Electronic spectra of the complexes in DMF medium were obtained in the range of 200-800 nm. Electronic spectrum is used to elucidate the structure of the metal complexes. The absorption of light in the visible region (400-800 nm) by a metal ion depends on the electronic transitions within the ion and also on the type and strength of ligand → metal bonding. Thus, the metal ions containing d-electrons (except those having 10 electrons in d- orbitals) give variable colors depending on the nature of the ligands attached with the metal ion.

The two peaks at 228 and 260nm corresponds to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the cadmium nicotinamide complex which provides information for the probable geometry as distorted octahedral.

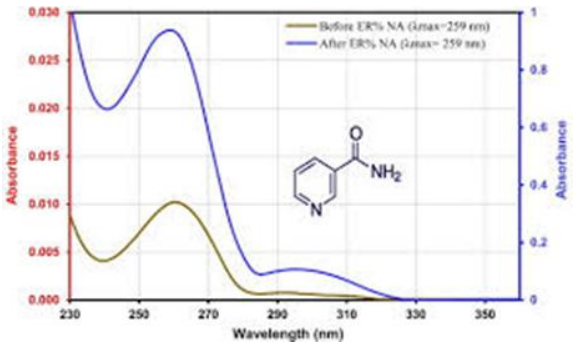


Fig 5.4 Electronic spectra for pure nicotinamide

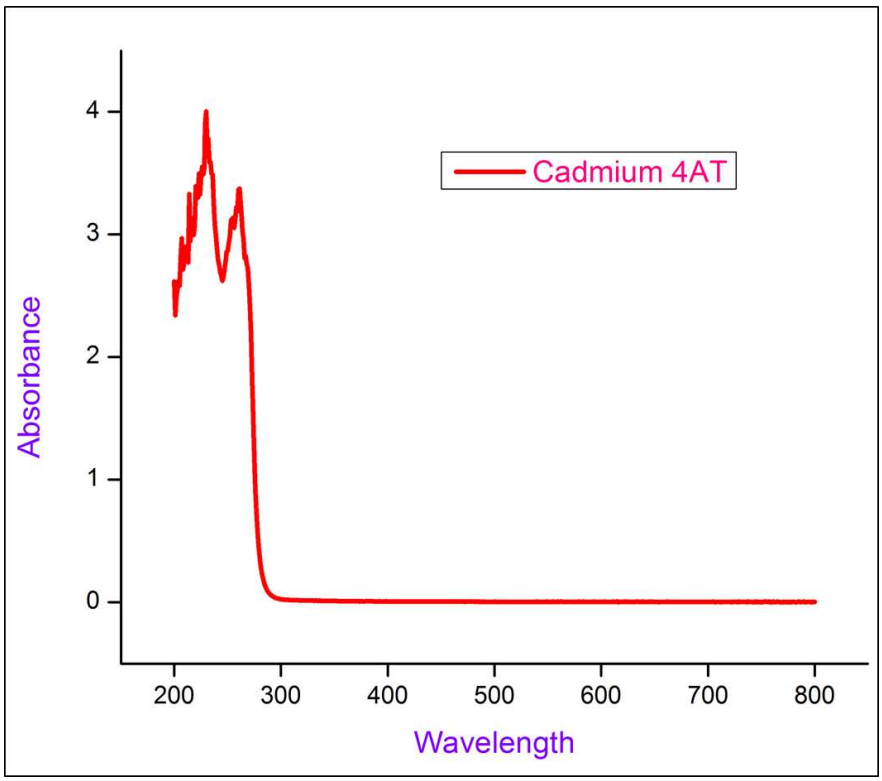


Fig 5.4.1 Electronic spectra for for the complex $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$

