Surface interaction and Corrosion inhibition of MS in 1M HCl and 0.5M H_2SO_4 using *Pouteria campechiana leaves*

Prema. S

(15PCH008)

Thesis Submitted to

Avinashilingam Institute for Home Science and Higher Education for Women,

Coimbatore-641 043

In Partial Fulfilment of the Requirements for the Degree of

Master of Science in Chemistry

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Signature of the

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PREMA.S

CONTENTS

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

PC	*Pouteria campechiana*
PCL	*Pouteria campechiana* leaf
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
MS	Mild steel
CR	Corrosion rate
IE	Inhibition efficiency
IC	Inhibition concentration
Ppm	Parts per million
Mpy	Mils per year
Θ	Surface coverage
I_{corr}	Corrosion current
E_{corr}	Corrosion potential
b_a	Anodic tafel slope
b_c	Cathodictafel slope
Cdl	Double layer capacitance
Rct	Charge transfer resistance
Rp	Polarization resistance
Rs	Solution resistance
mV	Milli volt
LPR	Linear polarization resistance
EIS	Electrochemical Impedance Spectroscopy
ML	Mass Loss

INTRODUCTION

INTRODUCTION

Elements are rarely found as pure metal in the nature. They are found in chemical combinations with one or more nonmetallic elements. These chemical combinations of metals are commonly known as ore. Three most common ores found in the earth's crust are Iron, copper and zinc. Significant energy must be expended to reduce the ore to pure metal. The energy can be applied via metallurgical or chemical means and is done through the process called smelting and refining. Additional energy are also used in the form of cold-working or heating and casting the pure metal into a working shape.

1.1 CORROSION

The word Corrosion, which can be simply defined as rust, is the tendency for metals to revert to their natural, lower energy state of ore. Corrosion is the reverse process of metallurgy.

Corrosion is a natural phenomenon, a chemical 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 (commonly metals) by chemically and/or electrochemical reaction with their environment.

Figure : 1.1 Corrosion

Metallic corrosion includes both oxidation and electrochemical process. In oxidation, metal is exposed to oxygen in the environment and so corrosion begins and in electrochemical process, the metal forms corrosion cells on its surface that greatly speed up the transformation of metal back to the ore state, and involves both chemical reactions and the flow of electrons. A basic electrochemical process drives the corrosion of metals that is galvanic action, where current is generated internally by physical and chemical reactions occurring among the components of the cell.

Though the studies of corrosion and corrosion science have been around for many years, the importance of learning continues to increase. In studies commissioned by the US Government, the annual corrosion cost was found to be 3% of the gross domestic product (GDP), or more than $400 billion. This suggests for the improvement in knowing of corrosion and how to decrease its presence in our society. Corrosion may possibly occurs in materials other than metals, such as in ceramics or polymers, in this case we call it as ‘degradation’ . Corrosion degrades the properties of materials and its structures including strength, appearance and permeability to liquids and gases.

1.2 TYPES OF CORROSION

There are several types of corrosion. Here are some common types of corrosion:

1.2.1 General corrosion

Stainless steel does not corrode easily as like ordinary carbon and alloy steels. However, with some chemicals, like acids, the passive layer of the metal may be attacked homogeneously depending on concentration and temperature and thus the metal loss take place. Hydrochloric acid and Sulphuric acid at some concentrations are exacting forceful towards stainless steel.

1.2.2 Galvanic Corrosion

Galvanic corrosion is the most common form of corrosion. It occurs when two dissimilar metals are in contact in the presence of an electrolyte. It can be avoided by separating the metals with a non-metallic insulator such as rubber.

Four elements that are necessary for corrosion to occur in a galvanic cell are:

- **Anode** – In this galvanic reactions electrons are generated - negative ions are discharged and positive ions are formed. Corrosion occurs at the anode.
- **Cathode** - This electrode receives electrons - positive ions are discharged, negative ions are formed. The cathode is protected from corrosion.
- **Electrolyte**– Current is carried. Electrolytes include aqueous solutions or other liquids.
- **Return Current Path** – It carries metallic pathway connecting the anode to the cathode. It is frequently the underlying metal substrate.

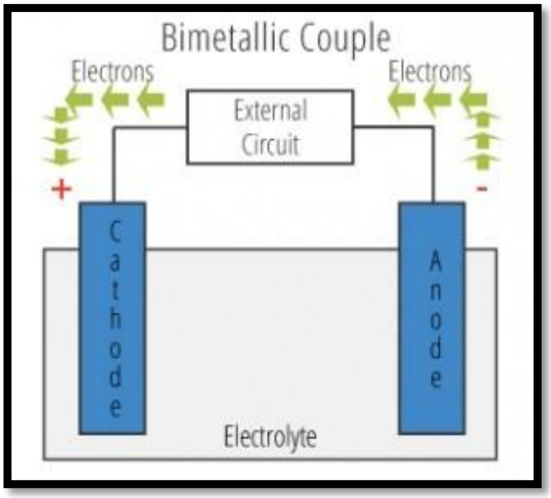


Figure 1.2. Schematic representation of electron flow in Galvanic Corrosion

All four elements anode, cathode, electrolyte and return current path are necessary for corrosion to occur. If any one of these elements is removed it will stop the flow of current and galvanic corrosion. When different metal is substituted for the anode or cathode it may result in the reverse of the current direction, resulting in a switch to the electrode experiencing corrosion.

1.2.3 Steel Corrosion

Microscopic areas of the uncovered steel become relatively anodic or cathodic to one another very easily. A large number of such areas can develop in a small section of the exposed steel. The corrosion process that takes place on a piece of uncoated steel is very complex. Factors such as variations in the composition/structure of the steel, presence of impurities due to the higher instance of recycled steel, uneven internal stress, and/or exposure to non-uniform environment all affect the corrosion process.

1.2.4 Pitting Corrosion

This type of corrosion occurs under certain conditions, wherethe corrosion take place in certain areas of the metal. These conditions include low concentrations of oxygen or high concentrations of chlorides (anions) that interfere with the alloy’s ability to reform a passivating film. In certain cases, most of the surface remains protected, but tiny fluctuations degrade the film in a few critical areas. Corrosion at these points is amplified and can cause pits.

1.2.5 Crevice corrosion

Crevice corrosion occurs in confined spaces where access of fluid from the environment is limited such as gaps and contact areas between parts, under gaskets or seals, inside cracks and seams and spaces filled with deposits. Stainless steel requires supply of oxygen to make sure that the passive layer can form on the surface. In very tight crevices, it is not always possible for the oxygen to gain access to the stainless steel surface thereby causing it to be vulnerable to attack. Crevice corrosion is avoided by sealing crevices with a flexible sealant or by using a more corrosion resistant grade.

1.2.6 Microbial corrosion

Microbial corrosion is commonly referred to as microbiologically influenced corrosion (MIC) it is caused by microorganisms. It take place in both metallic and non-metallic materials in presence or absence of oxygen. In absence of oxygen sulfate-reducing bacteria are active and produce hydrogen sulfide causing sulfide stress cracking. Some bacteria may directly oxidize iron to iron oxides and hydroxides in presence of oxygen. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

1.2.7 High-temperature corrosion

In this case deterioration of a metal take place due to heating. This type of corrosion occurs when a metal is subjected to a hot atmosphere in the presence of oxygen, sulfur, or other compound capable of oxidizing the material.

1.2.8 Stress corrosion cracking (SCC)

This is a rare form of corrosion which requires a very specific combination of tensile stress, temperature and corrosive species, often the chloride ion, for it to occur. SCC can occur in hot water tanks and swimming pools. Another form known as sulphide stress corrosion cracking (SSCC) is associated with hydrogen sulphide in oil and gas exploration and production.

1.2.9 Intergranular corrosion

This is a rare form of corrosion. When the Carbon level in the steel is too high, Chromium can combine with Carbon to form Chromium Carbide. This takes place at a temperatures between about 450-850 deg C. This process is known as sensitisation and it occurs during welding process. The Chromium available to form the passive layer is effectively reduced and corrosion can occur. It is avoided by choosing a low carbon grade the so-called 'L' grades or by using a steel with Titanium or Niobium which preferentially combines with Carbon.

1.3 CORROSION RATE

Corrosion rate of the steel in soil can be determined by the pH, moisture content and chloride levels in the environment. Corrosion rates of the steel in various environments are given below,

In Atmosphere

Metallic corrosion take place most easily when the metal is exposed to the atmosphere.. The atmospherically exposed metals depends on five main factors such as temperature, humidity, rainfall, sulfur dioxide (pollution) concentration in the air, and air salinity. These factors are the main contributor to corrosion.

Marine (water)

A less common environment for metal is submerged in or exposed to water. Moisture is highly corrosive to most metals including steel, aluminum, and zinc.The parameters that affect corrosion of metals in water include pH level, oxygen content, water temperature, agitation, the presence of inhibitors, and tide conditions.

Pipeline

Depending on the nature of the product being carried, exposure conditions, operating conditions (24/7 v. sporadic), and commitment to maintenance, corrosion in pipeline may vary.

(a) **(b)**

Figure 1.3 Corrosion in (a) Marine (b) Pipelines

1.4 CORROSION TESTING

Three general methods of corrosion testing are:

- Service history,
- Field performance, and
- Accelerated corrosion tests.

1.4.1 Service history

It is reliable and available for long period, but the data in the service history may change with the exact conditions the material is exposed to currently.

1.4.2 Field performance corrosion testing

It is similar to service history, but usually involve examining performance variable over a shorter period such as one to five years. Once the data is collected, one can extrapolate it to provide a somewhat scientific prediction of performance to 10, 20, or even 50 years. Extrapolating the variable performance to 10, 20 or even 50 years to some extent provides scientific prediction of long-term performance.

1.4.3 Accelerated corrosion test

This test is commonly used to test the corrosion rate and gives quicker results. There are two common testing methods used to study the corrosion on a piece of steel:

Ultrasonic testing is a non-destructive test with very high sensitivity detection of internal flaws in steel and changes in thickness. In ultrasonic pulse-waves are sent into the steel to determine if any changes are occurred, indicating corrosion.

A *scanning electron microscope (SEM)* focuses a beam of electrons on a surface that when reflected back yield discernable information about the surface condition and topography of the tested sample. Characteristic applications of SEM are detecting micro-cracking and molecular composition of the material or coating applied over the material.

1.5 CORROSION CASE STUDIES

- **Bhopal gas tragedy**

Bhopal disaster in India is one of the world ‘s worst industrial disasters occurred at 2-3 December 1984 at the Union Carbide India Limited in Bhopal, Madhya Pradesh, over 500,000 people were exposed to methyl isocyanate gas and other chemicals. The

Bhopal disaster was a result of a combination of legal, technological, organizational and human errors. Its all because of the corroded pipelines**. (http://corrosion-doctors.org/Pollution/bhopal.html)**

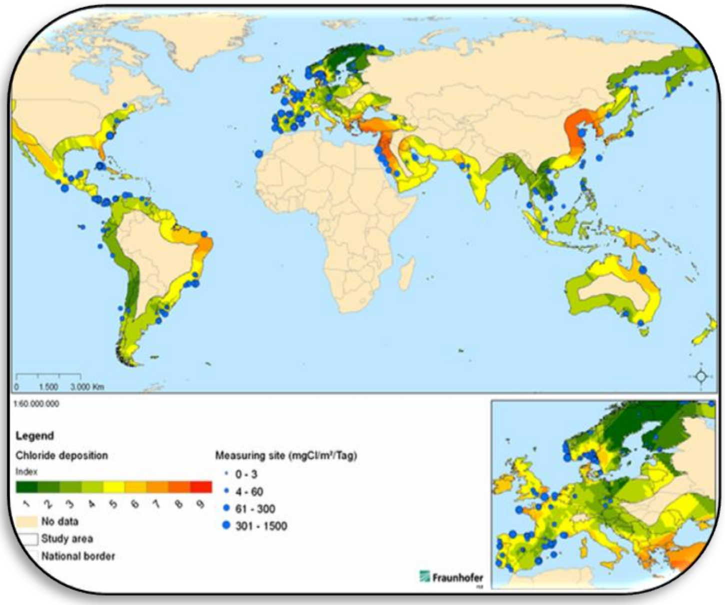


Figure 1.4 Corrosion world wide

- **Light Poles - Massachusetts**

In 2012 at Massachusetts two poles on a major bridge completely failed and had to be removed. Other poles have been observed to have completely broken from their base due to corrosion at the bottom of the pole. Some poles on Route 128 were visually examined and found to have completely rusted bases. Some poles are just missing from their bases and have exposed wires.

- **Oil Spill Caused by the Corroding Tanker Erika**

This accident took place in 1999, involved the Maltese tanker Erika, which broke apart and subsequently sank about 70 kilometers off the coast of Brittany, France. The ship carried around 30,000 tons of oil, and nearly two-thirds of it spilled into the ocean when Erika sank.It was one of the worst shipping accidents in history. The environment suffered tremendously, as this accident spilled more oil than what was spilled worldwide in 1998.**(https://hubpages.com/technology/)**

- **Tappan Zee Bridge - New York**

In 2009 engineering assessment found that the Tappan Zee's rate of deterioration is "unusually high." The bridge's drainage system was designed to dump water onto the substructure below the highway, causing major corrosion in crucial components like its "stringers," horizontal beams that hold up the deck, and joints. Major cracking has also been observed on the causeway's outer columns, reappearing soon after repairs. - **(New York Times, Jan. 13, 2013)**

Figure 1.5 Light poles affected by corrosion

1.6 CORROSION INHIBITORS

Due to the corrosion process there are numerous lose in industries, to combat it prevention is the best way. There are various methods used to prevent the degradation of metal surface among that corrosion inhibitor is one of the best method. A **corrosion inhibitor** is a substance or mixtures that, when added to a material minimize the corrosion.

Corrosion inhibitors are one of the practical and cost effective methods of controlling metallic corrosion. Inhibitors may be inorganic or organic substances. Inorganic substances suitable as metal corrosion inhibitor easily oxidize the metal to form an impervious layer which prevent direct ions-metal interaction and hence retard the rate of metal dissolution in the medium. The organic counterpart, on the other hand, possess features including presence of heteroatoms and/or double bonds, large surface area, active centre, etc. which upon adsorption on the metal surface will blanket a large area of the metal and thus isolate it from the aggressive ions present in the environment. (**Lebe Nnanna *et al*., 2016)**

1.6.1 GREEN INHIBITORS

Green inhibitors are biodegradable and do not contain heavy metals or toxic compounds. Plant is one of the sources of cheap, readily available, and non-toxic green corrosion inhibitors. Plant products are organic in nature, and contain certain phytochemical including tannins, flavonoids, saponins, organic and amino acids, alkaloids, and pigments which could be extracted by simple less expensive procedures. Extracts from different parts of plant have been widely reported as effective and good metal corrosion inhibitors in various corrosive environment.

Inhibitors are commonly used to prevent metal dissolution as well as acid consumption and retard the corrosive attack on metallic materials. Plant extract is rich source of naturally synthesized chemical compounds, readily available low-cost and eco-friendly, and can be obtained through simple extraction process with low cost as well as biodegradable. (**Lebe Nnanna *et al.*, 2016).**

The present work reports on the inhibitive effect of *Pouteria Campechiana* Leaves extracts for mild steel in hydrochloric acid and Sulphuric acid.

1.7. PLANT DESCRIPTION

Figure 1.*6 Pouteria campechiana leaf*

Other names : Canistel, Chesa, Egg fruit, Yellow sapota.

Origin of the plant : The canistel is an evergreen tree native to southern Mexico and Central America. It is cultivated in other countries such as Brazil, Taiwan, Vietnam, Indonesia and the Philippines.

1.7.1 SCIENTIFIC CLASSIFICATION OF PLANT

Kingdom	Plantae
Division	Angiosperms
Class	Eudicots
Subclass	Asterids
Order	Ericales
Family	Sapotaceae
Genus	Pouteria

Table 1.1 Scientific classification of the plant

1.8 OBJECTIVES

- To select and utilize an eco-friendly, commercial, natural plant material as corrosion inhibitor for mild steel in acid medium.
- To find out the phyto constituents present in the investigated plant extract.
- To evaluate the corrosion studies of mild steel in 1M HCl and 0.5M H_2SO_4 in the presence of *Pouteria campechiana* leaf extract using the conventional weight loss method and electrochemical measurements.
- To correlate the results obtained by mass loss and electrochemical techniques
- To ascertain the effectiveness of the inhibitors using surface analytical techniques.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

A literature review is very essential for a research work to gain a sound knowledge about the particular field. Through this one can know the works related to their research.

The present study on **“Surface interaction and corrosion inhibition of MS in 1M HCl and 0.5M H_2SO_4 using *Pouteria campechiana* leaves”** is reviewed under the following topics.

2.1. Natural products as inhibitors

2.2. Organic compounds as inhibitors

2.3. Corrosion behaviour of mild steel with varying parameters

2.3.1 .Effect of concentration of the inhibitor

2.3.2. Influence of exposure time

2.3.3.Temperature effect

2.4.Kinetic analysis

2.5. Polarization behavior

2.1. Natural products as inhibitors

Natural products such as Opuntia extract, *Aleovera* leaves, *Orange* and *Mango*peels, *Onion, garlic* and *bitter* gourd, *Papaia, Poinciana pulcherrima, Cassia occidentalis, Datura stramonmium* seeds, *Calotropis procera, Azydracta indica* and *Auforpio turkiale sap have been tested as corrosion inhibitors for mild steel in acidic media***.**

These plant extract exhibited an inhibition efficiency of 90%. The corrosion inhibition activity in many of these plant extracts could be due to the presence of heterocyclic constituents like alkaloids, flavonoids etc. The presence of tannins, cellulose and polycyclic compounds also enhanced the film formation over the metal surface, there by inhibiting aiding corrosion **(Pandian Bothi Raja, Mathur Gopalakrishnan Sethuraman, 2007).**

- The effects of various plant extracts such as papaya, *Poinciana pulclcherrima, Cassia occident ails* and *Datura stramonium* seeds and papaya, *calotropis procera B, Azydracta* *indica* and *Auforpia turkiala* sap on the dissolution of mild steel in HCl solution was evaluated.The study revealed that all extracts except those of *Auforpio turkiale* and *Azydracta indica* reduced the corrosion with an efficiency of 88%-96% in 1N HCl**. [Fabrizio Zucchi and Ibrahim Hashiomar (1984)].**

- Aqueous extracts of Henna *(Lawsonia inermis)* leaves powder was evaluated as corrosion inhibitors for steel and commercial aluminum in saline, acidic and alkaline waters by **Al-Sehaibani (2000).** Weight loss measurements showed that the extracts can inhibit efficiently the corrosion of steel for 37days in HCl with 96% efficiency and for aluminum in NaOH up to 99.8% while no inhibition occurred for steel or aluminum in NaCl solutions.
- **El-Etre and Abdallah (2000)**, evaluated the inhibitive action of natural honey on the corrosion of C-steel, used in manufacture of petroleum pipelines, in high saline water. The inhibition efficiency was calculated using weight loss measurements and potentiodynamic polarization technique. It was found that, natural honey exhibited a very good performance as inhibitor for steel corrosion in high saline water.
- **Loto and Mohammed (2000)** investigated the inhibitive effect of the barks, nuts and apples of the cashew tree on the corrosion inhibition of mild steel in HCl medium using weight loss and electrochemical measurements. The apple juice extract was found to exhibit good corrosion inhibition efficiency.
- **Loto *et al.*, *(*2001)** investigated the corrosion inhibition effect of *Bitter* leaf (*Vernonia Amygdalina*) solution extract on the corrosion mild steel in 0.5M HCl and H_2SO_4 at ambient temperature of 28°C and elevated temperature 80°. The work was performed using the weight loss method. Studies revealed that bitter leaf acted as a very good inhibitor.
- *Nerium oderum (flower), Lantana camara (leaves), Aglemermolus* extracts were studied by **Mohan *et al.*, (2001),**as corrosion inhibitor for mild steel in 10% HCl by using weight loss measurements. The results inferred that inhibition increases with increase in concentration and decreases with temperature. The maximum efficiency reported for these extracts are as follows *Lantana camara* (100%), *Nerium oderum* (flower 100%), *Aeglemer mould* (90%).

