Ixora coccinea as an eco- friendly corrosion inhibitor for mild steel in 1M HCl & 0.5M H_2SO_4 solution

Janani .D.R

(14PCH002)

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
Supervisor

Signature of the 27/4/16
Head of the Department

Dr. R. RAJALAKSHMI
M.Sc., M.Phil., B.Ed., Ph.D.,
Professor & Head Department of Chemistry
Avinashilingam Institute for Home Science
and Higher Education For Women
Coimbatore - 641 043

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Introduction

INTRODUCTION

Corrosion is a general term used to describe various interactions between a material and its environment leading to degradation in the material properties. Interaction with ambient oxygen can cause the formation of oxide layers via diffusion controlled growth. These may passivate the material against further oxidation.

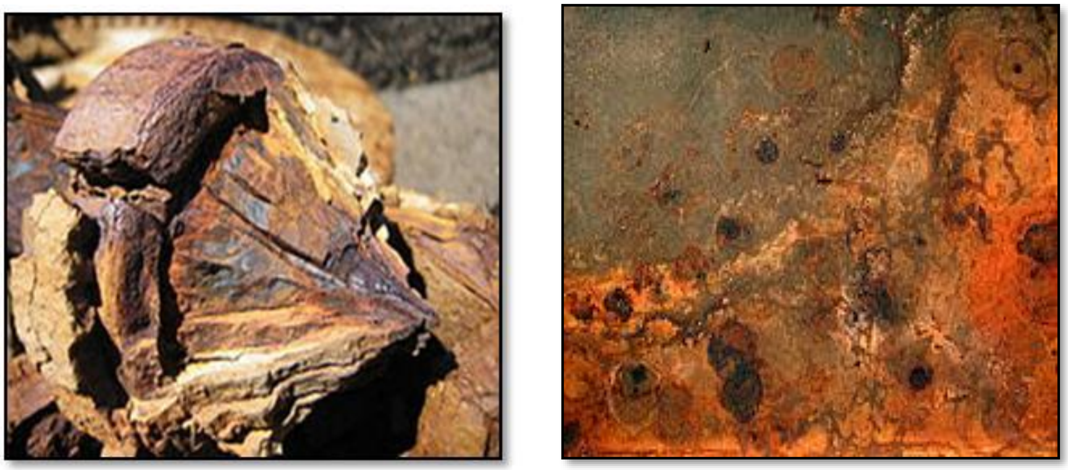


Figure 1.1.Corrosion

1.1 CORROSION………….

- The destructive attack of a metal by the environment, by chemicals, or electrochemical processes is called as the corrosion.
- Corrosion is the surface wastage that occurs when metals are exposed to reactive environments.
- Corrosion is the result of interaction between a metal and environment which results in its gradual destruction.

1.2 ELECTROCHEMISTRY OF CORROSION

The rusting of iron is an electrochemical process that starts with the transfer of electrons from iron to oxygen.

The key reaction is the reduction of oxygen

$$O_2 + 4e^- + 2H_2O \longrightarrow 4\,OH^-$$

The oxidation of iron that may be described as follows:

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

The following redox reaction also occurs in the presence of water and is crucial to the formation of rust.

$4\ Fe^{2+} + O_2 \longrightarrow 4Fe^{3+} + 2O^{2-}$

Additionally the following acid –base reactions affect the course of rust formation

$Fe^{2+} + 2\ H_2O \longrightarrow Fe\ (OH)_2 + 2\ H^{+}$

$Fe^{3+} + 3\ H_2O \longrightarrow Fe\ (OH)_3 + 3H^{+}$

Dehydration reaction will be taking place,

$Fe(OH)_2 \longrightarrow FeO + H_2O$

$Fe\ (OH)_3 \longrightarrow FeO(OH) + H_2O$

$2FeO\ (OH) \longrightarrow Fe_2O_3 + H_2O$

The final product is the formation of the rust.

1.3. FACTORS AFFECTING CORROSION

Many factors affect the type, speed, cause, and seriousness of metal corrosion. Some of the major factors that influence corrosion are as follows.

Climate

Temperature considerations are important because the speed of electrochemical attack is increased in a hot, moist climate.

Size and Type of Metal

It is a well known fact that some metals will corrode faster than others. Thick structural sections are more susceptible to corrosive attack than thin sections because variations in physical characteristics are greater.