5.5 NMR SPECTRA

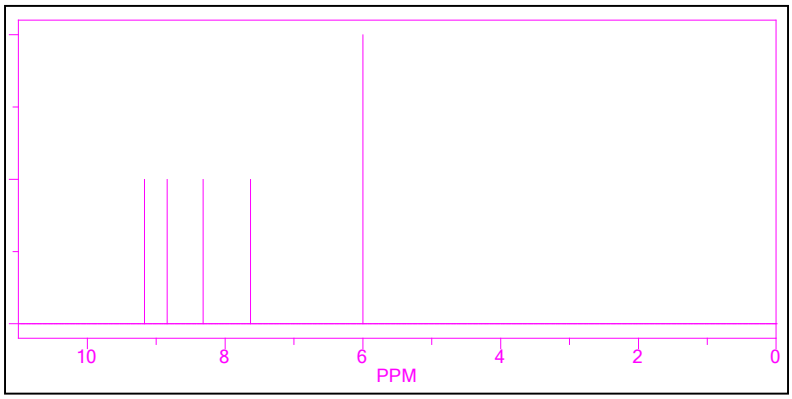


Figure. 5.5 NMR spectrum for the complex $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$

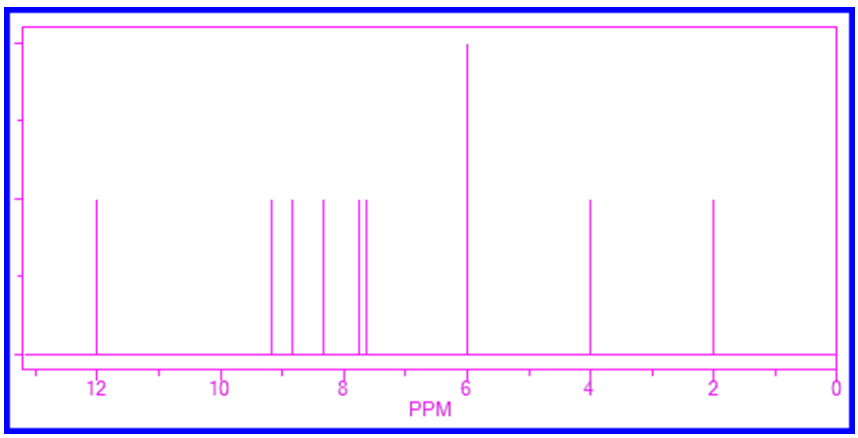


Figure. 5.5 NMR spectrum for the complex $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$

A comparison of ^1H NMR spectra of the metal complex and their respective ligand were done. The proton peaks at δ 2.0 were assigned to NH protons of amine group. The peaks at δ 6 and 7.6 and 8.3 were assigned to pyridine ring protons in both the pure nicotinamide and cadmium complex which confirms the formation of complex. The peaks at 9.1 were also

attributed to the C=O of the pyridine ring. Hence the presence of these peaks shows the coordination occurs at pyridine ring nitrogen. The NMR peak values for cadmium complex were given in the following table.

S. No	Peak value	Assignment
1.	2.0	N-H
2.	6	C-H protons of Carbonyl group
3.	7.6	Pyridine ring
4.	8.3	Pyridine ring

5.6 Structure of the complex

Based on above investigation the probable structure may be distorted octahedral in which the nicotinamide acts as a monodentate ligand with Pyridine ring nitrogen coordination and 4-amino triazole coordinates to the metal atom with amino grou.

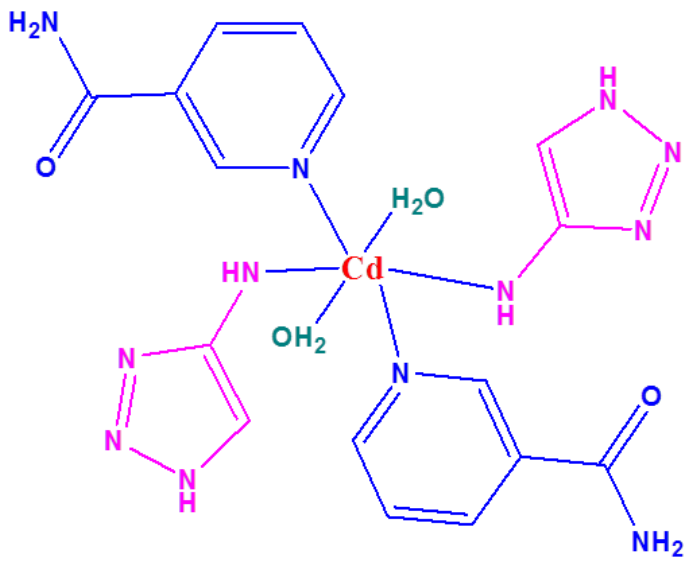


Figure. 5.6 Structure of the $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$