- The acid corrosion of *Andiographis Paniculata* was tested for its corrosion inhibitive nature by weight loss method, Tafel polarization method and impedance studies by **Ramesh *et al., (*2001)**. The results revealed that this plant extract had the potential to serve as corrosion inhibitor.
- **Sahoo *et al.,* (2001)** observed the corrosion inhibition of mild steel in aqueous environment by Neem extract through electrochemical and weight loss measurements. Experimental results indicated that the inhibition efficiency increased with increasing inhibitor concentration.
- **Sethuraman *et al.,* (2001)** observed the effect of *solonum triblobatum* extract on corrosion of mild steel in 5% HCl by weight loss measurement. It was found that inhibitor efficiency increased with increase in concentration and temperature. The presence of solanaces alkaloid in the plant was found to be responsible for the inhibition of mild steel.
- **Fabrizio Zucchi and Ibrahim Hashi Omar (2002)** studied the effect of various plant extracts like *Papaia, Poincianaz pulcherima, Cassia occidentalis, Datura stramonium seeds, Caltropis procera B, Azydracta indica, Autrpio turkiale sap* on dissolution of mild steel in HCl by electrochemical and weight loss measurements. It was noted that the inhibitive action was due to the products of hydrolysis of the protein content of these plants.
- The Biocidal and inhibitive effects of aqueous extract of *Azardiracta indica* on mild steel in fresh water environment was noticed by **Mohanan *et al.,* (2002)** using weight loss measurements. The retardation of corrosive effect depended on the concentration and stability of the extract. The inhibition activity is due to the adsorption of natural compounds.
- **Rajalakshmi *et al.,* (2002)** investigated the performance of acid extracts of *Ficus benghalensis* bark on the corrosion inhibition of mild steel in 1M HCl and 0.5M H_2SO_4 by weight loss and electrochemical techniques. The presence of anthrocyanin compounds, flavanoidal compounds and reducing sugars in the bark extract may be responsible for the inhibitive action. The efficiency of the inhibitor was noticed to increase with increase in concentration of the inhibitor.

- Water extracts from leaves of ***date palm, phoenix dactylifera, henna, lawsiniainermis, corrozea mays*** were tested as corrosion inhibitors for steel, aluminium, copper and brass in acid solutions using weight loss, solution analysis and potentiodynamic studies by **Rehan (2003)**. ***Date palm*** and ***henna*** extracts were found to be highly effective in reducing the corrosion rate of steel in acid chloride solutions and aluminum in NaOH solutions.
- **Orubite and Oforka (2004)** reported the inhibition of corrosion of mild steel in HCl solution using the leaves of ***Nypa fruticans wurmb*** by weight loss and hydrogen gas evolution methods.Maximum inhibition efficiency of 75.11% was observed with ***Nypa fruticans*** wurmb extract.
- The effectiveness of ***Khillah (Ammivisnaga) seeds*** on the corrosion of S × 316 steel in HCl solution was determined using weight loss measurements as well as potentiostatic technique by **El –Etre (2005).** The inhibition efficiency increased as the extract concentration increased.
- **Oguzie *et al.*, (2005)** investigated the efficiency of ***Telfaria occidentals*** extract as a corrosion inhibitor for mild steel in 2M HCl and 1M H_2SO_4solutions using hydrogen gas evolution technique. The results showed that the inhibition efficiency increased with increasing extract concentration.
- **Chauhan and Gunasekaran (2006)** investigated the inhibitive action of ***Zenthoxylum alatum*** plant extract on the corrosion of mild steel in 5% and 15% aqueous HCl, using weight loss and EIS methods and reported that corrosion inhibition efficiency increases on increasing plant extract concentration till 2400 ppm. The Plant extract was found to reduce the corrosion of steel more effectively in 5% HCl than in 15% HCl.
- Natural oil extracted from ***Pennyroyal Mint*** *(Mentha eulogiums, PM)* was evaluated as corrosion inhibitor of steel in molar HCl by **Bouyanzer *et al.*, *(*2006)**using weight loss, electrochemical polarization and EIS methods**.**The inhibition efficiency was found to increase with increasing oil content to attain 80% at 2.76 g/ L.
- The leaves extract of ***Datura stramonium*** was studied as a possible source of green inhibitor for corrosion of mild steel in HCl and H_2SO_4 media using weight loss and electrochemical techniques. The studies revealed that the plant extracts act as a good

inhibitor in both the acid media and had better inhibitive capacity in H_2SO_4 medium (**Raja *et al.*, 2007).**

- **El – Etre (2007)** investigated the inhibitive action of the aqueous extract of the root of ***shirsh el zallouh (Ferula harminis)*** toward the corrosion of C- steel in HCl solution. The addition of the extract was found to enhance the inhibition efficiency with increasing extract concentration.
- Inhibition of the corrosion of mild steel by ethanol of ***Musa acuminate*** peel has been studied using thermometric method of monitoring corrosion. Inhibition efficiency of the extract was found to vary with concentration, temperature, period of immersion, P^H and electrode potentials. Physical adsorption mechanism was proposed for the adsorption of the inhibitor. **Eddy, *et al.*, (2008)**
- **Oguzie (2008)** studied the corrosion inhibiting properties of extracts of ***Occimum vridis, Telferia occidentails, Azadirachta indica*** and ***Hibiscus sabdariffa*** as well as extracts from the seeds of **Garcinia kola** on the corrosion of mild steel in 2M HCl and 1M H_2SO_4 using gasometric techniques and reported that inhibition efficiency increased with increase in extract concentration
- Corrosion inhibition effect of the extract of black pepper on mild steel (MS) in 1 M H_2SO_4 media revealed that the corrosion rate significantly reduced with increasing concentration of the extract. **Pandian Bothi Raja and Mathur Gopalakrishnan Sethuraman (2008).**
- Corrosion inhibition effect of ***Justiciia gendarussa*** extract on mild steel in HCl medium was investigated by weight loss and electrochemical techniques. Inhibition efficiency of 93% was achieved with plant extract at 25^0C. AFM and ESCA confirmed the adsorption of ***justiciia gendarussa*** extract on mild steel surface **Satapathy et al., (2009)**
- Methanolic extract of ***Artemisa pallens*** was tested as corrosion inhibitor for mild steel in 4N HCl and conc. HCl. FI.IR studies were carried out in conc.HCl. The inhibition efficiency was found to be 93% at 1.5 g 1-1 in 4N HCl and 96% at gl –1 in conc. HCl**. [Patchaiah kalaiselvi *et al.*, (2010)].**
- Investigations of **Rosliza *et al.*, (2010)** using natural honey as corrosion inhibitors revealed that natural honey acted as a very good inhibitor towards corrosion of Al-Mg-Si alloy in sea water.

2.2. Organic compounds as inhibitors

- Three lactones including dihydrofuran-(2, 3, 4) - one tetra-hydro-2H-pyran-2-one and oxepan-2-one were tested as corrosion inhibitors for mild steel in 1M HCl at different concentration. A comparison of the results showed that oxepan-2-one acted as the best inhibitior and its inhibition efficiency reached maximum of 85%.**Tebbji *et al.*, (2007)**
- **Fengling Xu *et al.*, (2008)** found that the DTE performed excellently as corrosion inhibitor mild steel in 1M HCl acid media and a maximum efficiency of 90.9% was observed at 1.0*10-3 M.
- Investigation of **Quraish *et al.*, (2008)** involving poly aniline-formaldehyde as an inhibitor revealed that it inhibits mild steel corrosion through adsorption mechanism. It is found to exhibit an efficiency of 90% at 10 ppm.
- The inhibition for performance of mebendazole, a drug on mild steel in molar HCl acid solution was studied by weight loss and electrochemical methods. A maximum inhibition efficiency 96.25% was observed in presence of 2.54*10-4 M inhibitor **Ishtiaque Ahamad and Quraishi *et al.*,(2009)**
- Corrosion inhibition of carbon steel in HCl and H_2SO_4 solution in the presence of benzimidazole derivatives such as benzimidazole (BI), 2-methylbenzimidazole ($2CH_2$-Br) and 2-mercaptobenzimidazole was investigated using potentiodynamic polarization technique. Result obtained show that the benzimidazole derivatives retard both the cathodic and anodic reactions in both acidic media, by virtue of adsorption on the carbon steel surface. **Alijourani, *et al.*,(2010)**
- Corrosion inhibition of copper in O_2 –saturated 0.5M H_2SO_4 solutions by four selected amino acids, namely glycine, alanine,valine, or tyrosine, was studied using Tafel polarization, linear polarization, impedance, and electrochemical frequency modulation at 30^0C protection efficiencies of almost 98% and 91% were obtaind with 50mm tyr and gly, respectively. **Mohammed Amin *et al.*, (2010).**

2.3. Corrosion behaviour of mild steel with varying parameters

2.3.1. Effect of concentration of the inhibitor

- The influence sodium dodecyl benzene sulfonate on the corrosion behaviour of an elaborated annealed Fe1lTi-20 alloy has been investigated in 0.5 M H_2SO_4 solution using electrochemical techniques. The inhibition occurs through adsorption of a surfactant on the metal surface without modifying the mechanism of corrosion process. The studied surfactant acts predominately as cathodic inhibitors by blocking effect on the cementite cathodic sites. The inhibition efficiency increased with increasing surfactant concentrations and decreased with increasing temperature. Maximum inhibition was observed at concentration above its critical micelle concentration. **Kellou –Kerkouche *et al.*, (2008)**

- ***Calotropis procera*** was found to exhibit significant corrosion inhibitive effect in sulphuric acid medium on mild steel. Inhibition was through adsorption of the Phytoconstituents on mild steel followed temkin adsorption isotherm. **Raja, Sethuraman (2009).**

2.3.2. Influence of exposure time

- The dissolution rate of mild steel increased remarkably with time in the presence of Tertiary arsines**,** phosphine and stibines. This linear variation of weight loss with time indicated the absence of any insoluble film formed on the surface of the metal during corrosion.**(Subramanian *et al.*, 1993).**
- The influence of ***Calendula officinalis*** towards the corrosion of mild steel in 1M HCl has been evaluated by weight loss method and polarization technique by **Subha *et al.*, (2006)**. The inhibition efficiency of the compound was found to vary with the concentration of the inhibitor (0.001 to 0.5 % w/v) and immersion time (1 hr – 24 hr). Good inhibition efficiency was found at 0.5% (w/v) concentration of the inhibitor for 2 hours (94.67%)

2.3.3 Temperature Effect

- The inhibition effect of ***Zenthoxylum alatum*** plant extract on the corrosion of mild steel in aqueous orthophosphoric acid was investigated by weight loss and electrochemical impedance spectroscopy (EIS). The plant extract exhibited a maximum of 88% inhibition efficiency on corrosion inhibition of mild steel.**Gunasekaranand , Chauhan (2004).**
- The inhibitive action of leaf extracts of ***Sansevieria trifasciata*** on aluminium corrosion in 2M HCl and 2M KOH solutions was studied using gasometric technique and the studies revealed a decrease in efficiency with rise in temperature.**Oguzie, (2006).**
- Corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by leaf extracts of ***Occimum viridis (OV)*** was studied using the geometric technique at temperatures of 30 and 60 °C. The extracts inhibited the corrosion process in both acid media and inhibition

efficiency increased with increasing of the extract concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives namely KCl, KBr, KI. **Emeka Oguzie (2006).**

- The inhibitive action of the root of ginseng on aluminium corrosion in HCl using weight loss method at 30-60^{0}C. Corrosion rate was found to decrease in the presence of inhibitor compared to the free acid solution .The inhibition efficiency increased with increase in concentration of the inhibitor but decreased with increase in temperature. A mechanism of physical adsorption of the root components on the surface of the metal is proposed for the inhibition.**Obot, Obi-Egbedi *et al.*, *(*2006).**

2.4. Kinetic analysis

- The aqueous extract of the leaves of henna (lawsonia) was tested as corrosion inhibitor of C-steel, nickel and zinc in acidic, neutral and alkaline solutions. Degree of inhibition depended on the nature of metal and the type of the medium. It was found that this adsorption followed Langmuir adsorption isotherm. **El-Etre, Abdallah and El-Tantawy (2004)**
- According to **Obot *et al.*, (2009)** the inhibition of corrosion for mild steel in H_2SO_4 by 2,3-diphenylbenzoquinoxaline was found to obey Langmuir adsorption isotherm equation suggesting that the inhibition efficiency increased with increase in the concentration of the inhibitor.
- The corrosion inhibitive effect of the extract of ***Aloe Vera*** leaves on zinc surface in 2M HCl solutions was carried out the inhibition efficiency decreased with increase with increasing the temperature. A. Vera extract obeyed the Langmuir adsorption isotherm. A first-order kinetic relationship with respect to zinc was obtained with and without the extract from the kinetics treatment of the data. **Olusegum Abiola and James (2010)**

2.5. Polarization measurement

- **Farooqi *et al.*,(1997)** reported the inhibitive effects of aqueous extracts of ***Jasminum auriculatum*** (leaves), ***Monocardia charantia*** (fruits) & ***Hibiscus*** **(**flower) on the corrosion of mild steel for cooling water system, using 3% NaCl water. The inhibition efficiencies of the extracts were compared with that of HEDP. All the extracts were found to inhibit corrosion and their inhibition efficiencies were HEDP (93%), ***Jasminum auriculatum*** (80%),***Monocardicacharantia*** (79%) and Hibiscus (76%).Polarization measurements shows that extract of jasmine was anodic while ***Monocardia charantia*** and Hibiscus were found to be cathodic.

- **Smita and Mehta*et al.*, (1998)** suggested that the acid extracts of ***Calotropis giganta*** latex inhibited the acid corrosion of mild steel effectively at 0.08% and the inhibition decreased with decrease in concentration. Electrochemical studies showed that inhibitor was mixed type and effective one.
- **Minhaj *et al.*,(1999)** investigated the inhibitive effects of aqueous extracts of *Eucalyptus* (leaves),*Hibiscus* (flowers),*Agarius* on the corrosion of mild steel for cooling systems using tap water by weight loss and polarization methods.The results showed that all the plant extract inhibit corrosion of mild steel and their inhibitive efficiencies were in the order: Agaricus(85%) > Hibiscus > Eucalyptus(74%).
- Corrosion inhibition of mild steel by the extracts of *Pongamia glabra* and *Annona squamosa* in HCl and H_2SO_4 media was studied by **Sakthivel *et al.*, (1999).** Weight loss, polarization, hydrogen permeation and impedance studies were carried out at various temperatures. Polarization studies inferred that, *Pongamia glabra* and *Annona squamosa* acted as mixed and cathodic inhibitors respectively.
- The effect of *cashew juice* extract on corrosion inhibition of mild steel in HCl was investigated by **Loto and Mohammed *et al,* (2000).** Weight loss and potential measurement techniques were used. The extracts from bark provided no inhibition while nut-juice extract accelerated corrosion. Apple juice extracts at a concentration of 2ml/100ml of 0.1M HCl gave good results of corrosion inhibition.
- **Maheswari *et al*., (2001)** investigated the inhibitive effect of acid extracts of flowers and leaves of *Thespesia populnea*on the corrosion of mild steel in 1M HCl. The mass loss method and potentiostatic studies revealed the effectsiveness of the extract. An efficiency of 94.87% was found for 0.35% extract at 333K.
- **Manohari and Rajalakshmi *et al*., (2001)** determined the effective performance of extracts of *Psidium gujava*(bark) and *Callistemon*(leaves) for mild steel in 1M HCl. The extracts were effective at high concentration and at room temperature. The polarization curves showed mixed type behaviour.
- **Adbel-Gaber *et al.*, (2005)** observed that the effects of extracts of Chamomile (*Chamaemelum Mixtum.L),*Halfabar (*Cymbopogon proximus*), Black cumin (*Nigella*

sativa L.), and kidney beanplants on the corrosion of steel in aqueous 1M H_2SO_4 using EIS and potentiodynamic polarization technique. Potentiodynamic polarization curves indicated that the plant extract up to a critical concentration. The adsorption of the extracts inhibited corrosion obeyed Langmuir,Florry –Hugins,and the Kinetic Thermodynamic model,were tested to clarify the nature of adsorption.

- The inhibitive effect of the extract of *khillah (Ammi visnaga)*seeds, on the corrosion of SX 316 steel in HCl solution was determined using weight loss measurements as well as potentiostatic technique. The inhibitive effect of khillah extract was discussed on the basis of adsorption of its components on the metal surface. Negative values of free energy of adsorption indicating the spontaneity of the adsorption process. Khillah extract was found to afford an efficiency of 99.3% at 300 ppm **(El-Etre *et al*., (2005).**
- Corrosion inhibition of mild steel 2M HCl and 1M H_2SO_4 by leaf extracts of *Occimum viridus* was studied using gasometric technique at temperatures of 30°C and 60°C and EIS, weight loss.The results indicated that the extract inhibited the corrosion process in both acid media and the inhibition efficiency increases with increase in concentration of inhibitor. Temperature studies revealed a decrease in efficiency with rise in temperature **(Emeka Oguzie *et al* ., 2005).**
- The efficacy of *Telfaria occidentals* extract as a corrosion inhibitor for mild steel in 2M HCl and 1M H_2SO_4 solutions, and the effect of temperature and the halide additives on the inhibition efficiency were investigated by **Oguzie *et al* ., (2005)**. Corrosion rate was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. The inhibition efficiency increased with increase in concentration of inhibitor but decreased with an increase in temperature. Synergistic effects increased the efficiency of the extract in the presence of halide additives in the order KCl<KBr<KI. Protonated species in the extract composition played a vital role in the inhibiting action.
- **Yan Li *et al.*, (2005)** explained the inhibition efficiency of Berberine extracted from *Coptis chinensis* on corrosion of mild steel in 1M H_2SO_4 studied by Weight loss, electrochemical techniques, surface analysis in the presence of inhibitor was done by scanning electron microscope (SEM) with energy disperse spectrometer (EDS). The weight loss results showed that berberine is an excellent corrosion inhibitor for mild steel immersed in 1M H_2SO_4.