Foreign Material

Among the controllable factors which affect the onset and spread of corrosive attack is foreign material which adheres to the metal surfaces. Such foreign material includes:

- Soil and atmospheric dust.
- Oil, grease, and engine exhaust residues.
- Salt water and salt moisture condensation.
- Spilled battery acids and caustic cleaning solutions.
- Welding and brazing flux residues.

1.4. CONSEQUENCES OF CORROSION

Corrosion has many serious economic, health, safety, technological, and cultural consequences to our society.

Material effects:

- **Plant shutdowns:** Shutdown of./ nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.
- **Loss of products :** leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards. It is well known that at least 25% of water is lost by leakage.
- **Loss of efficiency:** Insulation of heat exchanger tubings and pipelines by corrosion products reduces heat transfer and piping capacity.
- **Contamination:** Corrosion products may contaminate chemical, pharmaceuticals, dyes, packaged goods, etc. with dire consequences to the consumers.
- **Nuclear hazards:** The Chernobyl disaster is a continuing example of transport of radioactive corrosion products in water, fatal to human, animal and biological life.

Economic effects

A number of countries have attempted to determine the national cost of corrosion. The most extensive of these studies was the one carried out in the United States in 1976 which found that the overall annual cost of metallic corrosion to the U.S. economy was $70 billion, or 4.2% of the gross national product.

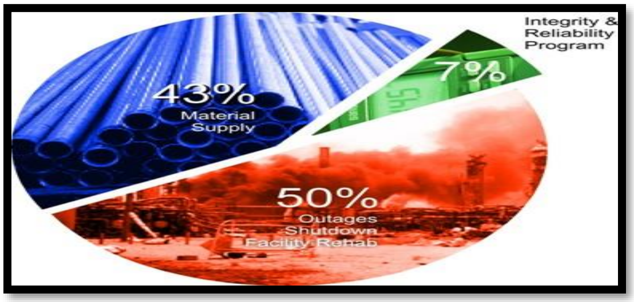


Figure 1.2. Economic effects due to corrosion

Health effects

Recent years have seen an increasing use of metal devices in the body, such as pins, plates, hip joints, pacemakers, and other implants. New alloys and better techniques of implantation have been developed, but corrosion continues to create problems.

Examples include failures through broken connections in pacemakers, inflammation caused by corrosion products in the tissue around implants, and fracture of weight-bearing prosthetic devices.

Safety effects

An even more significant problem is corrosion of the structures, which can result in severe injuries or even loss of life. Safety is compromised by corrosion contributing to failures of bridges, aircraft, automobiles, gas pipelines etc., the whole complex of metal structures and devices that make up the modern world.

Technological effects

The economic consequences of corrosion affect technology. A great deal of the development of new technologies are held back by corrosion problems because materials are required to withstand, in many cases simultaneously, such as higher temperatures, higher pressures, and more highly corrosive environments. In many of these instances, corrosion is a limiting factor preventing the development of economically or even technologically workable systems.

Cultural effects

International concern was aroused by the disclosure of the serious deterioration of the artistically and culturally significant gilded bronze statues in Venice, Italy. Corrosive processes will accelerate the deterioration of precious artifacts such as those in Venice by the highly polluted environments that now are prevalent in most of the countries of the world.

1.5.COST OF CORROSION

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere, air, water, soil and in every environment, we encounter. There is no single figure for loss to the nation due to corrosion. It can be a minimum of 3.5% of the nations GDP. Losses due to corrosion could be around Rs. 2.0 lakh crores per annum in India. Corrosion has a huge economic and environmental impact on all facets of national infrastructure; from highways, bridges, buildings, oil and gas, chemical processing, water and waste water treatment and virtually on all metallic objects in use. This cost was determined by analyzing 26 industrial sectors, in which corrosion is known to exist, and extrapolating the results for a nationwide estimate.