5.7 Antibacterial study

The antibacterial screening of the free isoniazid and the Thiocyanate complexes against E.Coli are shown in Fig. The antibacterial screening was performed by Disc Diffusion method to find whether the complex can act as a therapeutic agent. In this method, the activity of the test compounds is expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibition. The antimicrobial studies showed that the ligands and their metal complexes exhibit considerable activity against the pathogenic bacterial strains. The results show that the complexes are more active than their parent ligands against the same microorganisms and as the concentration increases the activity also increases.

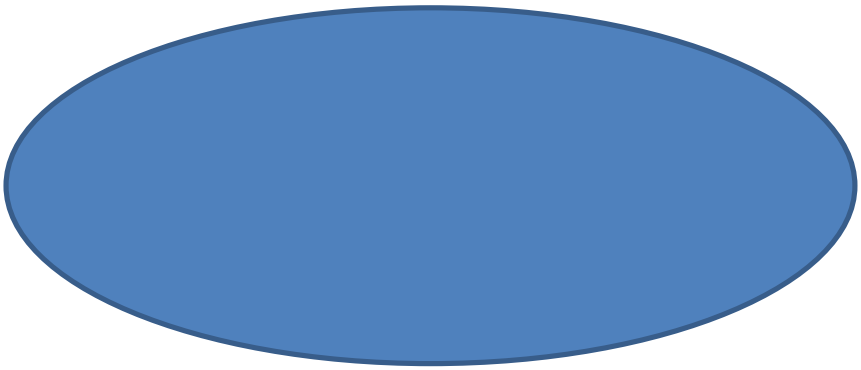


Figure. 5.6 Antibacterial activity of the $[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$complex

CONCLUSION

Conclusion

In the present study, the mixed ligand complex of cadmium has been prepared using Nicotinamide and 4-aminotriazole ligands. The analytical methods and physicochemical parameters have been found out and molar conductivity measurements predicted the non – electrolytic nature of the complex.

The electronic spectra of the complex were recorded and the corresponding transitions predict the probable geometry of the cobalt complex.

The IR spectra of the pure ligand and the complex were recorded and the metal ligand coordination peaks were observed. Nicotinamide acts as a monodentate ligand coordinated with pyridine ring nitrogen. 4- aminotriazole ligand coordinates by the amino group at 4^{th} position. The presence of water molecules inside the coordination sphere were predicted by the presence of broad I R peak at 3450cm-1.

Based on the above results and discussions, the most probable formula and geometry is given as follows.

$[Cd(NA)_2(4\text{-}AT)_2(H_2O)_2]$ - Distorted Octahedral

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ISSN 0973-0303

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ISSN 0973-0303

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ISSN 0973-0303

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Issue - 3 : Section(C) - Mathematics

Jamal Academic Research Journal: an Interdisciplinary (JARJ)

Special Issue

JARJ: COMPENDIUM OF POST GRADUATE DISSERTATIONS : *Mathematics*

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Compendium of the Post Graduate Dissertations: Mathematics 2019

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2	A STUDY ON LABELING AND ANTIMAGIC LABELING ON SOME GRAPHS	K.S.KANZUL FATHIMA	M.MAHALAKSHMI
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ISSN 0973-0303

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Vol - 1 (Spl) :2019
Issue - 1 : Section(C) – Microbiology