- Berberine extracted from *Coptis chinensis* was tested for corrosion of mild steel in 1 M H_2SO_4 From the Potentiodynamic curves, it can be seen that berberine suppressed both cathodic and anodic processes. The polarization resistance increased with the increasing inhibitor concentration. **Yan Li**, **Peng ZhaoQiang Liang and Baorong Hou (2005).**
- The effect of extracts of Chamomile (*Chamaemelum mixtum* L.), Half bar (*Cymbopogon proximus*), Black cumin (*Nigella sativa* L.), and Kidney bean (*Phaseolus vulgaris* L.) plants on the corrosion of steel in aqueous 1 M sulphuric acid were investigated. Potentiodynamic polarization curves indicated that the plant extracts behaved as mixed-type inhibitors. ***Abdel-Gaber et al., (2006).***
- **Lakshmi *et al.*, (2006),**investigated the inhibitive action of seed powder extract of *Brassica jencea* (mustard seed) on the corrosion of mild steel in HCl and H_2SO_4 by weight loss technique. It was shown that the mustard seed powder acted as a better inhibitor in H_2SO_4 medium than HCl medium.
- ***Quinine,*** a natural product, was investigated as a corrosion inhibitor for low carbon steel in 1M HCl solution. EIS, potentiodynamic polarization methods were used to study the inhibition action in the temperature range 20-50°C.The result proved the inhibition efficiency was found to increase up to 96% at 20°C**.(Mohamed Ismail *et al.*, (2006).**
- According to **de Souza and Spinelli (2008)** the naturally occurring biological molecule caffeic acid acted as an excellent inhibitior on the corrosion of mild steel in 1 M H_2SO_4 by decreasing the cathodic reaction area and modifying the activation energy of the anodic reaction.
- **Ebenso *et al., (2008)*** observed the corrosion inhibition of mild steel by ethanol extract of *Piper guinensis* (EEPG) using gravimetric, gasometric and thermometric methods. The results of the study reveals that the different concentrations of ethanol extract of *Piper guinensis* (EEPG) inhibit mild steel corrosion.
- The inhibition of the corrosion of mild steel by ethanol extract of *Musa sapientum peels*in H_2SO_4 was studied by gasometric and thermometric methods. The results of the study revealed that different concentrations of ethanol extract of *M. sapientum* peels inhibited mild steel corrosion. **Eddy *et al.*, (2008).**
- **Rajalakshmi. *et al.,*(2008)** studied the role of seed extracts of *Phaseolus aureus* on corrosion of mild steel in 1M HCl by weight loss method and potentiodynamic

polarization technique. The Potentiodynamic polarization results reveal that the seed extract behaved like mixed type inhibitor. Maximum inhibition efficiency of Phaseolus aureus in 1M HCl was found to be 93%.

- The inhibition effect of bis-thiadiazole (BTDS) derivatives against the corrosion of mild steel in 1M HCl solution was studied by weight loss, electrochemical impedance spectroscopy [EIS] and potentiodynamic polarization methods. All the BTDS exhibited >90% inhibition efficiency at concentration as low as 40 ppm. Polarization curves indicate that they were mixed type of inhibitors. **Ashish kumar singh and Quraishi (2009).**
- **Christy Ezhilarasi *et al*., (2009)** studied the influence of the addition of the extract of naturally occuring *Hibiscus syriacus linn* and the flavonoid component Rutin on the corrosion of mild steel in 1M hydrochloric acid by weight loss measurement, gasometric and polarization study in the presence and absence of quaternary ammonium salt. It was observed that the extract of the plant and Rutin reduced the corrosion rate and it was reported that the inhibition efficiency increases with increase in inhibitor concentration.
- **Nnabuk Eddy *et al.,* (2009)** investigated the inhibitive and adsorption properties of ethanol extract of *Terminalia catappa* for the corrosion of mild steel in H_2SO_4 using weight loss, hydrogen evolution, and infrared methods of monitoring corrosion. The studies revealed that the inhibition efficiency of the inhibitor increased with increasing concentration but decreased with increasing temperature and it obeyed the Langmuir adsorption isotherm. The inhibition potential of ethanol extract of *T.catappa* was attributed to the presence of saponin, tannin, phlobatin, antharaquinone, cardiac glycosides, flavonoid, terpene, and alkaloids in the extract.
- **Umoren *et al., (2009)*** studied the corrosion inhibition of aluminium in HCl solution in the presence of exudate gum from *Raphia hookeri* at the temperature range of 30-60^{0}C using weight loss and thermometric techniques. It was found that the inhibition efficiency increases with increase in temperature. The exudate gum was found to obey Temkin adsorption isotherm.
- **Aisha *et al*., (2010)** studied the corrosion and corrosion inhibition of mild steel in 1.0 M H_2SO_4 containing 10% ethyl alcohol (EtOH) by ***Zizyphus Spina-Christi* (*ZSC*)** extracts (aqueous extract and alcoholic extract) has been studied using chemical techniques

(hydrogen evolution (HE) and mass loss (ML)) and electrochemical techniques (electrochemical impedance spectroscopy(EIS) and potentiodynamic polarization(PDP)). The effect of acid concentration on the corrosion rate of mild steel increases with acid concentration (0.25-1.5) M showing first order corrosion reaction without changing the reaction mechanism, and the results showed that when the concentration of ***ZSC*** extracts (aqueous extract and alcoholic extract) increased the rate of steel corrosion is decreased, which indicates that the inhibition of the corrosion process is produced. Electrochemical impedance spectroscopy results showed that the corrosion and corrosion inhibition of steel occurred mainly by charge transfer. The electrochemical results of polarization also showed that the extracts of ***ZSC*** plant act as mixed type inhibitors, they retarded both cathodic and anodic reaction. The experimental results from chemical and electrochemical studies were found to fit Langmuir isotherm.

- **Mohd. Hazwan Hussinand Mohd. Jain Kassim., (2010)** investigated inhibition of the corrosion of mild steel in aqueous solutions by ethyl acetate extract of *Uncaria gambir* containing catechin using weight loss, Potentiodynamic polarisation measurements, electrochemical impedance spectroscopy (EIS) and scanning electron microscope technology with energy dispersive X-ray spectroscopy (SEM-EDX). Inhibition was found to be highest at a concentration of 150 ppm in solutions with a pH of 5. The results obtained showed that the ethyl acetate extract of U.Gambir acted as a mixed-type inhibitor and could serve as an effective corrosion inhibitor of mild steel in aqueous solution.
- **Okafor *et al.*, (2010)** investigated the inhibitive action of leaves (LV), root (RT) and seeds (SD) extracts of *Azadirachta indica* on mild steel corrosion in H_2SO_4 solutions using weight loss and gasometric techniques. The results obtained indicated that the extracts functioned as good inhibitors in H_2SO_4 solutions. Inhibition efficiency was found to increase with extracts concentration and temperature, and followed the trend: SD > RT > LV.
- According to **Solomon *et al.*, (2010)** the adsorption of the carboxymethyl cellulose on to the mild steel surface followed Langmuir and Dubin Radush Kevich adsorption isotherm models. The inhibition mechanism was further corroborated by the values of activation parameters obtained from the experimental data

- **Sivaraju & Kannan., (2010)** The inhibition effect of alcoholic extract on mild steel corrosion in 1N phosphoric acid has been studied *Acalypha indica L***.** by mass loss and polarization techniques between 303 K and 333K.The inhibition efficiency increased with increase in concentration of plant extract. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared to blank. The adsorption of inhibitor on mild steel surface was found to obey Temkin's adsorption isotherm.
- **Tedjani Yahia Namoussa *et al*., (2010)**The inhibitive action of aqueous extract of ***Tamarix gallica*** on the corrosion of mild steel in 1m sulphuric acid was assessed by weight-loss method and polarization technique. Polarization curves revealed that the plant extract behave as mixed-type inhibitors. inhibition efficiency increased with extract concentration up to a critical value. the results show that the extract solution of the plant could serve as an effective inhibitor for the corrosion of steel in sulphuric acid medium.
- **Vinod kumar *et al*., (2010)** analysed the corrosion inhibition effect of acid extract of the pericarp of the fruit ***Garcinia mangostana*** on mild steel in hydrochloric acid medium. Using weight-loss data, corrosion rate (CR) and thermodynamic parameters such as energy of activation for corrosion of mild steel (E), heat of adsorption of the inhibitors on the metal surface (Q) and change in free energy (ΔG) were calculated. The study revealed that the pericarp extract of the fruit G. mangostana is a non-toxic, cost-effective corrosion inhibitor for mild steel in acid medium.
- **Vivek Sharma *et al., (*2010)** investigated the effect of extract of *Musa paradisiaca* on corrosion inhibition of mild steel in aqueous 0.5 M sulphuric acid by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency was found to increase with increase in concentration of the extract. Polarization measurement indicates that *Musa paradisiaca* acts as a mixed type inhibitor and the inhibition efficiency decreases with rise in temperature.
- **Khalid Hasa*n et al*., (2011)** investigated the inhibition of corrosion of mild steel usin*g Paniala* ***(Flacourtia jangomas)*** extract in 1M HCl and 0.5M H_2SO_4 solutions was investigated by weight loss method at 30 degree C. The result showed that corrosion rate significantly decreased in presence of the extract and inhibition efficiency increased with increasing concentration of the extract. In case of HCl maximum inhibition efficiency

(98%) was noticed at 5% v/v inhibitor concentration and no considerable change in inhibition efficiency was observed after this concentration and in 0.5M $_{H2}S_{O4}$, it was found 95% efficiency at the same concentration of inhibitor.

- Corrosion inhibition effect of alkaloids extract from ***Palicourea guianensis*** plant (AEPG) on C38 steel in 1M HCl medium has been investigated by potentiodynamic polarization and electrochemical impedance spectroscopy. The polarization studies showed that AEPG acts as mixed-type inhibitor. The electrochemical impedance spectroscopy showed that the charge transfer resistance increases and the double layer capacitance decreases on increasing plant extract concentration. The inhibition efficiency of the extract obtained from impedance and polarization measurements was in a good agreement and was found to increase with increasing concentration of the extract. Inhibition efficiency of 89% was achieved with 100 mg L-1 of AEPG at 25 °C. The obtained results showed that, the *Palicourea guianensis* extract could serve as an effective inhibitor for the corrosion of steel in acid media. The adsorption of AEPG obeys the Langmuir adsorption isotherm**.Lebrini *et al*., (2011).**
- **Rajiv Prakash *et al*., (2011)** investigated the effect of plant extract of Papaveraceae family Argemone mexicana for use as a low cost and efficient corrosion inhibitor for mild steel in acidic environment. Weight loss and electrochemical methods were used to study the corrosion. Nearly 80% corrosion inhibition was observed at around 200 mg L^{-1} inhibitor concentration and maximum (92.5%) for 500 mg L^{-1} extract concentration in 1 M HCl. Inhibition mechanism is studied using UV–vis, electrochemical, and surface imaging techniques.
- **Sangeetha *et al*., (2011)** studied the inhibition efficiency (IE) of ***Phyllanthus amarus*** extract (PAE)-Zn^{2+}system, in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of Cl-, has been evaluated by weight loss method. Weight loss study reveals that the formulation consisting of 2 mL of PAE and 25 ppm of Zn^{2+} has 98% inhibition efficiency in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl-. Synergistic parameters suggest that a synergistic effect exists between PAE and Zn^{2+}. Polarization study reveals that this system functions as mixed type of inhibitor controlling the cathodic reaction and anodic reaction to an equal extend. AC impedance spectra reveal that a protective film is formed on the metal

surface. The FTIR spectra reveal that the protective film consists of Fe^{2+}-phyllanthus complex.

- **Shuduan Deng *et al.*, (2011)** investigated the inhibition effect of *Ginkgo* leaves extract (GLE) on the corrosion of cold rolled steel (CRS) in 1.0–5.0 M HCl and 0.5–2.5 M H_2SO_4 solutions by weight loss, potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) methods. The results showed that GLE is a good inhibitor, and exhibits more efficient in 1.0 M HCl than 0.5 M H_2SO_4. The adsorption of GLE on CRS surface obeyed Langmuir adsorption isotherm. GLE acts as a mixed-type inhibitor in 1.0 M HCl, while a cathodic inhibitor in 0.5 M H_2SO_4.
- Corrosion inhibition effect of ***Vernonia amygdalina*** extract on aluminium in 0.5 M HCl solution was studied using gravimetric method at 40^{o}C temperature. The results revealed that *V.Amygdalina* could be used as an ecofriendly corrosion inhibitor for Aluminium in HCl solution. The corrosion inhibition efficiency of the extract increases with concentrations in the corrosion media. The surface coverage of the extract obeyed Langmuir adsorption isotherm. **Ajanaku Kolawole Oluseyi *et al*., (2012)**
- **Babatunde *et al*., (2012)** reported the inhibitive effect of leaf extract of ***Irvingia gabonensis*** on the corrosion of aluminum in 1M HCl solution was investigated using chemical method at 30, 35 and 40°C respectively. The inhibition efficiency for the extract increased with increasing concentration of the extract and decreased with increase in temperature. The adsorption of the inhibitor molecules on Aluminium surface was found to obey Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed based on the thermodynamic parameters that govern the inhibition process.
- **Ben Hmamou *et al*., (2012)** studied the effectiveness of *Chamomile* extract (CE) as corrosion inhibitor for C38 steel in 1 M HCl using Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM) studies. The effect of temperature on the corrosion behavior of C38 steel in 1 M HCl with addition of plant extracts was studied in the temperature range of 298–328 K. Inhibition efficiency of 88% was achieved with 7g/L CE at 298 K. It is evident from the results of this study that CE inhibits the corrosion in 1 M HCl through adsorption process following Langmuir adsorption isotherm.

- **Ananth Kumar *et al*., (2013)** The corrosion inhibitive action of flower extracts of *Magnolia champaca flower* on mild steel corrosion in 0.5 M H_2SO_4 solution was studied using weight loss method, potentiodynamic polarization and EIS measurements. The results obtained indicate that the extracts functioned as good inhibitors in 0.5 M H_2SO_4 solution. Inhibition efficiency was found to increase with extract concentration. The adsorption of constituents in the plant extract on the surface of the metal is proposed for the inhibition behavior.
- Leaves of ***Punica granatum*** extract (LPGE) as green inhibitor for the corrosion of mild steel in 1M HCl solution was studied using weight-loss and potentiodynamic polarization measurements. The results obtained revealed that LPGE has fairly good inhibiting properties for mild steel corrosion in 1M HCl solution, with efficiency of around 94 % at a concentration of 1 g/L. The inhibition was of a mixed anodic–cathodic nature. **Abboud *et al*., (2013).**
- **Chauhan *et al*., (2013)** studied the Corrosion inhibition of Zn in HCl by *Nictanthes* plant extract The natural plant product used as a medicine namely marigold were tested as corrosion inhibitor of Zn in 0.5M HCl. The Cyclic-Voltametry, potentiometry technique data suggested that the inhibition efficiency increases with the concentration of extract.
- The inhibitive effect of the extract of ***Salvia judica*** on aluminum corrosion in 1 M NaOH solutions was investigated by using the weight loss method at different temperatures. It was found that the extract play as corrosion inhibitor for aluminum corrosion in 1 M NaOH solution. The inhibition action of the extract was discussed in view of Langmuir and Temkin adsorption isotherms. It was found that the adsorption of the extract on aluminum surface is a spontaneous process. **Eyad Nawafleh *et al*., (2013).**
- **Hemalatha *et al*., (2013)** investigated the corrosion inhibitive action of flower extracts of ***Nelumbo nucifera*** *flower* on mild steel corrosion in 1 N H_2SO_4 solution was studied using weight loss method, Potentiodynamic polarization and EIS measurements. The results obtained indicate that the extracts functioned as good inhibitors in 1 N H_2SO_4 solution. Inhibition efficiency was found to increase with extract concentration. The adsorption of constituents in the plant extract on the surface of the metal is proposed for the inhibition behavior.

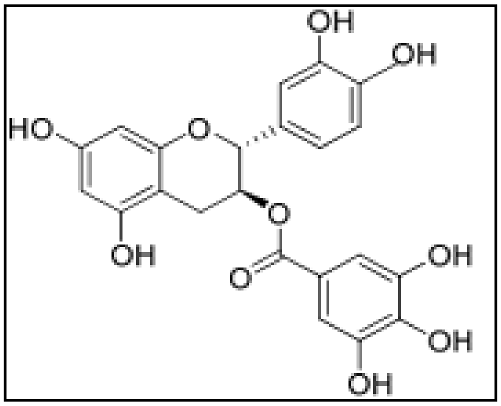
- **Onuegbu *et al.*, (2013)** reported the use of ***Eupatorium odoratum*** (E.O) as corrosion inhibitor of mild steel in 1M H_2SO_4 acid. The effects of temperatures on the inhibition efficiency of ***Eupatorium odoratum*** were also tested at temperature of 30^0C and 60^0C respectively. The weight losses of the mild steel were taken for complete four days, for the two temperatures. The rates of corrosion of the mild steels were found to increase with increase in concentration of the acid and also decrease with increase in concentration of the ***Eupatorium odoratum***.
- Extract of ***Clerodendrum phlomidis*** leaves was investigated as corrosion inhibitor of mild steel in 0.5M HCl using conventional weight loss method and scanning electron microscopic studies. The weight loss results showed that all the plant extracts are excellent corrosion inhibitors, Scanning electron microscopic studies provided the confirmatory evidence of improved surface condition, due to the adsorption, for the corrosion protection. **Pruthviraj *et al.*, (2013).**
- The extract of ***Adhatoda vasica*** in aqueous 0.5 M H_2SO_4 was systematically investigated by **Ramananda Singh (2013)** to ascertain its inhibitory effect on corrosion of mild steel and its mechanism of the inhibition by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency of ***Adhatoda vasica*** on corrosion of mild steel in 0.5 M H_2SO_4 solution increases on increasing in its concentration and decreases with rise in temperature. Potentiodynamic Polarization measurements show that ***Adhatoda vasica*** act as mixed type inhibitor.
- **Kamaraj *et al.*, (2014)** investigated the effect of ***Podophyllum hexandrum*** fruit extract as an inhibitor for mild steel in 1N HCl using weight loss method. The corrosion coupons were immersed in 1N HCl solution containing varying inhibitor concentrations (1%, 2%, 3%, 4% and 5% v/v) within a period of 1-4 hours. From the result, it was found that the adsorption of ***Podophyllum hexandrum*** fruit extract reduced the corrosion rate in acid medium. The inhibitive action of this plant extract has been found to be significant. The most suitable inhibitor concentration was found to be 5% for an inhibition efficiency of 89%. The inhibition is attributed to physical adsorption.
- **Krishnaveni and Ravichandran., (2014)** studied the effect of ***Morinda tinctoria*** *(MT)* ***leaves*** extract on the corrosion inhibition of Al in acid medium. The inhibition studies were carried out on Al in 0.5 mol/L HCl using mass loss and electrochemical techniques.

Parameters, such as concentration of the inhibitor, concentration of the acid, temperature and concentration of halide ions, were varied and optimized. Increase of the temperature and concentration of acid can decrease the performance of the inhibitor. Thermodynamic parameters show that the physisorption of the inhibitor molecules on Al surface obeyed Langmuir isotherm.