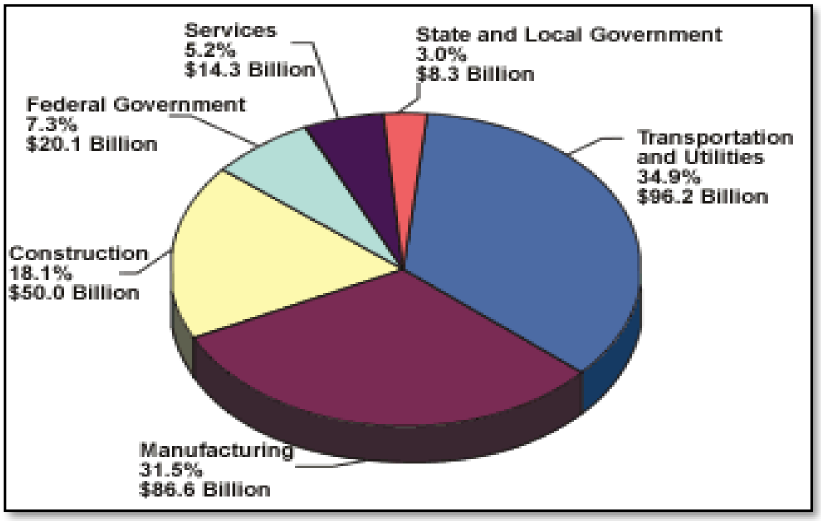


Figure 1.3. Cost of corrosion

1.6. VARIOUS FORMS OF CORROSION

TYPES	DEFINITION
GALVANIC CORROSION 	This type of corrosion occurs with an electrolyte like seawater. Metals have different values of electrical potentials. When they become electrically connected and put in an electrolyte, the more active metal which has a high negative potential corrodes fast.
PITTING CORROSION 	This occurs because of random attacks on particular parts of the metal's surface. This makes holes which are large in depth. These holes are called "pits". The pit acts as the anode while the undamaged part of the metal is the cathode. For example, it can be very harmful in gas lines

STRESS CORROSION CRACKING 	It is a complex form of corrosion which arises due to stress and corrosive environment. This generates brittle and dry cracks in the material. The stress is developed in the material due to bending or stretching of the material. It also affects only at a particular section of material
INTERGRANULAR CORROSION 	In the granular composition of metals and alloys, grains (small crystals) are present and their surfaces join with each other. This forms the grain boundaries. The Intergranular corrosion is developed on or near the grain boundaries of a metal.
CREVICE CORROSION 	It is also known as concentration cell corrosion. This is due to the trapping of liquid corrosive between the gaps of the metal. Crevice corrosion is similar to pitting corrosion. It's very difficult to detect crevice corrosion. It can be initiated by materials like gaskets, fasteners, surface deposits, washers, threads, clamp etc.
FILIFORM CORROSION 	It is a type of concentration cell corrosion. This develops on coated metallic surfaces with a thin organic film. The corrosion generates the defect on the protective coating of metallic surface. Filiform corrosion is a very specific process because it only affects the surface's appearance, not the metallic material.

FRETTING CORROSION 	It is a form of erosion-corrosion. It shows as the combined effect of corrosion and fretting of metal. Due to this corrosion, the material surface starts to disappear. Oxidation is the main cause of fretting corrosion. It can be controlled by using lubricates, controlling movement etc.

1.7.CORROSION IN VARIOUS INDUSTRIES:

Corrosion Science provides a medium for the communication of ideas, developments and research in all aspects of this field and includes both metallic and non-metallic corrosion. Corrosion is a huge issue for materials, mechanical, civil and petrochemical engineers. In recent years, numerous failures of industries due to corrosion is a commonly noted report.

The aerospace & defense industry

The particular demands of the aerospace industry have created a manufacturing environment with a very high and proper regard to optimizing corrosion performance, as a result of which the safety record has been exemplary and the efficiencies of operation have been outstanding. Failure of military systems in action due to materials or corrosion failure is a much feared phenomenon and is dealt with by reliability, a wider topic that arose from the needs of defense industry.

The Automotive Industry

It has been said that no other consumer product suffers corrosion so much from environmental factors as the automotive industry. A mild steel car body suffers from high and low temperatures, from precipitation and from increasing concentrations of reactive components in the atmosphere and along the road.

The Nuclear Industry

The nuclear industry has most of corrosion problems of other industries and some that are all of its own. Right from the start, the potential for disaster was recognized and tackled head-on by adopting high grade materials in many parts of systems. For boiling water reactors and pressurized water reactors, average capacity loss incurred in

1982 was 5%-8%. It is estimated that corrosion problems have cost the nuclear utility industry more than 5 billion dollars since 1980.