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COMPENDIUM OF THE POST GRADUATE DISSERTATIONS: MICROBIOLOGY - 2019

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8.	ANTIBACTERIAL ACTIVITY AND MOLECULAR DOCKING ANALYSIS OF VITEX NEGUNDO AGAINST MULTIPLE DRUG RESISTANT PSEUDOMONAS AERUGINOSA	Dr. M. MOHAMED MAHROOP RAJA	AJITH S
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10.	UTILIZATION OF PADDY STRAW EXTRACT AS CELLULOSE SUBSTRATE FOR THE PRODUCTION OF BIOETHANOL USING CELLULOLYTIC A.NIGER	Dr. H.VAJIHA BANU	AYISHA CHITIKA N
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Special Issue

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Compendium of the Post Graduate Dissertations(2019): Management studies

S.No.	Title of the Project	Name of the Guide	Name of the Candidate
1	A STUDY ON SERVICE QUALITY WITH SPECIAL REFERENCE TO BIG BAZAAR KERALA	Dr. U. SYED AKTHARSHA	ABDUL AZIZ M
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Jamal Academic Research Journal: an Interdisciplinary (JARJ)

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Compendium of the Post Graduate Dissertations: NUTRITION AND DIETETICS-2019

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1.	Nutritional status, food habits and physical activity pattern of the selected adolescent girls (17-19 years)	Dr.M.Angel	R.Bhuvaneswari
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ISSN 0973-0303

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Special Issue

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2	Solvation Studies on Optically Active 1-Acetyl-5-Nitroindoline And 5-Nitroisatin Molecules In Polar And Non-Polar Solvents	Dr. A. S. Haje Hameed	K. Alphaaristo
3	Period Doubling Bifurcations, Homoclinic Orbits and Mixed Mode Oscillations in A Modified Wein's Bridge Oscillator	Dr. A. Ishaq Ahamed	A. Gokulakannan
4	Visible Light Photocatalytic Activity of TiO_2 Nanoparticle for The Degradation of Rhodamine B	Mr. A. Mohamed Saleem	O. Bahnam Shareef
5	Spectroscopic Studies [Ftir, Nlo, Homo-Lumo] And Anti-Microbial Analysis Of (2e)-3-(1h-Indol-2-Yl)-N-Phenylprop-2-Ethanone Molecule Using Density Functional Theory Method	Dr. S. Abbas Manthiri	B. Sudharsan
6	Green Synthesis of TiO_2 and Zn Doped TiO_2 Nanoparticles Using Aloe Vera Plant Extract	Dr. J. Ebenezar	R. Kishor Kumar
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ISSN 0973-0303

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Jamal Academic Research Journal: an Interdisciplinary (JARJ)

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JARJ: COMPENDIUM OF POST GRADUATE DISSERTATIONS : *Physics*

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ISSN 0973-0303

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2	A STUDY ON QUALITY OF WORK LIFE AMONG THE EMPLOYEES OF HOTEL LE TEMPS FORT IN	Dr. N ANTONY PRAKASH	A. NOORULLAH HASSAN
3	A STUDY ON PROBLEMS FACED BY TRANSGENDER	Mr. M. RAJALINGAM	K. RAVICHANDRAN
4	A STUDY ON PERFORMANCE APPRAISAL AMONG THE EMPLOYEES OF HOTEL LE TEMPS FORT IN	Dr. N ANTONY PRAKASH	K.ALHAMTHAN
5	A STUDY ON PARENTS AND CHILD RELATIONSHIP AMONG RURAL ADOLESCENCE BOYS	Mr. M. RAJALINGAM	RAZACK
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7	A STUDY ON EMPLOYEES WORK LIFE BALANCE IN Q MED HOSPITAL IN TRICHY	Dr. K.SHEIK FAREETH	S. NOOR NISHA

ISSN 0973-0303

Part D : Life Sciences
Vol - 1 (Spl) :2019
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Special Issue

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3	ISOLATION AND PURIFICATION OF GENOMIC DNA FROM MAMMALIAN CELLS USING RAPID NON- PHENOLIC METHOD	Dr. K. PRABAKAR	MR. MUNAVAR

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