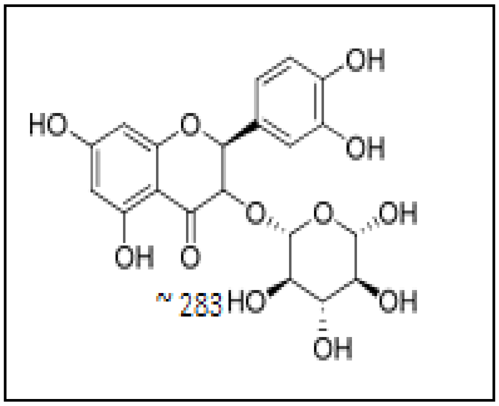
- The inhibition property of ***Ruta graveolens*** extract (RGE) on the corrosion of carbon steel in 1M HCl solution was investigated using potentiodynamic polarization and weight loss techniques. The percentage inhibition increased with the increase of the concentration of the extract. At a concentration of 2.0g/l, the percentage inhibition reached about 94.34% at 25°Cand 6 hours. The inhibition efficiency decreased with the increase of temperature. The results showed that the adsorption of the extract on the carbon steel surface obeys Langmuir isotherm. **Mahir Majeed *et al*., (2014).**
- **Pasupathy *et al*., (2014)** investigated the extract of the leaves and berries of ***Solanum nigrum*** as a green corrosion inhibitor for zinc in 0.5N HCl by using weight loss, gasometric and thermometric methods. Results obtained showed that the extract of ***Solanum nigrum*** offered good protection against corrosion of zinc metal and exhibited high inhibition efficiencies. The inhibition efficiency was found to increase with increase in the extract concentration. The adsorption of the inhibitor molecules on the zinc metal surface obeyed Temkin adsorption isotherm.
- The corrosion inhibition of mild steel in H_2SO_4 solution in presence of ***Juniperus*** plant at a temperature range of 30 to 60°C was studied using chemical (Hand WL) and electrochemical (PDP and EIS) methods. ***Juniperus*** plant acts as an inhibitor in the acid environment. The inhibition efficiency increases with increase in inhibitor concentration but decreases with an increase in temperature. The inhibitive effect of the ***Juniperus*** plant could be attributed to the presence of some compound in the plant which is adsorbed on the surface of the mild steel. ***Juniperus*** plant was found to conform to the Frumkin adsorption isotherm and Temkin adsorption isotherm at all the concentration levels and temperature studied. The phenomenon of physical adsorption is proposed from the activation parameters obtained. Thermodynamic parameters revealed that the adsorption process was spontaneous. **Saedah Al-Mhyawi (2014)**

Phytochemical constituents of *Pouteria campechiana*:

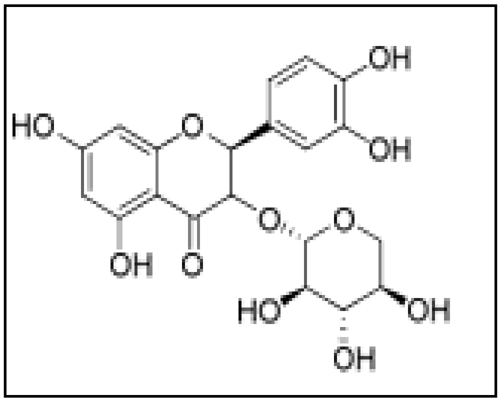
The crude ethanolic extract of the leaves of ***Pouteria Campechiana*** was evaluated for its phytochemical nature, the major constituents reported are Myricetin-3-O-α-L-arabinopyranoside, Myricetin-3-O-α-L-rhaminopyranoside, Quercetin-3-O-α-L-rhamnopyranoside, Taxifolin-3-O-α-L-rhamnopyranoside, Trans-taxifolin-3-O-α-L-arabinopyranoside, Taxifolin-3-O-α-L-arabinofuranoside and Quercetin-3-O- β-Arabinopyranoside. **Moustafa H Baky *et al.*, *(*2016)**



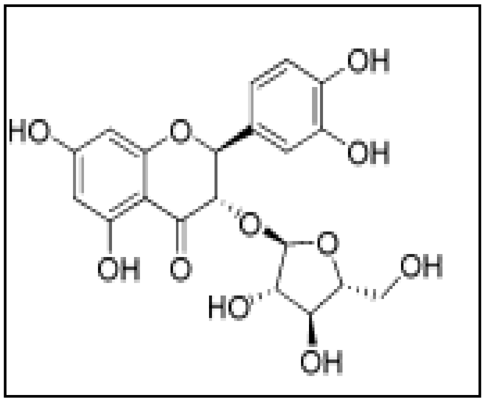
(+)-Catchin-3-O-gallate



Taxifolin-3-O-α-L-rhamnopyranoside



Trans-taxifolin-3-O-α-L-arabinopyranoside



Taxifolin-3-O-α-L-arabinofuranoside

Thus it can be noticed that the selected plant has abundant phytochemical constituent which will aid in corrosion inhibition of metals. Further investigations are warranted to prove its role in corrosion inhibition of mild steel in acid media.

MATERIALS AND METHODS

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In any research work materials and methods are adopted to determine the research work qualitatively and quantitatively. In the present study, efforts have been taken to study the inhibitive action of the ***Pouteria campechiana*** leaves extract as corrosion inhibitor for mild steel (MS) in 1M HCl and 0.5 M H_2SO_4.The study was elaborated in following steps.

3.1. SELECTION OF SAMPLE

Mild steel was selected because it is widely used in engineering materials particularly for the structure and automobile applications due to low cost and easy availability. MS suffers from severe corrosion in destructive environment, which needs to be protected. Hence the MS were studied using the green inhibitor through various methods.

3.2. PREPARATION OF SAMPLE

Regular sample of area 1x5 cm^2 have been cut from a large sheet of mild steel. A hole was drilled in the specimen, mechanically polished, degreased, washed with de ionized water, it is then thoroughly dried and kept in desiccator for weight loss tests. The mild steel specimens used in the following percentage elemental of composition as shown below.

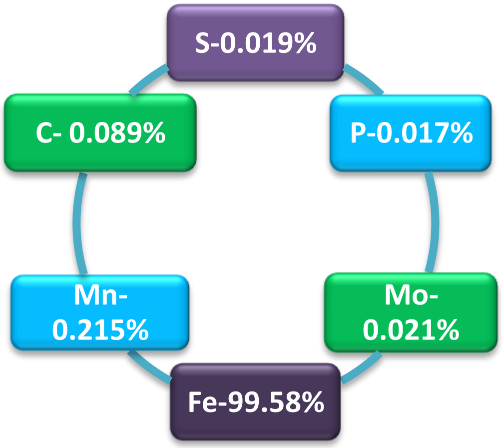

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Figure 3.1 Elemental composition in Mild steel

3.3. TEST MEDIUM

Acid are one of the widely used solutions in chemical laboratories and also in several industrial processes for the processing like pickling, acid cleaning, acid de-scaling and oil wet cleaning etc ,hence the samples are tested in acidic condition. Experiments were performed in 1M HCl and 0.5 M H_2SO_4 solution. The acids used were of LR grade.

3.4. SELECTION OF INHIBITOR

The inhibitors were selected on the following consideration,

- ✓ Less expensive
- ✓ Possess no threat to the environment
- ✓ Non-toxic
- ✓ Easily available
- ✓ Bio-degradable
- ✓ Eco-friendly

3.5. PREPARATION OF THE INHIBITOR

The extract was prepared by refluxing 25g of ***Pouteria campechiana*** leaves in 500 ml of HCl and 0.5M H_2SO_4 for three hours and kept overnight for cooling. The cooled extract was filtered and made up to 500ml with 1M HCl and 0.5M H_2SO_4 to get 5% extract of inhibitor.

3.6. PHYTOCHEMICAL SCREENING

Phytochemical examinations were carried out for all the extracts as per the standard methods. **(Prashant Tiwari *et al.*, Jan-March 2011)**

1. Detection of alkaloids: Extracts were dissolved individually in dilute Hydrochloric acid and filtered.

a) Mayer's Test: Filtrates were treated with Mayer's reagent (Potassium Mercuric Iodide). Formation of a yellow coloured precipitate indicates the presence of alkaloids.

b) Wagner's Test: Filtrates were treated with Wagner's reagent (Iodine in Potassium Iodide). Formation of brown/reddish precipitate indicates the presence of alkaloids.

c) Dragendroff's Test: Filtrates were treated with Dragendroff's reagent (solution of Potassium Bismuth Iodide). Formation of red precipitate indicates the presence of alkaloids.

d) Hager's Test: Filtrates were treated with Hager's reagent (saturated picric acid solution).Presence of alkaloids confirmed by the formation of yellow coloured precipitate.

2. Detection of carbohydrates: Extracts were dissolved individually in 5 ml distilled water and filtered. The filtrates were used to test for the presence of carbohydrates.

a) Molisch's Test: Filtrates were treated with 2 drops of alcoholic α-naphthol solution in a test tube. Formation of the violet ring at the junction indicates the presence of Carbohydrates.

b)Benedict's Test: Filtrates were treated with Benedict's reagent and heated gently. Orange red precipitate indicates the presence of reducing sugars.

c) Fehling's Test: Filtrates were hydrolysed with dil. HCl, neutralized with alkali and heated with Fehling's A & B solutions.Formation of red precipitate indicates the presence of reducing sugars.

3. Detection of saponins

a) Froth Test: Extracts were diluted with distilled water to 20ml and this was shaken in a graduated cylinder for 15 minutes. Formation of 1 cm layer of foam indicates the presence of saponins.

b) Foam Test: 0.5 gm of extract was shaken with 2 ml of water. If foam produced persists for ten minutes it indicates the presence of saponins.

4. Detection of phytosterols:

a) Salkowski's Test: Extracts were treated with chloroform and filtered. The filtrates were treated with few drops of Conc. Sulphuric acid, shaken and allowed to stand. Appearance of golden yellow colour indicates the presence of triterpenes.

b) Libermann Burchard's test: Extracts were treated with chloroform and filtered. The filtrates were treated with few drops of acetic anhydride, boiled and cooled. Conc. Sulphuric acid was added. Formation of brown ring at the junction indicates the presence of phytosterols.

5. Detection of phenols

Ferric Chloride Test: Extracts were treated with 3-4 drops of ferric chloride solution. Formation of bluish black colour indicates the presence of phenols.

6. Detection of tannins

Gelatin Test: To the extract, 1% gelatin solution containing sodium chloride was added. Formation of white precipitate indicates the presence of tannins.

7. Detection of flavonoids

a) Alkaline Reagent Test: Extracts were treated with few drops of sodium hydroxide solution. Formation of intense yellow colour, which becomes colourless on addition of dilute acid, indicates the presence of flavonoids.

b) Lead acetate Test: Extracts were treated with few drops of lead acetate solution. Formation of yellow colour precipitate indicates the presence of flavonoids.

8. Detection of proteins and aminoacids

a) Xanthoproteic Test: The extracts were treated with few drops of conc. Nitric acid. Formation of yellow colour indicates the presence of proteins.

b) Ninhydrin Test: To the extract, 0.25% w/v ninhydrin reagent was added and boiled for few minutes. Formation of blue colour indicates the presence of amino acid.

3.7. TECHNIQUES EMPLOYED

- Mass loss methods
- Electrochemical measurement

3.8. MASS LOSS METHODS

It is one of the oldest techniques of monitoring corrosion rate and is carried out by exposing the weighed metal coupons in the test media for a period of time. It is then removed and weighed. The weight loss obtained for the coupons are then measured.

In the current study pre weighed coupons were immersed in triplicate with the help of glass hook into a beaker containing 100ml of 1 M HCl acid with and without inhibitor for a particular period of time. The coupons are then washed, dried and reweighed. The average weight loss of coupons was recorded. Varying the parameters such as concentration, time of immersion and temperature the experiments were conducted

- Concentration (0.1% - 0.7%)
- Time of immersion (1/2 h, 1h, 3h, 6h, 12h & 24h)
- Temperature (303K-353K)

3.8.1. Determination of corrosion rate

Many expressions are available to express the corrosion rate. The widely used expression is measured in mils per year using formula,

$$\mathbf{C.R\ (mpy) = 3.45 * 10^{6}\ x\ W/\ D\ x\ A\ x\ T\ \ldots\ldots\ldots\ldots\ldots\ldots\ (3.1)}$$

Where,

W-Weight loss in g

D-Density of mild steel in g/cm^2

A-Area of the sample in cm^2

T-Exposure time in hours

3.8.2. Determination of percentage of inhibition and surface coverage

The percentage of inhibition efficiency and surface coverage were calculated by using the following equation,

$$\mathbf{I.E\ (\%) = w_o\text{-}\ w/w_o\ x\ 100}$$

$$\mathbf{\theta = w_o\text{-}\ w/w_o\ x\ 100\ \ldots\ldots\ldots\ldots\ldots\ldots\ (3.2)}$$

Where,

w_o - corrosion rate without inhibitor in g

w – Corrosion rate with inhibitor in g

Determination of thermodynamic parameters,

The change in free energy (ΔG) of adsorption of the inhibitors can be calculated by using the following equation (Abdel.A and Saied.A., 1981)

$$\mathbf{Log\ C = [\log \theta/\ (1\text{-}\theta)] - \log B\ \ldots\ldots\ldots\ldots\ldots\ldots\ (3.3)}$$

Where,

$\text{Log } B = -\ 1.74 - (\Delta G/2.303\ RT)$

θ is the surface coverage, C is the concentration of inhibitor, and R is the gas constant 8.314 J/mol, T is the temperature in K

The value of enthalpy of adsorption ΔH and entropy of adsorption ΔS were obtained from the basic thermodynamic equation (I.E) Gibbs Helmholtz equation

$$\mathbf{\Delta G = \Delta H - T\Delta S\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3.4)}$$

A plot of ΔG versus T will be a straight line with intercept ΔH and slope ΔS.

3.8.3. Adsorption isotherm

Corrosion inhibition is a surface process with specific adsorption of inhibitor on the metal surface. In recent years, attempts have been made to understand the nature of interaction between the inhibitor and metal surface in term of adsorption isotherm. The knowledge of the adsorption behavior of the inhibitor is important for definition of its active mechanism. The dependence of surface coverage on concentration is through the following adsorption isotherms.

Langmuir [log (θ / 1-θ) Vs log C]

Temkin [θ Vs log C]

3.8.4. Activation energy (E_a)

The activation energy at different concentration of the inhibitor at various temperatures was determined by plotting log CR Vs 1/T. (Arrhenius plot). From the slope of the plot activation energy (E_a) was calculated using the following formula.

E_a = -2.303 x R x slope of the Arrhenius plot

Where,

R is the gas constant 8.314 J/mole

3.8.5. Activation Parameters

An alternative formulation of Arrhenius equation is

$\mathbf{CR} = (\mathbf{RT/Nh}) \; \mathbf{exp} \; (\mathbf{\Delta Sa/ R}) \; \mathbf{exp} \; (\mathbf{\Delta Ha/ R})$ …………………… **(3.5)**

Where,

h is Planck's constant

N is Avogadro number

ΔSa is entropy of activation

ΔHa is enthalpy of activation

A plot of log (CR/T) Vs 1/T gave a straight line with a slope of - ΔHa /2.303R and an intercept of log(R/Nh + ΔSa/2.303R) from which the values of ΔHa and ΔSa were calculated.

3.9. ELECTROCHEMICAL METHOD

3.9.1. Polarization techniques

Electrochemical studies were carried out using conventional three electrode cell with large area of platinum foil as counter electrode saturated calomel electrode (SCE) as reference electrode and sample was as working electrode.Electrochemical measurements was done by using Biologic EC Lab software version 10.4.

Before starting the measurements the electrode potential was allowed to stabilize for 30 minutes. Polarization studies were conducted at a scan rate of 2mV/sec from -0.1 to -1mV with respect to the corrosion potential in the presence and absence of the inhibitor. 1sq.cm.of polished mild steel surface was exposed and the electrochemical studies are carried out at 303K.

3.9.2. Tafel plot

In the Tafel plot technique, a controlled scan can be applied, extending in both the anodic and the cathodic directions of corrosion potentials for a few hundred milli volts. The linear region of the plot (applied potential Vs log current) is projected to intersect. This defines corrosion current (I_{corr}) and the corrosion potential (E_{corr}) and the slope of the linear region is the Tafel slopes (ba and bc).

The inhibition efficiency was calculated using the following equation,

$$\mathbf{I.E\ (\%) = \frac{I_{corr}\,(blank) - I_{corr}\,(inhibited)}{I_{corr}\,(blank)} * 100 \ \ldots\ldots\ldots\ldots\ldots\ldots..\ (3.6)}$$

I.E from LPR technique

$$\mathbf{I.E\ (\%) = \frac{R_p(inhibited) - R_p(blank)}{Rp\ (inhibited)} * 100 \ \ldots\ldots\ldots\ldots\ldots\ (3.7)}$$

Where,

R_p (inhibited) and R_p (blank) are linear polarization resistance in the presence and absence of the inhibitor respectively.

3.9.3. Impedance spectroscopy

In this method an AC signal of 5-10mV of frequency 10KHz to 10MHz is applied to the system. Impedance date can be presented in the form of Nyquist or Bode plot. From the data, the R_{ct} and Cdl are obtained.

The I.E can be calculated using the equation,

$$\mathbf{I.E\ (\%) = \frac{R_{ct}(inhibited) - R_{ct}(blank)}{R_{ct}(inhibited)} * 100 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3.8)}$$

R_{ct} (inhibited) and R_{ct} (blanck) are charge transfer resistance in the presence and absence of the inhibitor respectively. With the help of the double layer capacitance Cdl, θ can be calculated using the equation,

$$\theta = 1 - \frac{C_{dl}\ (\text{inhibited})}{C_{dl}\ (\text{blank})} \quad \text{……………………..} \quad (3.9)$$

Where,

C_{dl} (inhibited) and C_{dl} (blank) are the double layer capacitance in the presence and absence of the inhibitor respectively.

3.10. SURFACE ANALYTICAL TECHNIQUES

3.10.1. FT-IR technique

FT-IR spectroscopy was carried out to glean information about the functional groups present in the investigated inhibitors. The samples for FT-IR studies were prepared by finely mixing the extract with spectroscopically pure KBr and then pressed by using a die so as to get a fine transparent pellet. The FT-IR spectrum was recorded for leaves of PCL extract with a frequency ranging from 4000 to 400 cm^{-1} using **Perkin Elmer FT-IR spectrophotometer** with the **SOFTWARE – OPUS version 6.5**. The interaction between the organic molecules and the metal surface has been studied by FT-IR spectra.

3.10.2. UV –visible spectrophotometric measurement

PC based double beam spectrophotometer 2202 was used to confirm the possibility of the metal- inhibitor complex formation on metal surface. UV-visible absorption spectrophotometric method was carried out on the prepared metal samples after immersion in 1M HCl with and without addition of 0.7% PCL inhibitor for 3h.

3.10.3. SEM surface analysis

Scanning electron microscopy (SEM) **JEOL MODEL JSM 6360** was used to examine the morphology of the metal surface in presence and absence of inhibitors. To understand the morphology on the MS surface in absence and presence of inhibitors, the following cases have been examined.

- Polished MS specimen.
- MS specimen dipped in 1M HCl acid medium.
- MS specimen dipped in 1M HCl acid medium containing 0.7% PCL inhibitor.

3.10.4. Laser Profilometer

Surface profiles and pores were studied using a **Zeta-20 3D Optical Profiler** was used. MS specimen that kept in a vacuum desiccator after the inhibition test were mounted on sample holder occurred under the objective of the Optical Profiler and the 3D photos were taken from the 100x magnified surface via operating program on computer. The MS specimens after exposure to 1 M HCl solution in the absence and presence of PCL extract for 3h were examined by Zeta 3D Profiler.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The present study entitled **"Surface interaction and corrosion inhibition of MS in 1M HCl and 0.5M H_2SO_4 using *Pouteria campechiana* leaves"** deals with the assessment of corrosion inhibitive nature of ***Pouteria campechiana*** leaves for mild steel in 1M HCl and 0.5 M H_2SO_4 acid medium. The results obtained from the study are dealt under the following sections.