The Electrical and Electronics Industry

Many might believe the electronics industry would be unaffected by corrosion but it is not so. Aluminium is used for tracks on most devices and aluminium corrodes. Corrosion of power cables has been a considerable problem. Many critical systems are required to in quite hostile environments namely temperature ranging from below 0° to 40° or humidity up
to 100% and cope with airborne particles and insects.

The Marine and Off-Shore Industry

The marine environment is probably the most aggressive common environment in which metals are expected to operate. The corrosion performance record is mixed. For decades unscrupulous owners have consistently cut purchase, operating and maintenance costs, taking advantage of the important international regulation of merchant shipping.

The Chemical Industry

Corrosion is an obvious and well-recognized problem for industrial chemical system handling; say hydrofluoric acid or hot concentrated NaOH solutions. Much care is taken to use the most efficient materials. The presence of an unexpected impurity or change in concentration of process chemical can result in sudden dramatic rise in corrosion rate. The single life-limiting factor for prosthesis or other medical implant is its corrosion performance in bio medical engineering.

The Food Industry

The food quality requirements lead most plants to select stainless steel as a material of choice. Assuming that the stainless steel consumption and cost in this industry is entirely attributed to corrosion, a total annual direct cost of corrosion is estimated at $2.1 billion..

1.8. CORROSION PROTECTION OF METALS:

Two methods of combating corrosion which are widely used are cathodic protection and chemical inhibitors. Both methods depend on controlling the charge on the metal surface, and this can be monitored by measuring the potential of the metal. The conditions needed to stop corrosion can then be predicted from an electrochemical phase diagram.

Cathodic protection:

It is affected by forcing the potential to a negative region where those metals is completely stable. This can be done by using a sacrificial anode made from a more reactive metal, or using an external power supply to change the amount of charge on the metal surface. Cathodic protection is well suited to steel structures in marine or underground environments.

Chemical inhibitors

There is a class of chemical inhibitors which work by removing electrons from the metal, thereby pushing the potential into a positive region where an oxide film spontaneously forms. This results in a stable, passive surface with a very low corrosion rate.

1.9. CORROSION INHIBITORS:

A corrosion inhibitor is a substance when added in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment. It is well known in surface chemistry that surface reactions are strongly affected by the presence of foreign molecules. Corrosion processes, being surface reactions, can be controlled by compounds known as inhibitors which adsorb on the reacting metal surface. The technique of adding inhibitors to the environment of a metal is a well known method of controlling corrosion in many branches of technology.

Green inhibitors:

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 of plant origin contain various organic compounds such as alkaloids, flavonoids, terpenoids, saponins, primary and secondary alcohols, quinones, fatty acids, steroids and other minor components. These compounds are known to have inhibitive action. Commonly, the inhibitive effect of plant extract is attributed to adsorption of organic substances on the metal surface therefore blocking active sites or even forming a protective barrier.

1.10. PLANT DESCRIPTION

Ixora coccinea

Figure 1.4. ***Ixora coccinea*** **plant**

Other names **:** jungle geranium, flame of the woods or jungle flame

Origin of the plant: It is a common flowering shrub native to Southern India and Sri Lanka.

Details of the plant: *I. coccinea* is a dense, multi-branched evergreen shrub, commonly 4–6 ft (1.2–2 m) in height, but capable of reaching up to 12 ft (3.6 m) high. It has a rounded form, with a spread that may exceed its height. The glossy, leathery, oblong leaves are about 4 in (10 cm) long, with entire margins, and are carried in opposite pairs or whorled on the stems. Small tubular, scarlet flowers in dense rounded clusters 2-5 in (5–13 cm) across are produced almost all year long.

Phytochemicals present in the plant:

Phytochemical studies have shown that the major compounds present in ***I.Coccinea*** are lupeol, oleic acid, linolic acid, ursolic acid,oleanolic acid, stearic acid and sitosterol.(***Joshi et al.,2013***)

1.10.1. SCIENTIFIC CLASSIFICATION

Table 1.1. Scientific classification of the plant

Kingdom	Plantae
Division	Angiosperms
Class	Eudicots
Subclass	Asterids
Order	Gentianales
Family	Rubiaceae
Subfamily	Ixoroideae
Tribe	Ixoreae
Genus	*Ixora*

1.11.OBJECTIVES

- To select an eco-friendly, cost effective, naturally occuring plant material as corrosion inhibitor for mild steel in acid medium.

- To utilize of the naturally occurring plant extracts such as *Ixora coccinea* in 1M HCl and 0.5M H_2SO_4.

- To carry out phytochemical screening for the investigated inhibitor- *Ixora coccinea* leaf extract.

- To evaluate the corrosion studies of mild steel in 1M HCl and 0.5M H_2SO_4 in the presence of *Ixora coccinea* leaf extract at room temperature and higher temperature using the classical mass loss method.

- To calculate the activation energy (E_a) and thermodynamic parameters (ΔH, ΔS, ΔG^0) using results of temperature study.

- To assess the mode of action of the inhibitor under study cathodic, anodic or mixed type by conducting potentiodynamic, polarization studies & impedance measurements.

- To evolve a suitable mechanism for the adsorption process. To correlate the results obtained by mass loss and electrochemical techniques.

Review of literature

REVIEW OF LITERATURE

Mild steel is one of the most widely used engineering materials particularly for the structural and automobile applications. However, it undergoes rusting easily in the humid atmosphere and its rate of corrosion is quite high in acidic environment. Corrosion is an inevitable natural process. It is also a serious engineering problem in this modern age of technological advancement and which accounts for economic losses and irreversible structural damage. Several efforts have been made to restrain the onset and thereafter-destructive effects of corrosion using several preventive measures. Out of several methods, use of inhibitors is one of the most practical methods for the prevention of corrosion particularly in acidic media.

Acid solutions are widely used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid de-scaling and oil wet cleaning etc. Corrosion inhibitors are generally used to reduce the corrosion rates. Most of the well-known acid inhibitors are organic compounds containing electron donor atoms particularly nitrogen, sulphur, oxygen in their functional groups with aromatic and heterocyclic rings. But unfortunately most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap, safe inhibitors of corrosion.

Thus a new branch of environmental chemistry has emerged which provides environmental friendly corrosion inhibitors specifically termed as 'Green inhibitors'.

This thesis seeks to investigate effective and environmentally safe inhibitors such as ICL on corrosion of mild steel in 1 M HCl and 0.5M H_2SO_4. In this direction a review of natural product as corrosion inhibitor is carried out.

2.1. Green corrosion inhibitors for mild steel

- **Emeka E.Oguzie (2008)** studied the inhibitive behaviour on mild steel in 2 M HCl and1 M H_2SO_4 by leaf extracts of ***Occimum viridis, Telferia occidentalis, Azadirachta indica*** and **1--*Hibiscus sabdariffa*** and extract seeds of ***garcinia kola*** by gasometric technique at $30^0$and 60^0C.Inhibition efficiency was found to increase with increase in extracts concentration. Synergistic effects increase with increased the inhibition efficiency in the presence of halide additives.

- **Quraishi *et al.*, (2010**) studied the inhibition of the corrosion of mild steel in HCl and H_2SO_4 solutions by the extract of ***Murraya koenigii*** leaves using weight loss, electrochemical impedence spectroscopy (EIS), linear polarization and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The effect of temperature, immersion time and acid on the corrosion behaviour of mild steel in 1 M HCl and 0.5M H_2SO_4 in the presence of extract were studied and the thermodynamic parameters (ΔQ, ΔH^*, and ΔS^*) were calculated.
- **Farooqi *et al***., (1997) investigated the inhibitive effects of aqueous extracts of *Jasminum auriculatum* (leaves),*Momordica charantin* (fruits) and *Hisbiscus* (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 (93%), *Jasminum auriculatum*(80%),*Momordica charantina*(79%). Polarization measurements show that extract of Jasminum was anodic while the extract of Momordica and Hisbiscus were found to be cathodic. Impedance measurements reflected the complex formation tendency of the extracts.
- **El-Etre *et al.*, (2007)** investigated the inhibitive action of the aqueous extract of olive leaves ***(Olea europaea L.)*** towards the corrosion of C-steel in 2M HCl solution by weight loss measurements, Tafel polarization and cyclic voltammetry. It was found that the extract acts as a good corrosion inhibitor for the tested system. The inhibition efficiency increased with increasing extract concentration and decreased with temperature. The experimental data obeyed the Langmuir adsorption isotherm.
- **Pandian Bothi Raja *et al.*, (2008)** observed the performance of ***Black pepper*** extract on mild steel in 1M H_2SO_4 by conventional weight loss studies (303-323 K), electrochemical studies Viz., Tafel polarization, AC impedance and scanning electron microscope (SEM) studies. Results of weight loss study revealed that Black pepper extract acts as a good inhibitor even at high temperature and it obeys Temkin adsorption isotherm.
- **Umorena *et al,* (2008)** evaluated the inhibition of aluminium corrosion in HCI by exudate gum from ***Raphia hookeri*** at temperature range of 30–60 ^{0}C was studied using weight loss and thermometric techniques. The inhibition efficiency increased with increase in inhibitor concentration but decreased with an increase in temperature. The exudate gum was found to obey Temkin adsorption isotherm.