4.1 Characterisation of *Pouteria campechiana* leaf extract

4.1.1 Phytochemical Screening

The qualitative phytochemical screening of the crude extract from *Pouteria campechiana* leaves were tested for the presence of reducing sugars, flavonoids, tannins, terpenoids, alkaloids, anthraquinones using standard procedure. (**Koul *et al*., 2008**)

Phyto constituents	Alkaloids	Phytosterols	Flavonoids	Saponins	Phlobatannnins	Steroids	Tannins	Carbohydrates	Terpenoids
Results	+	+	+	+	–	+	–	+	+

+Present ; - Absent

Table 4.1: Phytochemical screening of crude PCL extract

The phytochemical analysis of the leaves extracts of PCL reflected the presence of saponins, flavonoids, alkaloids, terpenoids and phenols. The presence of these active phytoconstituents in the extracts may have great influence on their corrosion inhibition property.

4.1.2 FT-IR Spectrophotometer

FT-IR of fine powder of PCL shows the presence of phenolic –OH (corresponds to 3297 cm^{-1}). The peak at 1635 cm^{-1} corresponds to C=O group, and a peak at 1446 cm^{-1} indicates the presence of C-H bend, whereas 1260 cm^{-1} corresponds to C- O stretching. The FT-IR peaks present accord well with the infra- red spectrum obtained from other researchers **(Hamman, 2008; Kumar & Mathur, 2013; Ray & Aswatha, 2013).**

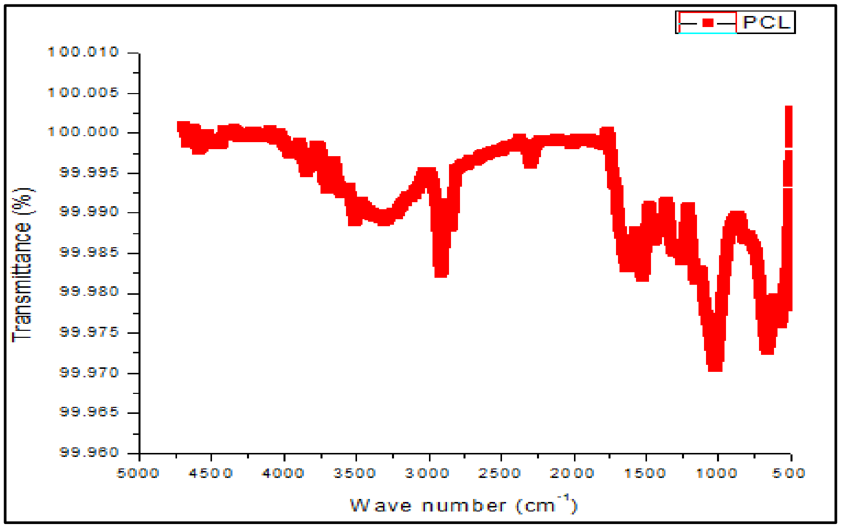


Figure 4.1. FT- IR spectral peak of crude PCL extract

4.2 Mass loss measurements

The acid extract of PCL in 1 M HCl and 0.5 M H_2SO_4 has been tried for its potency in the retardation of corrosion of mild steel. It has been evaluated using the following parameters by mass loss method.

- ✓ Concentration of the inhibitor
- ✓ Immersion time and
- ✓ Temperature variation

4.2.1 Effect of inhibitor concentration in 1M HCl

The effect of the addition of PCL extract on the corrosion of mild steel in 1 M HCl solution has been studied using mass loss method at 303 K.

Table 4.2 gives values of the rate of corrosion (mpy) and inhibition efficiency (IE %) for corrosion of mild steel in 1 M HCl in the presence of PCL extract as green inhibitor at different concentrations. A maximum efficiency of 81.2 % is obtained at 0.7% concentration of the inhibitor.

4.2.1.1 Impact of immersion time

Mass loss of mild steel at specific time intervals, in the absence and presence of PCL concentration in 1M HCl acid at ambient temperature of 303 K has been studied. The values of mass loss (W), corrosion rate (R) and the percentage inhibition efficiency (%IE) are presented in Table 4.2.

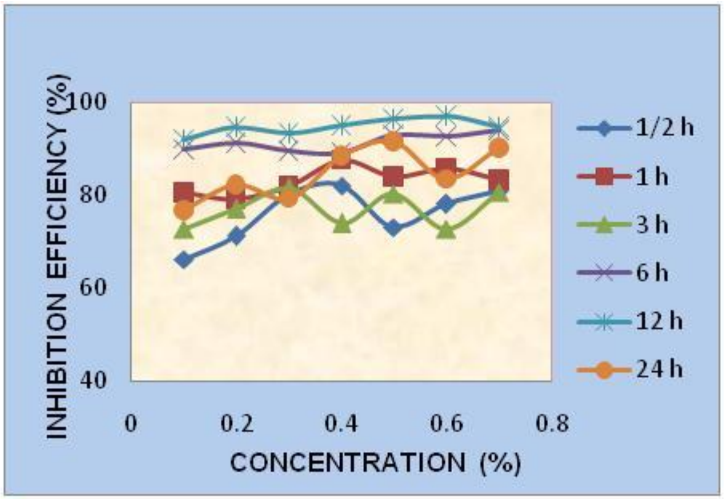


Figure 4.2. IE of MS in 1 M HCl at different concentration of PCL

The corrosion rates decreased progressively in 1M HCl with increase in PCL concentration. Figure 4.2 shows the variation of mass loss, corrosion rate and percentage inhibition efficiency versus exposure time at different concentrations of PCL extract. The curves obtained show a progressive increase with the addition of PCL at all concentrations in 1M HCl. The inhibitor is able to afford a maximum efficiency of 97 % at 12 h of immersion time (0.7 % conc).

Table 4.2: Variation of inhibition efficiency with PCL concentration for time of immersion in 1M HCl

S No	Conc (%)	Corrosion rate and inhibition efficiency											
		½ h		1 h		3h		6h		12 h		24 h	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mp y)	IE (%)
1.	Blank	861	-	904	-	712	-	671	-	800	-	266	-
2.	0.1	290	66.3	174	80.7	193	72.8	68	89.8	62	92.2	65	76.7
3.	0.2	247	71.2	187	79.2	162	77.2	58	91.3	42	94.7	47	82.2
4.	0.3	170	80.1	162	82.1	130	81.6	69	89.6	52	93.4	54	79.3
5.	0.4	153	82.2	149	83.5	184	74.1	71	89.3	38	95.2	30	88.4
6.	0.5	230	73.3	144	83.9	139	80.4	46	93	28	96.4	25	90.3
7.	0.6	187	78.2	127	85.8	193	72.9	48	92.8	41	94.8	43	83.6
8.	0.7	162	81.2	110	87.7	136	80.8	40	93.9	23	**97**	22	91.6

4.2.1.2. Effect of temperature

Presented in Table 4.3, is the corrosion rate of mild steel samples in the presence and absence of PCL extract in 1 M HCl solution at temperature range 303K to 353 K. The corrosion rate values increased as the temperature of the reacting system increases. Dissolution of the mild steel occurs more rapidly as temperature increases reflecting an increase in corrosion rate as temperature increases. It is noted that at elevated temperature, reacting molecules collide faster leading to more consumption of the reactant and formation of the product. Increase in corrosion rate results to decrease in inhibition efficiency.

Figure 4.3, represent the Inhibition efficiency of Mild steel in 1 M HCl at different temperature of PCL extract. It is observed that as the concentration of the extract increases, the inhibition efficiency also increases. At increased concentration, the interaction between the extract molecules and the mild steel samples would have increased thereby leading to better protection of the samples. The results obtained show that the values of inhibition efficiency of PCL extract decrease with increase in temperature. At higher temperature desorption of the adsorbed molecules of the extract occurs leading to the exposure of the surface of mild steel to the acid environment resulting in increase in corrosion rate and decrease in inhibition efficiency. Decrease in inhibition efficiency with increase in temperature is termed physical adsorption. From Table 4.3, it can be noticed that the efficiency decreases with increasing temperature but stabilizes at 353 K to afford an efficiency of 85.9% (0.7% conc of inhibition).

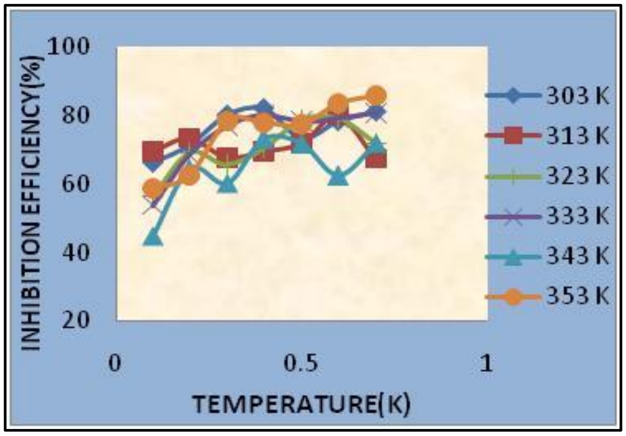


Figure 4.3. IE of MS in 1 M HCl at different temperature of PCL

Table 4.3: Variation of inhibition efficiency with PCL concentration at different temperature in 1M HCl

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		303K		313K		323K		333K		343K		353 K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	861	-	2217	-	3573	-	6635	-	7890	-	24223	-
2.	0.1	290	66.3	673	69.6	1560	56.3	3070	53.7	4350	44.9	10039	58.5
3.	0.2	247	71.3	588	73.5	1100	69.2	2098	68.4	2797	64.5	9118	62.3
4.	0.3	171	80.2	716	67.7	1228	65.6	1535	76.9	3130	60.3	5220	78.4
5.	0.4	154	82.2	673	69.6	1057	70.4	1313	80.2	2123	73.1	5356	77.8
6.	0.5	230	73.3	622	71.9	750	78.9	1441	78.3	2226	71.8	5492	77.3
7.	0.6	188	78.2	725	67.3	997	72.1	1381	79.2	2951	62.6	3974	83.6
8.	0.7	162	81.2	443	79.9	742	79.2	1287	80.6	2200	72.1	3411	85.9

4.2.2. Effect of inhibitor concentration in 0.5M H_2SO_4:

From Table 4.4, and Figure 4.4, it's clear that the corrosion rate of mild steel in the blank is higher in comparison with the blank containing PCL. The CR decreased when the concentration of inhibitor increased.

The inhibition efficiency of PCL extracts increases as a function of their concentration. This result suggests that an increase in extract concentration increases the number of inhibitor molecules adsorbed onto the mild steel surface and reduces the surface area that is available for the direct acid attack on the metal surface.

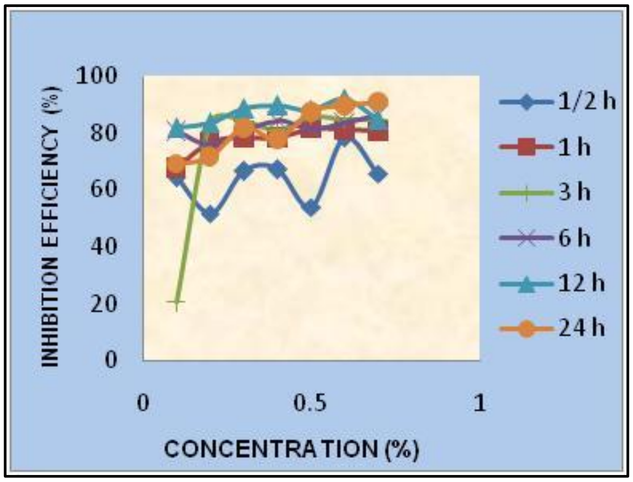


Figure 4.4. IE of MS in 0.5 M H_2SO_4 at different concentration of PCL

4.2.2.1 Impact of immersion time

Figure 4.4 shows the inhibition efficiency of mild steel in 0.5 M H_2SO_4 at different concentration of PCL extract. This shows that as the corrosion rate decreases the inhibition efficiency increases. In this study maximum inhibition efficiency obtained is 91.9 % at 12 h of immersion time.

Table 4.4: Variation of inhibition efficiency with PCL concentration for time of immersion in 0.5 M H_2SO_4

S. No	Conc (%)	Corrosion rate and inhibition efficiency											
		½ h		1 h		3 h		6 h		12 h		24 h	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	1151	-	1185		1131	-	1003	-	1124	-	915	-
2.	0.1	409	64.4	383	67.6	897	20.7	191	80.9	205	81.7	282	69.1
3.	0.2	554	51.8	277	76.6	184	83.7	245	75.6	185	83.5	259	71.6
4.	0.3	383	66.7	255	78.4	177	84.3	190	81	129	88.5	166	81.8
5.	0.4	375	67.4	255	78.4	214	81	156	84.4	117	89.6	202	77.9
6.	0.5	528	54.1	230	80.6	157	86.1	184	81.7	134	88	113	87.6
7.	0.6	392	65.9	221	81.3	172	84.8	164	83.6	171	84.8	95	89.7
8.	0.7	247	78.5	217	81.6	170	84.9	137	86.3	91.33	**91.9**	81	91.2

4.2.2.2. Effect of temperature

The influence of temperature on the corrosion behaviour of steel/acid in the presence and absence of PCL at various concentrations is investigated by mass loss in the temperature rang 303-353 K during ½ h of immersion. The collected curves in Fig 4.5 shows the evolution of corrosion rate with concentration at different temperatures. The results also indicate that for a given temperature, the corrosion rate of steel decreased with increasing inhibitor concentration. The values of inhibition efficiency obtained from the mass loss for different inhibitor concentrations and at various temperatures in 0.5M H_2SO_4 are given in Table 4.5, and Fig 4.5, It is clear that inhibition efficiency increased with increase in inhibitor concentration. The maximum value of inhibition efficiency (IE%) obtained for PCL is 92.1 % at 343 K.

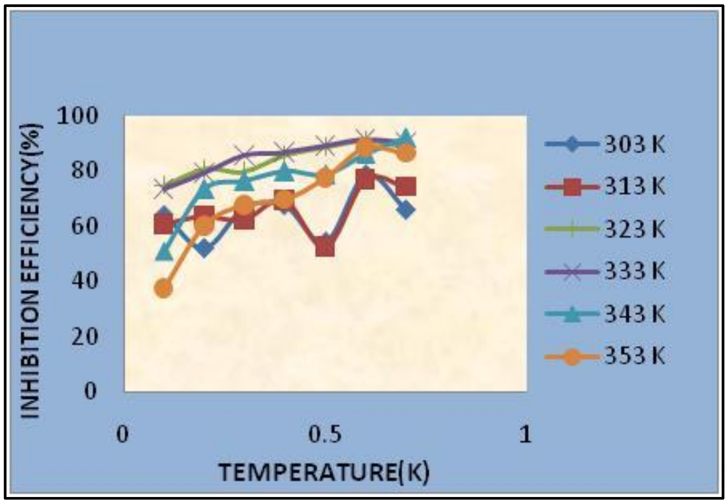


Figure 4.5. IE of MS in 0.5 M H_2SO_4 at different temperature of PCL

Table 4.5: Variation of inhibition efficiency with PCL concentration at different temperature in 0.5 M H_2SO_4.

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		303K		313K		323K		333K		343K		353 K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	1151		2217		5595		12239		17545		30876	
2.	0.1	409	64.4	870	60.8	1407	74.8	3258	73.4	8597	51	19302	37.5
3.	0.2	554	51.8	810	63.5	1083	80.6	2575	79	4708	73.2	12316	60.1
4.	0.3	384	66.7	835	62.3	1142	79.6	1748	85.7	4187	76.1	9962	67.7
5.	0.4	375	67.4	682	69.2	818	85.4	1629	86.7	3548	79.8	9373	69.6
6.	0.5	529	54.1	1057	52.3	631	88.7	1330	89.1	3770	78.5	6943	77.5
7.	0.6	392	78.5	571	76.9	503	91	1083	91.1	2439	86.1	3599	88.3
8.	0.7	247	65.9	511	74.2	631	88.7	1202	90.2	1390	**92.1**	4205	86.4

4.2.3. Adsorption behaviour

Adsorption isotherms are of the general form shown in Equation

$$f\,(\theta, x)\exp(-2a\theta)=KC \quad \text{……………………….. (Eq 4.1)}$$

where f(θ, x) is the configurational factor subject to the physical model and assumption responsible for the derivation of the isotherm, θ is the surface coverage, C is the inhibitor concentration, “a” is the molecular interaction parameter and K is the equilibrium constant of adsorption process.

The conventional form of the Langmuir isotherm is,

$$[\ /1-\theta] = K_{ads}C \quad \text{……………………… (Eq 4.2)}$$

and rearranging gives

$$\theta=[K_{ads}C/\ 1 + K_{ads}C] \quad \text{……………………. (Eq 4.3)}$$

where θ is the value of surface coverage on mild steel, C is PCL concentration in the acid solution and K ads is the equilibrium constant of the adsorption process.

4.2.3.1: Langmuir adsorption isotherm

Linear plots of log θ / 1- θ Vs log C are obtained with the slopes in the range close to unity (Figures 4.6 and 4.7) . This suggests that the inhibitor molecules occupy the adsorption sites on the metal surface. The slight divergence of the slopes from unity is due to the molecular interaction among the PCL molecules on the metal surface and changes in the values of the Gibbs free energy relative to the surface coverage.