- **Smita and Metha *et al.,*** (1998) suggested that the acid extracts of Calotropis giganata 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.

- The inhibitive effects of aqueous extracts of Eucalyptus (leaves), Hisbiscus(flower), and Agaricus on the corrosion of mild steel for cooling systems using tap water was investigated by weight loss and polarization methods **(Minhaj A *et al.,* 1999)**. The results showed that all the plant extract inhibit corrosion of mild steel and their inhibitive efficiencies were in the order: Agaricus(85%) >Hibicus(79%)> Eucalyptus(74%).

- The effect of Cashew juice extract on corrosion inhibition of mild steel in HCl medium was carried out using weight loss and potential measurements techniques. The extracts from bark, provided no inhibition while nut-juice extract accelerate corrosion. Apple juice at a concentration of 2ml/100ml of 0.1M HCl gave good results of corrosion inhibition (**Loto , Mohammed *et al.,* 2000)**.

- **El-Etre and Abdulah *et al.,* (2000)** evaluated the inhibitive action of natural Honey on corrosion of C-steel, which was 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 good performance as inhibitor for steel corrosion in high saline water.

- **Ramesh *et al.,* (2001)** has investigated the corrosion inhibition efficiency of *Andiographis peniculata* extract on acid corrosion of mild steel.The inhibitive effect was studied by weight loss method,Tafel polarization method and impedance studies.The results revealed that this plant extract has the potential to serve as corrosion inhibitor.

- The inhibition effect of amino acids (alanine, glycine and leucine) against steel corrosion in HCl solutions was explained using potentiodynamic polarization method **(Ashassi-sorkhabi ,Majidi *et al.,* 2002)**. Corrosion data such as corrosion rate, corrosion potential (Ecorr) and corrosion resistance (Rp) were determined by extrapolation of the cathodic and anodic tafel region. The effect of inhibitor concentration and acid concentration was studied.

- **Rajalakshmi *et al.*, (2002)** investigated the performance of acid extracts of *Ficus benghalensis* bark on the corrosion inhibition of mild steel in1M HCl and 0.5M H_2SO_4 by weight loss and electrochemical techniques. The presence of anthocyanin compounds, flavonoid compounds and reducing sugars in the bark extract could inhibit the corrosion of mild steel in acid medium.

- Extract of *Ricinus Comunis* leaves were tested for corrosion inhibitory effects towards mild steel in 100 ppm sodium chloride solution. The anticorrosion efficiency of plant extracts was studied by weight loss, electrochemical polarization and impedance measurements. Corrosion inhibition efficiency was found that 84% in 300ppm of plant extract concentration. Polarization measurements indicate that extract act as mixed type of inhibitor **(Ananda Louise sathyanathan *et al.*, 2005).**

- The inhibitive action of the aqueous extract of olive (*Olea europaea* L.) leaves toward the corrosion of C-steel in 2 M HCl solution was investigated by **El-etre (2007)** using weight loss measurements, Tafel polarization, and cyclic voltammetry. It was found that the extract acted as a good corrosion inhibitor for the tested system. The inhibition efficiency increased with increasing extract concentration. The adsorption of extract components onto the steel surface was found to be a spontaneous process and to follow the Langmuir adsorption isotherm. The results of cyclic voltammetry showed that the presence of olive extract decreases the charge density in the transpassive region. The inhibition efficiency was greatly reduced as the temperature increased.