4.2.3.2. Temkin adsorption isotherm

Efforts are also carried out to plot θ Vs log C and the results indicate that the MS/acidic solution interface furnishes a straight line suggesting that the adsorption of PCL extract on the MS/acidic solution interface obey Temkin isotherm

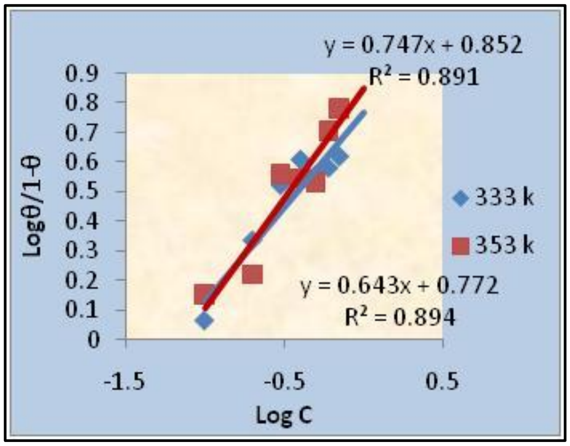


Figure 4.6. Langmuir adsorption for HCl

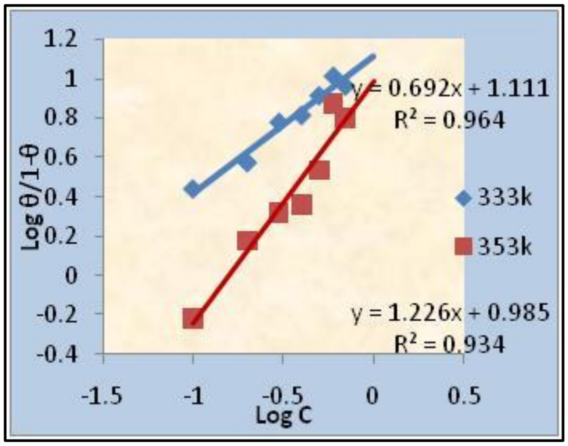


Figure 4.7.Langmuir adsorption for H_2SO_4

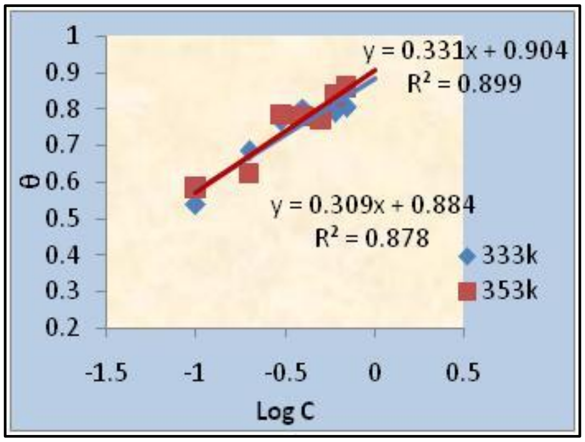


Figure 4.8.Temkin adsorption for HCl

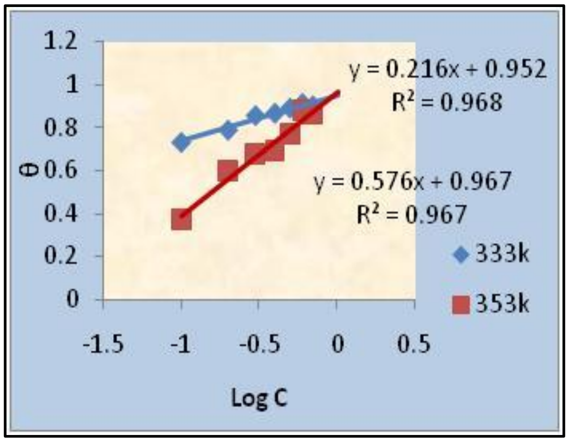


Figure 4.9.Temkin adsorption for H_2SO_4

4.2.3. Kinetic parameters

4.2.3.1 Activation energy (Ea)

Adsorption is an important process in corrosion inhibition because the inhibition of metal corrosion by organic molecules is often due to adsorption of the inhibitor molecules onto the metal surface thereby blocking the active sites that are susceptible to corrosion reaction. A better understanding of the adsorption behaviour of an inhibitor can be achieved by investigating the thermodynamics of the adsorption process. The dependence of the corrosion rate on temperature can be expressed using the Arrhenius equation:

$$\mathbf{Log\ C_R = log\ A - E_a/2.303\ RT\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (Eq\ 4.4)}$$

where CR is the corrosion rate (mpy), Ea is the apparent activation energy, R is the molar gas constant (8.314 $JK^{-1}\cdot mol^{-1}$), T is the absolute temperature and A is the frequency factor. The values of the standard enthalpy and entropy of activation, ΔH* and ΔS* respectively can be calculated from the transition state equation:

log (C_R/T)=[log(R /Nh)+ (ΔS* 2.303R)]+(−ΔH* 2.303R)(1 /T) ……………(Eq 4.5)

where h is Planck's constant and N is the Avogadro number. The Arrhenius plots (log CR vs. 1/T) and the transition state plots (log (CR/T) vs. 1/T) for mild steel corrosion in 1M HCl and 0.5 M H_2SO_4 without and with various concentrations of PCL are shown in Figures 4.10, 4.11, 4.12 and 4.13 respectively. Both the Arrhenius and the transition state plots are found to exhibit adequate linearity.

The values of the apparent activation energy (Ea) are calculated from the slope of the Arrhenius plots (slope = −Ea/2.303R), while the values of ΔH* and ΔS* were respectively obtained from the slope (slope = −ΔH*/2.303R) and intercept (intercept = log(R/Nh) + ΔS*/2.303R) of the transition state plots.

The values of Ea, ΔH* and ΔS* are listed in Table 4.6. It is obvious from the results that the values of Ea generally increase at initial concentration and decreases with increasing concentration of the inhibitors. An increase in Ea with increase in inhibitor concentration is an indication of physical adsorption process at the initial stage of inhibition and it suggests increase in inhibition efficiency with increase in concentration of the inhibitors.

4.2.3.2 ΔH and –ΔS

The values of enthalpy, ΔH* and entropy, ΔS* of activation were calculated from the plots of log CR/T vs. 1/T (Figure 4.11). The results in Table 4.6. shows that the values of ΔH* are positive both in the absence and presence of the inhibitor, which implies the endothermic nature of mild steel dissolution process for both instances. The negative values of ΔS* obtained in some cases indicate that the formation of the activated complex in the rate determining step is an associative process rather than dissociative and suggest a decrease in disorderliness as the reaction proceeds from reactants to activated complex .

The positive values of ΔS* obtained in the presence of PCL suggest that the rate-determining step represents a more disordered arrangement, which may involve the decomposition of some intermediate products of corrosion reaction such as dissociation of adsorbed chloride ions or water molecules from the steel surface in order to allow for adsorption of the inhibitor molecules.

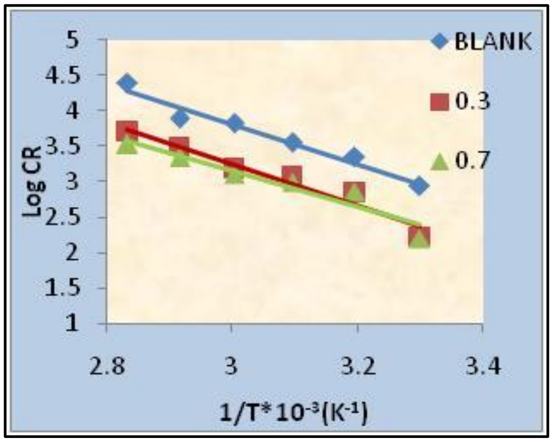


Figure 4.10 Arrhenius plot (HCl)

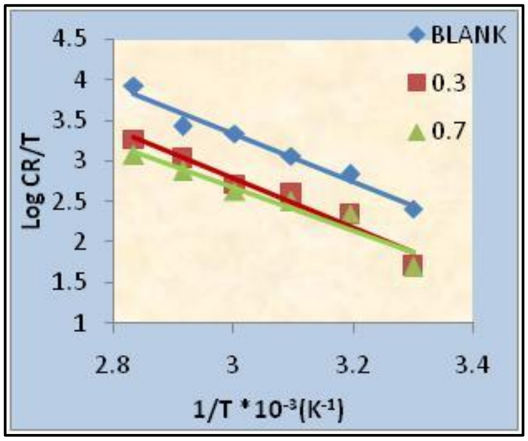


Figure 4.11.Transition state plot (HCl)

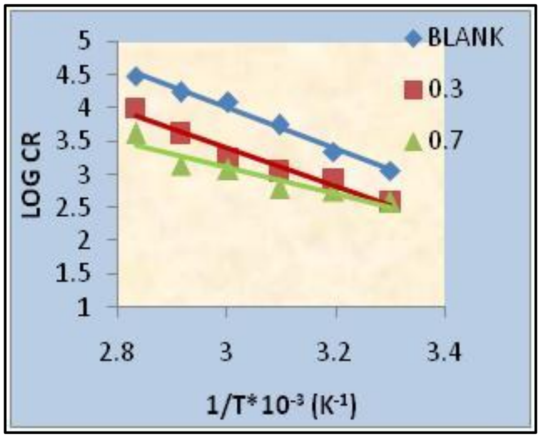


Figure 4.12. Arrhenius plot (H_2SO_4)

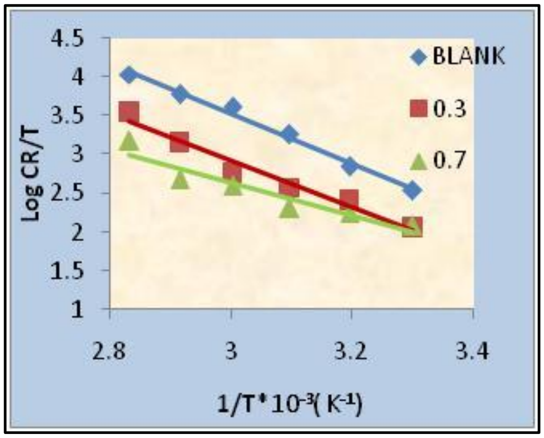


Figure 4.13.Transition state plot (H_2SO_4)

Table 4.6 : Values of Ea, ΔHa and ΔSa of MS in various concentrations of PCL in 1M HCl / 0.5M H_2SO_4

S.NO	Conc V/V (%)	Activation energy -Ea k J/ mol		ΔHa kJ/ mol		ΔSa J/ mol	
		HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4
1.	Blank	53.6	59.8	56.4	62.5	35.4	57.5
2.	0.1	61.1	68.3	63.8	71	50.9	75.3
3.	0.2	59.3	54.5	62	57.3	43.1	31.5
4.	0.3	55.6	54.4	58.4	57.1	30.8	29.8
5.	0.4	54.7	54.7	57.4	57.4	26.7	29.5
6.	0.5	51.6	43.7	54.3	46.4	17.5	-4.1
7.	0.6	55	47.7	57.7	50.4	26.9	3.9
8.	0.7	48.2	38.1	51	40.8	6.6	-24.5

4.2.4. Thermodynamic parameters

A plot of ΔG^oads versus T is linear (Figure 4.14) for mild steel acid corrosion in the presence of various concentrations of investigated extract in both acid media. The slope of the straight lines are equal to ΔS^oads and intercept equal to ΔH^oads.

Figure 4.14 clearly shows the dependence of ΔG^oads on T, indicating the good correlation among thermodynamic parameters. The negative values of ΔG^oads ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. The enthalpy and entropy for the adsorption of PCL extract on mild steel are deduced from the thermodynamic basic equation (3.3).

In the present investigation, the values of ΔG^oads suggest a strong adsorption of PCL extract components on to the mild steel surface in both studied acid media. The calculated ΔG°ads values, at all studied temperatures, are given in Table.4.7

Generally, values of ΔG°ads up to -20 kJ mol^{-1} are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than -40 kJ mol^{-1} involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co- ordinate type of bond (which indicates chemisorption). The calculated standard free energy of adsorption values in the studied temperature domain are in the range of -40.56 to -38.91 kJ mol^{-1}. These values are in frontier between the two mode of adsorption, therefore, it can be concluded that the adsorption is a competitive phenomenon between chemical and physical adsorption . The enthalpy and entropy of adsorption (ΔH°ads and ΔS°ads) has been calculated using equation 3.4.

An endothermic adsorption process (ΔH°ads > 0) is due to chemisorption while an exothermic adsorption process (ΔH°ads < 0) may be attributed to physisorption, chemisorption or a mixture of both. When the process of adsorption is exothermic, physisorption can be distinguished from chemisorptions according to the absolute value of ΔH°ads. For physisorption processes, this is usually lower than -40 kJ mol^{-1} while its value is around -100 kJ mol^{-1} for chemisorption. Base on the results of the present work, the calculated ΔG°ads and ΔH°ads values for inhibitor show that adsorption mechanism is not completely physical or chemical and a combination of physisorption and chemisorption exists between the inhibitor and metal surface. ΔS°ads values are found to be negative meaning that the process of adsorption is accompanied by a decrease in entropy , leading to an orderly arrangement of adsorption of phytoconstituents on the metal surface. **Bouanis M *et al., (*2016)**

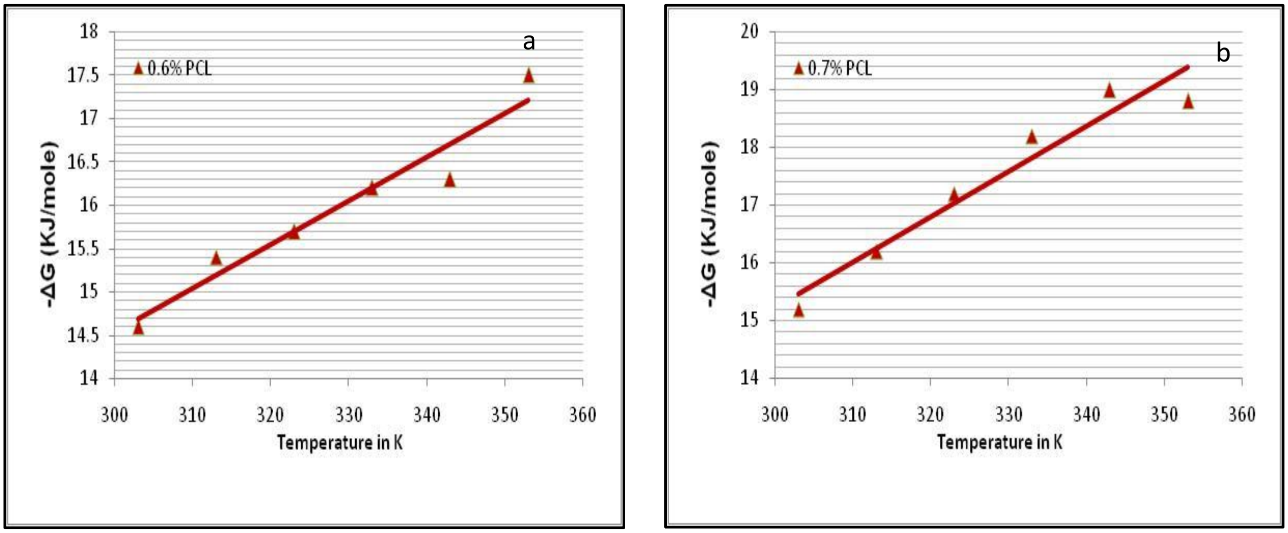


Figure 4.14. Plot of ΔG° vs T(a) for 1M HCl (b) for 0.5 M H_2SO_4 medium

Table 4.7: Values of -ΔG°, -ΔH° and ΔS° of MS in various concentration of PCL extract in 1M HCl and 0.5 M H_2SO_4 medium

S.NO	Concentration of inhibitor V/V (%)	Free energy of adsorption - ΔG° (k J / mol)						Δ S° (J/ mol)	Δ H° (kJ/ mol)
		303K	313 K	323 K	333K	343 K	353K		
1 M HCl									
1.	0.1	17.6	18.6	17.6	17.9	17.4	19	-9.8	-14.8
2.	0.2	16.4	17.3	17.2	17.7	17.7	17.4	-19.7	-10.8
3.	0.3	16.6	15.5	15.7	17.7	16.1	18.5	-37.7	-4.3
4.	0.4	16.2	15	15.5	17.5	16.9	17.6	-41.4	-2.9
5.	0.5	14.4	14.7	16.6	16.6	16.1	16.9	-4	0.1
6.	0.6	14.6	15.4	15.7	16.2	16.3	17.5	-34.5	-4.3
7.	0.7	14.7	13.2	14.3	16	15.1	17.6	-63.2	5.6
0.5 M H_2SO_4									
1	0.1	17.6	17.5	19.9	20.3	18.1	16.5	9.6	-21.5
2	0.2	14.3	16	18.9	19.2	18.9	17.2	-65.8	4.1
3	0.3	14.9	14.9	17.6	19.4	18.2	17	-63.3	3.8
4	0.4	14.2	14.9	17.9	18.8	17.9	16.4	-59.5	2.8
5	0.5	12.2	12.5	18.2	18.8	17.1	16.9	-108.5	19.6
6	0.6	14.6	14.9	18.3	18.9	18.1	18.7	-86.4	11.1
7	0.7	15.2	16.2	17.2	18.2	19.0	18.8	-120.6	23

4.3. Electrochemical measurements

4.3.1. Potentiodynamic studies

The kinetics of anodic and cathodic reactions occurring on mild steel electrode in 1M HCl solutions with different PCL extract concentrations are studied through the polarization measurements. The results are depicted in Figure 4.15 and the electrochemical parameters are tabulated in Table 4.8. In acidic solutions, the anodic reaction of corrosion is the passage of metal ions from the metal surface into the solution, and the cathodic reaction is the discharge of hydrogen ions to produce hydrogen gas or to reduce oxygen. The inhibitor may affect either the anodic or the cathodic reaction, or both. Since the anodic Tafel slope (ba) and cathodic Tafel slope (bc) of PCL are found to change with inhibitor concentration, this indicates that the inhibitor affected both of these reactions.

A compound can be classified as an anodic- or a cathodic-type inhibitor when the change in the Ecorr value is larger than 85 mv. Since the largest displacement exhibited by PCL is 40 mv , it may be concluded that this molecule should be considered as a mixed-type inhibitor, meaning that the addition of PCL affects both the anodic dissolution of mild steel and the cathodic hydrogen evolution reaction.

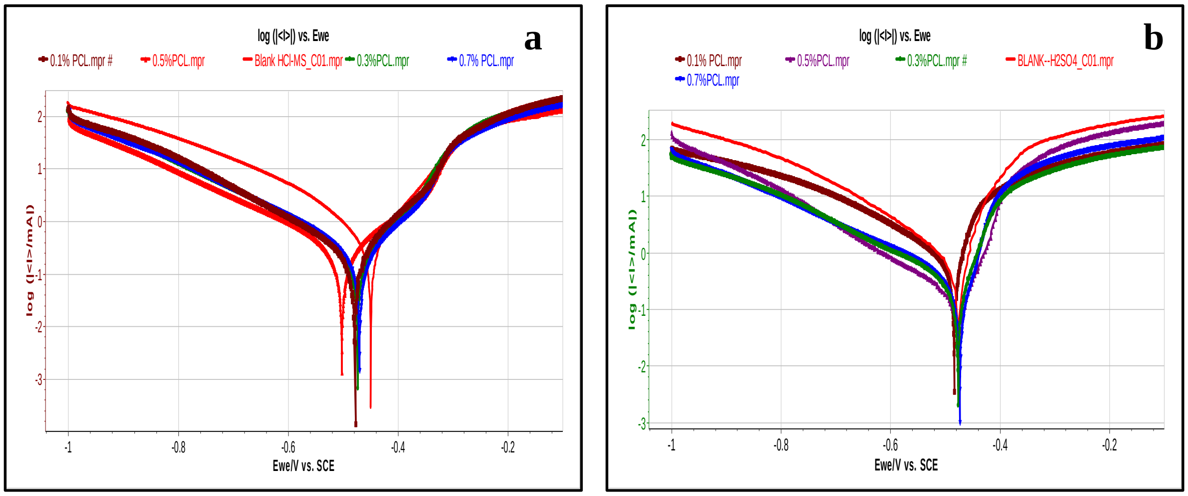


Figure 4.15. Potentiodynamic polarization curve for MS in a) 1M HCl b) 0.5M H_2SO_4 in presence and absence of PCL extract

Close examination of Table 4.8 shows that an increase in inhibitor concentration decreases the Icorr values. A maximum inhibition efficiency of 79.1 % (1M HCl) and 84.6 % (0.5M H_2SO_4) is achieved when the concentration of extract is 0.7%.

Table 4.8. Linear polarization parameters of MS in 1M HCl and 0.5 M H_2SO_4 in presence of PCL extract

S.No.	Conc. of inhibitor in (%)	Tafel polarisation parameters					Linear polarisation resistance parameters	
		E_{corr} mV/ SCE	I_{corr} A/cm^2	b_a mV/ decade	b_c mV/ decade	IE (%)	R_p Ohm/cm^2	IE (%)
1M HCl								
1.	Blank	-457	584	85	142		3.4	
2.	0.1	-441	206	67	138	64.7	53	93.6
3.	0.3	-458	195	80	158	66.7	87	96.1
4.	0.5	-435	182	66	133	68.8	102	96.7
5.	0.7	-474	122	65	121	79.1	113	96.9
0.5M H_2SO_4								
1.	Blank	-538	2734	66.8	163		23.8	
2.	0.1	-513	938	99.9	165.1	65.7	43.5	45.3
3.	0.3	-525	464	71.1	141	83.0	56.9	58.2
4.	0.5	-575	456	79.2	181.1	83.3	80.9	70.6
5.	0.7	-494	421	71.5	133.7	84.6	119	80

The $R_p$values have shown an increase in values from 93.6 % to 96.9 % in 1M HCl solution and from 45.3 % to 80 % in 0.5M H_2SO_4 solution .Increase in R_p values with increasing inhibitor concentration confirmed the process of adsorption of PCL extract in mild steel surface.

4.3.2. Electrochemical Impedance Spectroscopy

EIS is one of the most successful techniques used to evaluate the effectiveness of an inhibitor. The corrosion behaviour of mild steel in 1M HCl and 0.5M H_2SO_4 acidic solution in the presence of PCL has been investigated by EIS method .Various impedance parameters such as charge transfer resistance (Rct), double layer capacitance (Cdl) and the corresponding IE calculated are given in Table 4.9.

The plots are not perfect semicircles, attributing to the non-homogeneity of the surface and roughness of the metal (**Bouklah *et al*., 2006).** Also, these plots show the increase in impedance response on MS with addition of PCL extract by their increasing diameters, corresponding to charge transfer resistance (Rct) values **(Musa *et al*., 2012**). Bode plots infer a single time constant.

The large charge transfer resistance could be due to a decrease in the active surface necessary for the corrosion reaction. The inhibition efficiency (% IE) calculated from the values of Rct, are found to be maximum at a concentration of 0.7% PCL. The extracts are found to afford a maximum efficiency of 89.3 % (1M HCl) and 89.4 % (0.5M H_2SO_4) respectively.

The value of C_{dl} decreases with increase in inhibitor concentration thus the thickness of protective layer increases. This can be attributed to the decrease in local dielectric constant and an increase in the thickness of the electrical double layer suggesting that PCL extract inhibit the mild steel corrosion by adsorption at the metal/acid interface.

The successive coverage of MS surface and growth of layer would have provided an effective corrosion inhibition. Thus the change in C_{dl} can result from a decrease in local dielectric constant and due to gradual displacement of H_2O molecules by adsorption of original molecules present in the PCL extract. **(Musa *et al*., 2012)**

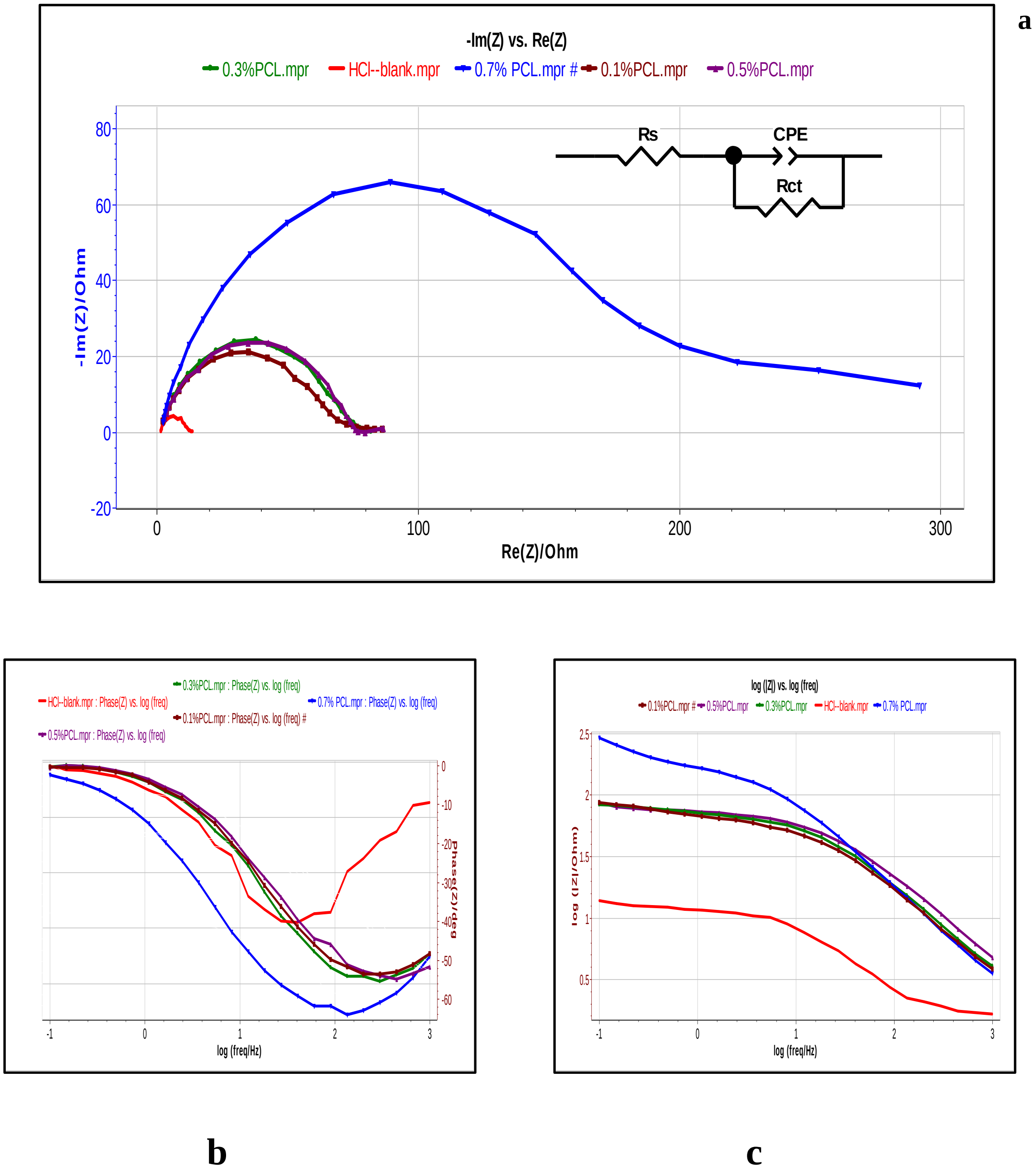


Figure 4.16. Nyquist diagrams for MS in 1M HCl (a-c) in the presence and absence of PCL extract

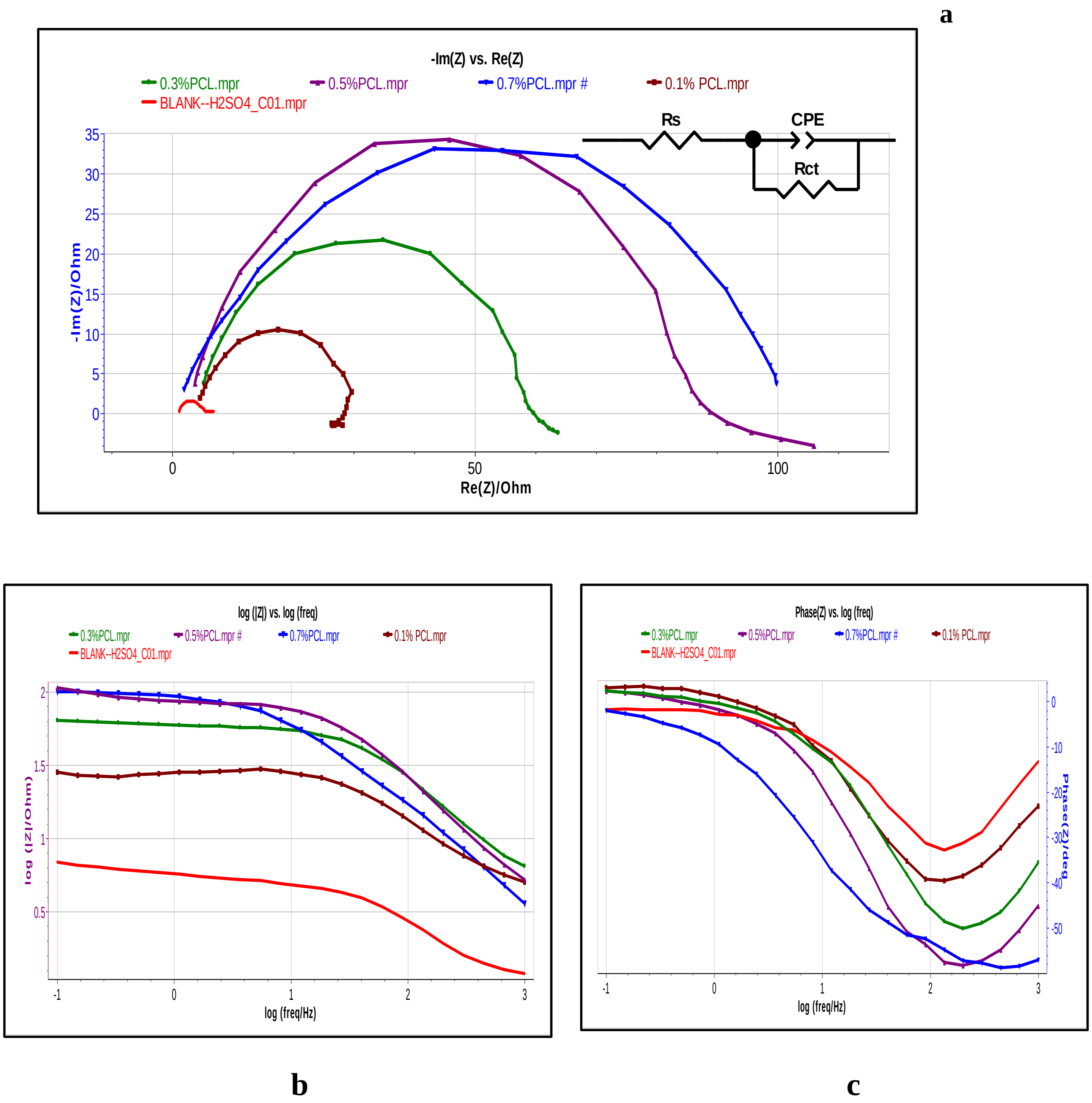


Figure 4.17. Nyquist diagrams for MS in 0.5 M H_2SO_4 (a-c) in the presence and absence of PCL extract.

Table 4.9: Electrochemical impedance parameters of MS in 1M HCl and 0.5 M H_2SO_4 in presence of PCL extract

S.No.	**Conc (%)**	**R_S (Ωcm^2)**	**R_{ct} (Ωcm^2)**	**IE (%)**	**C_{dl} ($\mu F/cm^2$)**	**Θ**
HCl						
1.	Blank	2.0	17.2		633	
2.	0.1	3.5	65.0	73.5	105	0.8341
3.	0.3	4.1	87.1	80.2	84.4	0.8666
4.	0.5	3.4	108.5	84.1	79.1	0.8750
5.	0.7	2.9	160.1	89.3	61.9	0.9022
H_2SO_4						
1.	Blank	1.2	8.9		375.0	
2.	0.1	6.2	27.6	67.8	199.4	0.4682
3.	0.3	6.1	57.3	84.5	85.8	0.7712
4.	0.5	3.2	59.6	85.1	52.5	0.86
5.	0.7	4.4	84.3	89.4	45.4	0.8789

4.3.3 Comparison between Mass loss and Electrochemical studies

The findings of electrochemical studies (polarization and EIS) were in fair agreement with those of gravimetric studies along with slight deviations, tabulated in Figure 4.17. This deviation is due to the fact that the gravimetric study is an average technique of calculating the % IE **(Bouklah *et al.*, 2006),** while an instantaneous efficiency can be calculated by the electrochemical studies performed.

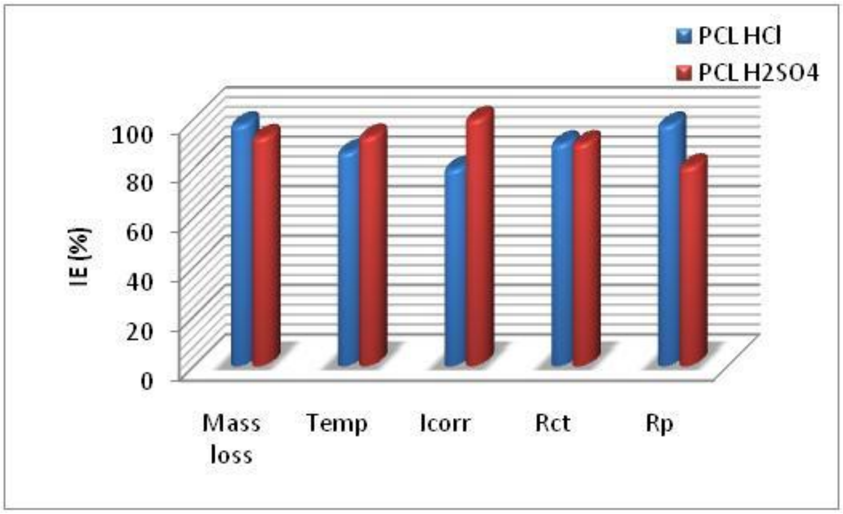


Figure 4.18.Comparison of IE in ML and ES in PCL extract

4.4 Surface Analytical Techniques

4.4.1 FT- IR Spectral analysis

The IR spectrum of the phytochemical compounds adsorbed on the metal surface reveal the presence of functional group peaks whose absorption frequencies correspond to carbonyl groups at 1635 cm^{-1} and 1603 cm^{-1}.

In the presence of the inhibitor, IR spectrum of the corrosion product **(Figure 4.19)** revealed that the –OH stretch (3908cm^{-1}) is shifted from (3297) cm^{-1}. From the spectra, it is observed that the C–H stretch of alkanes and C–C stretch (in–ring) of aromatics appear at 2921 cm^{-1}.

From the crude plant extract to the corrosion product of PCL shifts are noticed for –C ≡ N stretch (2326 cm^{-1} to 2324 cm^{-1}), C-H bend (1446 cm^{-1}) and C-O stretch (1027cm^{-1}). The shift in the absorption frequencies of the inhibitor on the metal surface strongly supports the interaction between the phytochemical compounds of the inhibitor and metal surface. Some missing bonds are there in corrosion products indicating that there is interaction (Fe-complex formation) between the leaves extract of and the surface of mild steel.

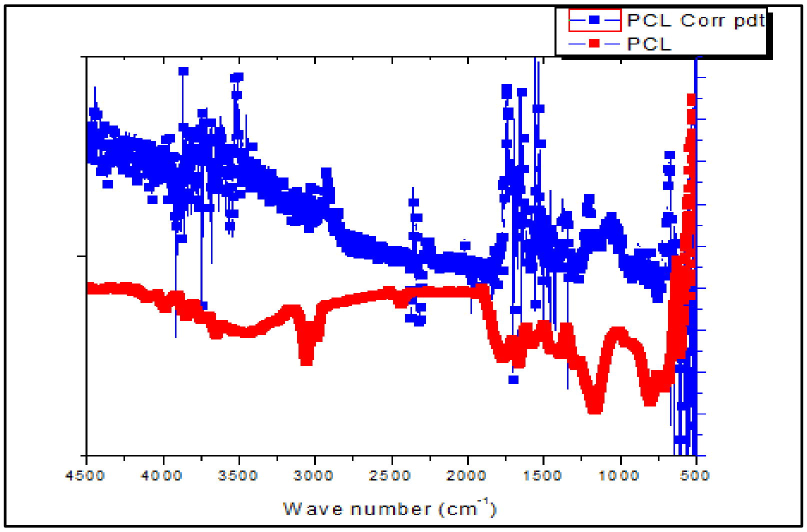


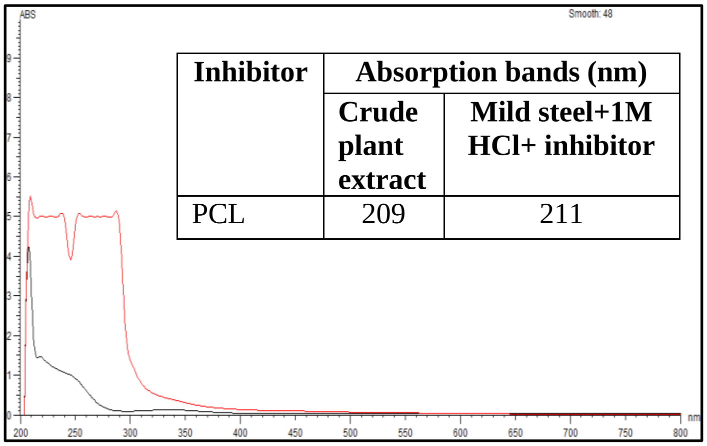
Figure 4.19. IR spectrum of PCL extract and corrosion products in 1M HCl

Table 4.10: IR spectrum of (a) acid extract of concentrate (b) adsorbed material of MS in the presence of PCL extract in 1M HCl

Powdered Plant material			**Corrosion product of PCL**		
Frequency cm^{-1}	**Assignment**	**Functional Groups**	**Frequency** cm^{-1}	**Assignment**	**Functional Groups**
3297	OH stretch	Alcohol	3908	O–H stretch, H–bonded	1°, 2° amines, amides
2921	C - H stretch	Alkanes	-	-	-
2326	-C≡N stretch	Aliphatic amines	2324	–C≡N stretch	Aliphatic amine
1635	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers	1603	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers
1446	C–H bend	Aliphatic amines		C-C in ring	Aromatics
	C–O-C stretch	Ethers	1410	C–H bend	Aliphatic amines
1260	C-O stretch	carboxylic acids	-	-	-
1027	C-O stretch	carboxylic acids		C-O stretch	carboxylic acids
	O–H bend	Alcohols	775	O–H bend	Alcohols

4.4.2 UV ANALYSIS:

In order to confirm the possibility of the formation of inhibitor-Fe complex, UV-Visible absorption spectra obtained from 1M HCl solution containing PCL extract before and after the mild steel immersion are shown in **Figure 4.20.** The electronic absorption spectra of PCL before immersion have absorption maximum at 209 nm which can be attributed to π- π* and n- π* transitions.



Inhibitor	**Absorption bands (nm)**	
	Crude plant extract	**Mild steel+1M HCl+ inhibitor**
PCL	209	211

Figure 4.20.UV analysis of PCL extract and 1M HCl + 0.7% PCL

After 3 hrs of immersion of mild steel, the change in the position of absorption maximum or the change in the absorbance values to 211 nm indicates that the complex formation between two species in solution. These experimental findings provide the formation of complex between Fe^{2+} and Fe^{3+} and confirm the inhibition of mild steel from corrosion.