- Corrosion inhibition effect of black pepper (BP) extract and its piperine isolated from BP on corrosion of C38 steel in 1 M HCl solution was investigated by **Dahmani *et al.*, (2010)** using weight loss method. Piperine was isolated by ethanol in yield 6 from ground BP. Results obtained from weight loss measurements indicated that the natural compounds tested exhibit higher efficiency exceeding 95% at 2g/L. The presence of piperine decreases hugely the corrosion rate and its inhibition efficiency (IE%) increases with concentration to attain 99 % at 10-3M. Piperine adsorbs on the steel surface according Langmuir isotherm.

- **Uwah *et al.*, (2013)** investigated the inhibitive action of ethanol extracts from leaves (LV), bark (BK) and roots (RT) of *Nauclea latifolia* on mild steel corrosion in H_2SO_4 solutions at 30–60 °C using weight loss and gasometric techniques. The extracts were found to inhibit the corrosion of mild steel in H_2SO_4 solutions and the inhibition efficiencies of the extracts follow the trend: RT > LV > BK. The inhibition efficiency increased with the extracts concentration but decreased with temperature rise. Physical adsorption of the phytochemical components of the plant on the metal surface is proposed as the mechanism of inhibition.

- The inhibition of low-carbon-steel corrosion in 1 M HCl and 0.5 M H_2SO_4 by extracts of *Dacryodis edulis* (DE) was investigated by **Oguzie *et al.*, (2010)** using gravimetric and electrochemical techniques. DE extract was found to inhibit the uniform and localized corrosion of carbon steel in the acidic media, affecting both the cathodic and anodic partial reactions. The corrosion process was inhibited by adsorption of the extracted organic matter onto the steel surface in a concentration-dependent manner and involved both protonated and molecular species.
- **Vijayalakshmi *et al.*, (2010)** investigated the inhibitory effect of extract obtained from destructive distillation of palmyra palm (*Borassus flabellifer* Linn.) shell on the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl was investigated using weight loss and electrochemical measurement techniques. The results show that the inhibition efficiency increases with increase of palmyra palm shell extract concentration. The maximum inhibition efficiency in 0.5 M H_2SO_4 and 1 M HCl was found to be 97.65% and 98.11% for a period of 24 h with 3%v/v concentration of the inhibitor respectively.
- **Lebrini *et al.*, (2010)** studied about alkaloids extract of *Annona squamosa* plant as possible corrosion inhibitor for C38 steel in molar hydrochloric acid (1 M HCl). Potentiodynamic polarization and AC impedance methods were utilized for the study. The corrosion inhibition efficiency increased on increasing plant extract concentration. Polarisation studies showed that *Annona squamosa* extract was mixed-type inhibitor in 1 M HCl. The inhibition efficiency of *Annona squamosa* extract was temperature dependent and its addition led to an increase of the activation corrosion energy revealing a physical adsorption between the extract and the metal surface. The adsorption of the *Annona squamosa* extract followed Langmuir's adsorption isotherm.
- **Sivaraju *et al.*, (2010)** reported the inhibition effect of *Acalypha indica* L. alcoholic extract (AIAE) on mild steel corrosion in 1N phosphoric acid by mass loss and polarization techniques between 303 K and 333K. 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. Potentiostatic polarization results revealed that Tribulus terrestris .L extract act as mixed type inhibitor. Surface analysis (FT-IR and SEM) was also carried out to establish the mechanism of corrosion inhibitor on mild steel corrosion in phosphoric acid medium.

- **Gopal ji *et al.*, (2011)** reported 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. This plant extract is selected for the study of corrosion inhibition in view of its rich source of organic inhibiting molecules as proteins, amino acids, tannins, phenolic compounds, saponins, and flavonoids and nonalkaloids organic compounds such as fused benzene rings, hetero Natom rings,- OCH3, and -OHgroups. A simple extraction method was adopted to obtain water-based plant extract. Inhibition mechanism was studied using UV-visible, electrochemical, and surface imaging techniques.

- The influence of *Xylopia ferruginea* leaves extract and partitions in different solvents on the corrosion behavior of mild steel (MS) in 1 M HCl was tested using weight loss method was reported **(Elyn Amira *et al.*, 2011)** . Potentiodynamic polarization studies clearly reveal that all inhibitors behaved as mixed-type inhibitors with predominant anodic effectiveness. The Nyquist plots showed that on increasing the inhibitor concentration, the charge transfer resistance increased and the double layer capacitance decreased. The adsorption of inhibitors on MS surface obeys the Langmuir adsorption isotherm. SEM studies confirmed that the corrosion protection of MS was by the adsorption of inhibitors. The effectiveness as corrosion inhibitors is in the order of chloroform partition (CP) > *n*-hexane partition (HP) > methanol extracts (ME).