4.4.3 SEM ANALYSIS

SEM images are recorded to investigate the changes occurred on the surface of the mild steel samples after 6 h immersion in 1 M HCl solution in the absence and presence of the inhibitor. Fig.4.21 (b) presents the micrograph obtained for a mild steel sample after exposure to blank solution, while Fig.4.21 (c) presents the surface morphology of mild steel specimens immersed in 1 M HCl medium containing 0.7% of PCL extract. Mild steel surface in the uninhibited solution is severely damaged and rough due to an aggressive attack of the corroding medium. Fig.4.21 (c) reveals that the corrosion marks on the inhibited samples decrease in presence of extract which also attests the inhibition ability and adsorption of the inhibitor on the mild steel surface. Moreover the parallel lines on the mild steel surface can be attributed to polishing scratches**. (A.Khadraoui, *et.al,* 2014)**

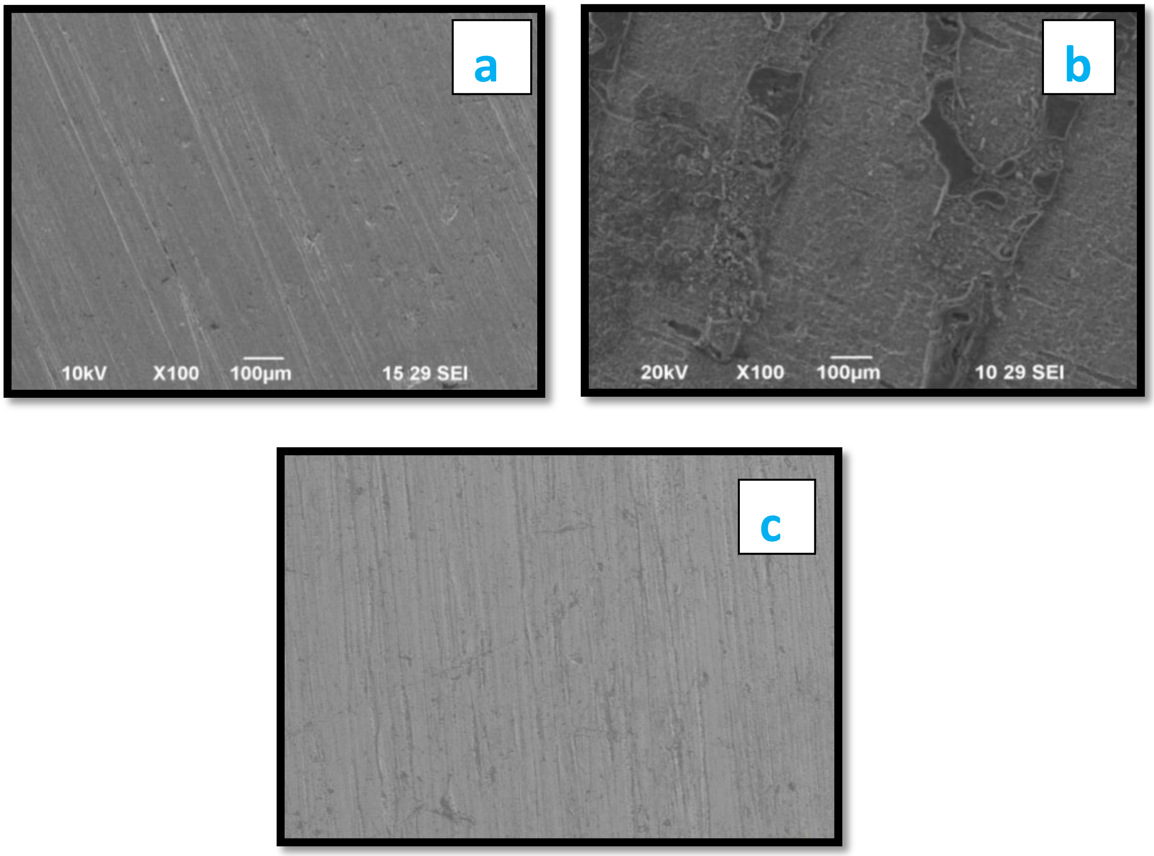
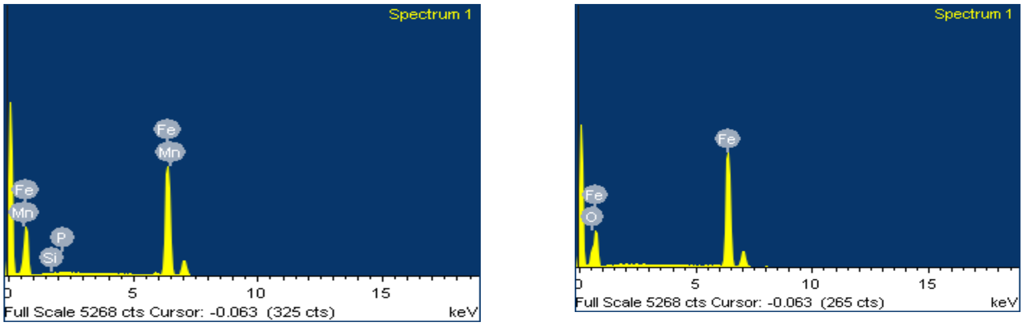


Figure : 4.21. Surface of MS in SEM analysis (a)Plain (b) Blank (MS in 1 M HCl) (c) 1M HCl + 0.7% PCL

4.4.4 EDX

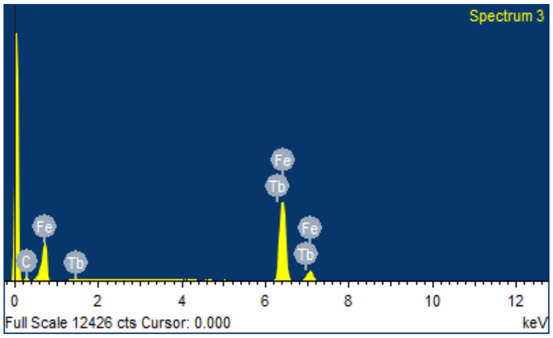
To determine the elements present in the mild steel surface after exposure to the PCL solution, the EDX spectra of the specimen were taken after 3 h immersion time Figure 4.22 represent the EDX spectra of mild steel specimen in presence of PCL at their optimum concentration. In presence of optimum concentration of PCL the EDX show addition signals for nitrogen suggesting that in the inhibited solution PCL adsorb on the metal surface and from protective surface film which is responsible for the appearance of pick for the nitrogen in the EDX spectra of inhibited mild steel specimen. Moreover , the signals corresponding to the oxygen (O) for inhibited mild steel specimen show comparatively high intensities. This finding suggest the adsorption of PCL on the mild steel surface resulting into increased intensity of signals corresponds to the oxygen. **Chandrabhan verma M *et al*., *(*2015)**



Element	Wt %	At %
Si	0.35	0.69
P	0.10	0.18
Mn	2.38	2.41
Fe	97.17	96.72

Element	Wt %	At %
O	9.89	27.70
Fe	90.11	72.30

Figure 4.22: EDX images of (a) Plain MS (b) MS in 1M HCl



Element	Wt %	At %
C	5.48	12.97
Fe	58.01	29.52
Tb	4.59	0.82
O	31.92	56.69

(c) 1M HCl + 0.7% PCL

4.4.5 LASER PROFILOMETER

3D Laser Profilometer is a powerful technique to investigate the surface morphology at nano to microscale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface.

The technique was employed to reveal the surface microstructure of metal after corrosion test. From the technique, average roughness Ra and Root mean square values can be determined. Fig.4.23 displays the three-dimensional image of mild steel surface immersed in 1M HCl solution without and with addition of 0.7% PCL for 3 h. Table 4.11 gives the corresponding average roughness Ra and RMS roughness (Rq) values. From Fig. 4.23(b), it can be seen that the corrosion pattern of mild steel in uninhibited 1M HCl solution was very rough. It is clearly shown in Figure 4.23(b) mild steel sample was badly damaged due to the acid attack on surface.

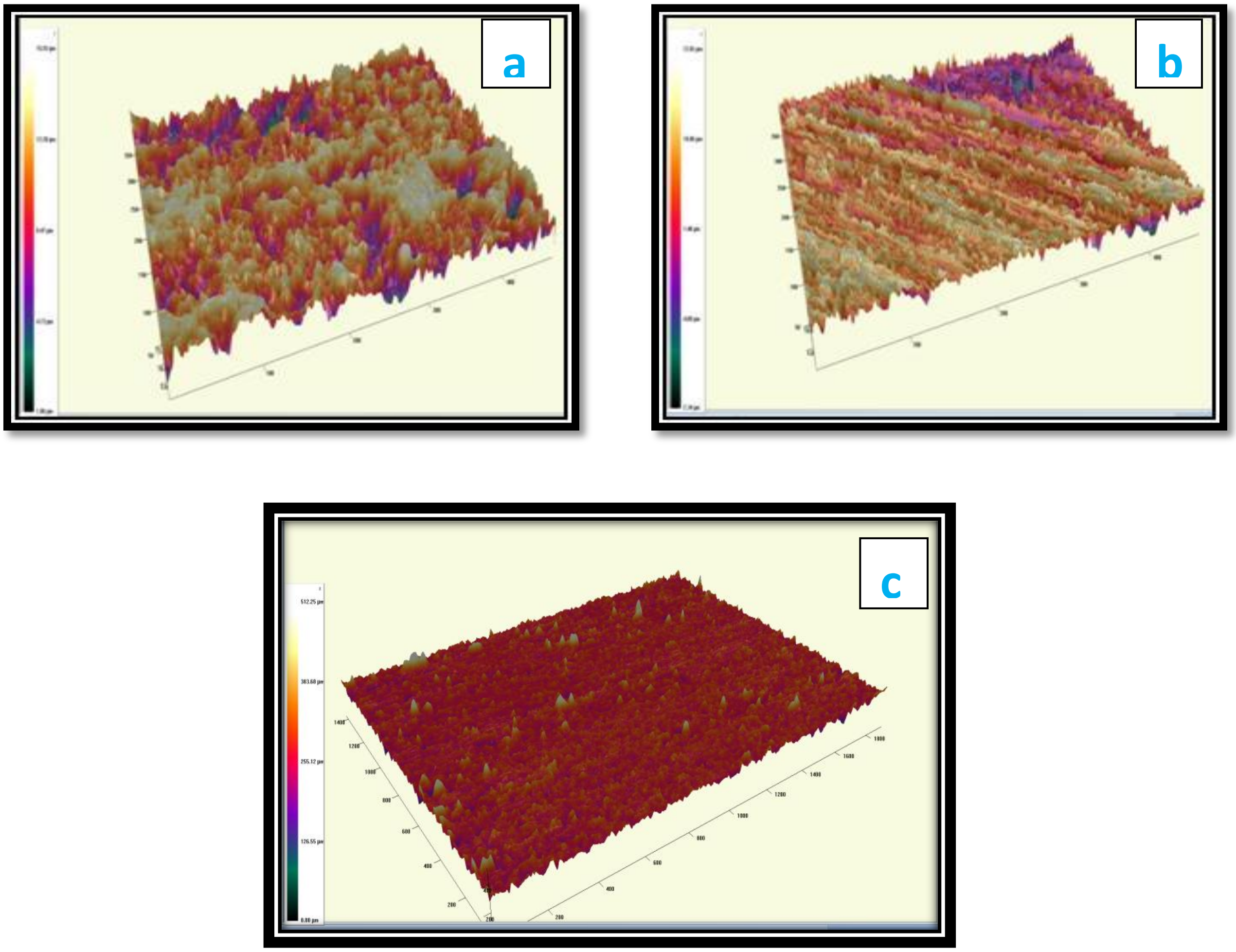


Figure 4.23. 3 D Laser images of (a) Plain (b) Blank (c) 1M HCl + 0.7 % PCL

Table 4.11: Roughness parameters of MS in presence and absence of PCL extract

Samples	Average Roughness Ra (µm)	Root Mean Square Roughness Rq (µm)
Plain MS	2.558	3.140
MS in 1M HCl	17.28	22.35
MS in 1M HCl + 0.7% PCL	9.3	11.7

By contrast, the corrosion morphology of mild steel in inhibited 1M HCl solution containing the inhibitor is smooth. The average roughness of the mild steel surface in uninhibited 1M HCl solution is about 17.28 µm and Rq is 22.35 µm as a result of the acid attack, while in the presence of PCL , Ra and Rq decreases to 9.3 and 11.7 µm respectively.

This indicates that the addition of the extract reduced the surface roughness. 3D Laser profilometer images and the roughness quantification are also consistent with SEM studies. This confirms that the corrosion inhibition on mild steel occurs through adsorption of the extract on it.

4.6 MECHANISM OF INHIBITION

Generally, the first stage in the corrosion inhibition mechanism is the adsorption of inhibitor molecules on the mild steel surface. The process of adsorption is influenced by the type of the aggressive electrolyte, the chemical structure of the inhibitor molecules, and the nature and charge of the metal. The charge on the metal surface is due to the electric field generated at the metal/ electrolyte interface. It is reported that in acid solutions the mild steel surfaces are positively charged with respect to their potential zero charge (PZC) (**Deng *et al.*, 2011**). PCL may adsorb on the mild steel surface by (i) electrostatic interaction of the inhibitor molecules with already adsorbed chloride ions (physisorption), (ii) vacant d-orbitals of metal surface atoms and unshared electron pairs of heteroatoms (chemisorption), or (iii) interaction of vacant the d-orbital of the inhibitor molecule with the d-electron of the metal surface (retro-donation).

In acidic medium the phytochemicals present in PCL molecules may adsorb through protonated heteroatoms (N, O, and S) and already adsorbed anions on the mild steel surface. Initially the protonated forms of PCL molecules in acid medium compete with H+ ions for electrons on the mild steel surface. The high electron density on the mild steel surface renders more negative charge to it. In order to relieve the surface from the high negative charge, the electron from the d-orbital of Fe may be transferred to the vacant π*-orbital (antibonding) of the PCL molecules and in turn strengthen their adsorption on the mild steel surface (**Xometl *et al.*, 2008**).

A schematic representation of the adsorption behavior of PCL extract on mild steel in acid solution shown in figure 4.24 The phytochemical components might be adsorbed on the positively charged metal surface through the active centers. Thus, a close packed triple layer will form on the metal surface and inhibit the entry of iron ions to the solution. Hence, with an increase in the positive charge on the metal surface, the adsorption of phytochemical components would increase and the phytochemical content in the solution would decrease (**Lewis *et al.*, 1994**). The formation of such protective film was confirmed by FT-IR and Scanning electron microscopic techniques. The calculated high inhibition efficiency may be attributed to strong adsorption ability of phytochemical components on mild steel surface.

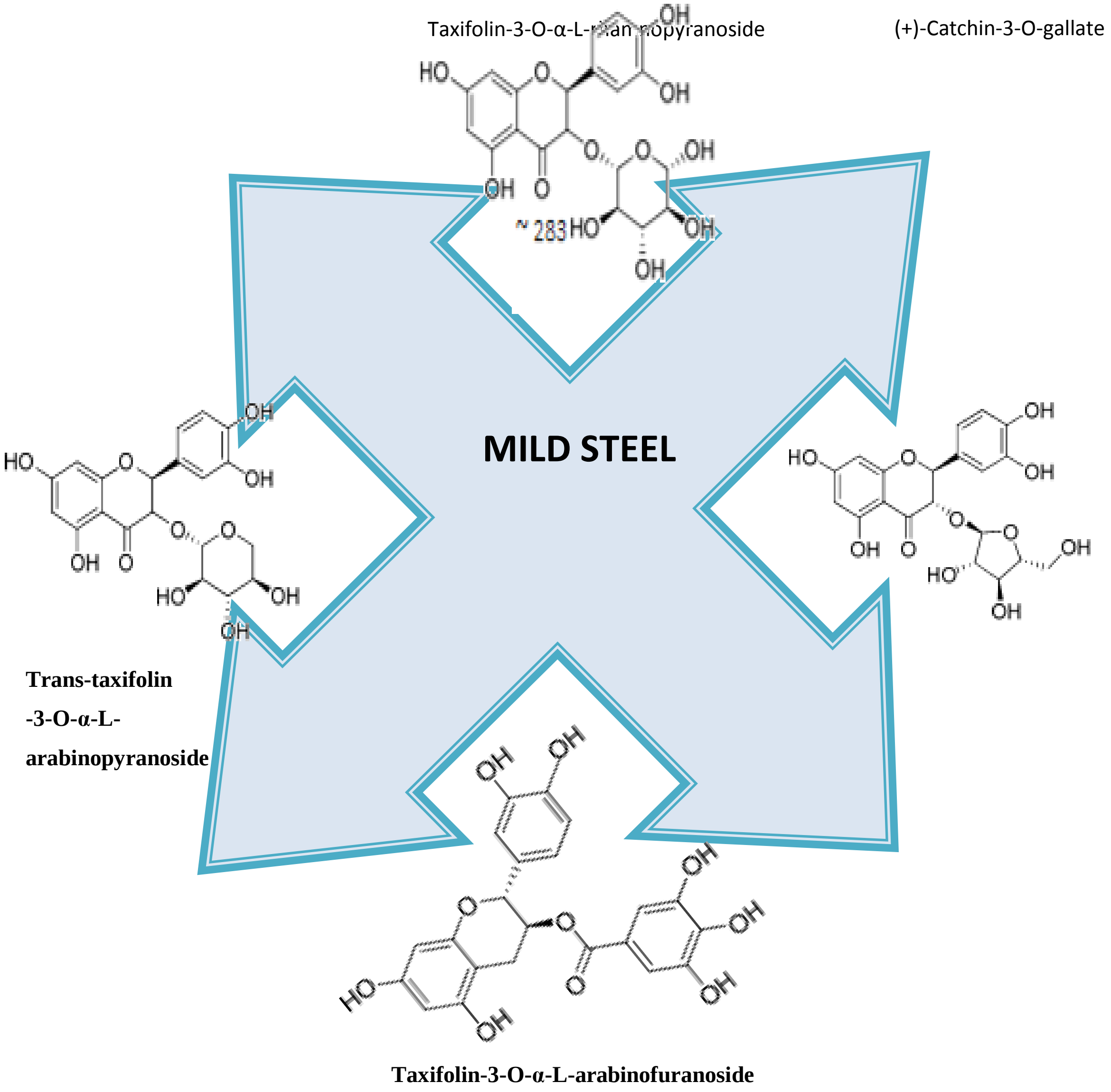


Figure 4.24. Schematic representation of the adsorption behavior of PCL extract on mild steel.

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

Corrosion inhibitors are economically feasible to mitigate the problems caused by corrosion. Environmental regulations in industrialized countries are increasing the pressure to eliminate, in the short term, a number of compounds

It is important to minimize or control metal corrosion technically, economically and environmentally, which is a major industrial problem. Green corrosion inhibitors are found to be effective from an ecological and environmental perspective and can play a major role over toxic inhibitors. It is still amazing that the anticorrosion efficiency of green corrosion inhibitors are equal to or even more effective than synthetic inhibitors. It is certain that natural compounds and plants products emerge out as effective inhibitors of corrosion in the coming years due to their biodegradability, easy availability, inexpensive and non-toxic nature. Natural products as green corrosion inhibitors having the limitation of their production volume on larges industrial scales, therefore, their economic aspects must be evaluated for industrial usage.

PCL acts as an excellent inhibitor for MS in 1M HCl and 0.5 M H_2SO_4 solution, and the extent of inhibition efficiency is directly proportional to the concentration of the inhibitor.

Inhibition efficiency increases with increasing inhibitor concentration and the maximum IE of 97% is obtained at 0.7 % concentration of the leaf extract of *Pouteria Campechiana* .

The adsorption of extract components follows Langmuir and Temkin adsorption isotherm.

From Icorr values a maximum inhibition efficiency of 79.1 % (1M HCl) and 84.6 % (0.5M H_2SO_4) is achieved when the concentration of extract is 0.7%.

Nyquist plots of MS in HCl and H_2SO_4 solutions containing plant extracts shows that charge transfer resistance increases with increasing of plant extract concentration and Cdl values decrease with increasing concentration of the inhibitors.

The inhibition efficiency (% IE) calculated from the values of Rct, are found to be maximum at a concentration of 0.7% PCL. The extracts are found to afford a maximum efficiency of 89.3 % (1M HCl) and 89.4 % (0.5M H_2SO_4) respectively.

In the current investigation the PCL extract plays a major role in reducing the metal dissolution as well as hydrogen evolution and protect the mild steel surface from corrosion. Thus PCL extract proved to be zero cost, eco-friendly and highly economical.

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