- **Loto (2011)** studied the effect of green tea extract as an organic 'green' inhibitor on the corrosion of mild steel in dilute sulphuric acid at ambient temperature. Weight loss/corrosion rate and potential measurement techniques were used for the experimental work. The results showed effective corrosion inhibition of the extract on the mild steel test specimens in the different concentrations of sulphuric acid used. The different acid strength used did not give any clear adverse corrosive effect on the performance of the inhibitor.

- **Nwabanne *et al.*, (2011)** investigated the inhibitive, thermodynamics and adsorptive properties of ethanol extract of *Vernonia Amygdalina* for the corrosion of mild steel in 0.4M HNO_3 solution using weight loss technique. The extract was to be a good inhibitor for corrosion of mild steel in HNO_3. Inhibition efficiencies obtained ranged from 40.57 to 50.74% and from 38.06 to 49.27% at 303 and 323K respectively. The inhibition efficiency of the extract decreased as temperature and time of immersion increased, but increased with increase in concentration of extract. The inhibition capacity of this extract was attributed to the presence of saponnin, tannin, alkaloid, anthraquinone, flavanoid, cardiac glycosides in the extract. Langmuir, Temkin, Frumkin and Flory-Huggins adsorption isotherms were found to confirm the adsorption characteristics of the inhibitor.

- The extract of *Ipomoea invulcrata* (IP) was studied as a possible source of green inhibitor for corrosion of aluminium in 1 M HCl at 30-60^{o}C using the conventional weight loss technique. The studies reveal that at constant acid concentration, the plant extract acted as an effective inhibitor for aluminium corrosion in acidic medium. Inhibition efficiency increased with concentration but decreased with increase in temperature and immersion time. The adsorption of IP was in accord with the Langmuir adsorption isotherm at all the temperature studied. The mechanism of physical adsorption is proposed for the inhibitory action of IP and is satisfactorily explained by both kinetic and thermodynamic parameters **(Obot *et al.*, 2010).**

- **Taleb Ibrahim *et al.*, (2010)** investigated the inhibitive action of eggplant peel extract toward the corrosion of mild steel in 2M HCl solution by employing weight loss measurements and electrochemical techniques. The results of both methods showed that the corrosion rate decreased and inhibition efficiency increased as the concentration of the eggplant inhibitor increased. The adsorption data were analyzed using various adsorption isotherm models and the results at temperatures of 25, 40 and 50°C have shown that the adsorption behavior of eggplant extract molecules was best described by the Langmuir adsorption isotherm.

- **Al-Turkustani *et al.*, (2011)** studied the inhibitive effect of water and alcoholic extracts of Medicago Sative (MS) on the corrosion of steel in 2.0 M H_2SO_4 containing 10% EtOH using chemical (weightloss (ML), hydrogen evolution(HE)), electrochemical (potentiodynamic polarization (PDP) and impedance spectroscopy (EIS)) techniques. The results showed that the inhibition efficiency increases with the increase of M. Sative (MS) concentration. The water and alcholic extracts of MS plant act as mixed type inhibitors with nearly the same efficiency. The inhibition action of M. Sative (MS) extracts was discussed in terms of their horizontal adsorption on the metal surface. The adsorption follows Langmuir adsorption isotherm.

- Corrosion inhibition of mild steel in 1 M H_2SO_4 by leaves and stem extracts of *Sida acuta* was evaluated by **Umoren *et al.*, (2011)** using chemical (weight loss and hydrogen evolution) and spectroscopic (AAS, FTIR and UV-V) techniques at 30–60°C. It was found that the leaves and stem extracts of S. acuta inhibited the acid induced corrosion of mild steel. The inhibition efficiency increases with increase in concentration of the extracts but decrease with rise in temperature. Inhibitive effect was afforded by adsorption of the extracts' components which was approximated by Freundlich adsorption isotherm. Inhibition mechanism is deduced from the temperature dependence of the inhibition efficiency and also from spectroscopic results.

- **Lebrini *et al.*, (2011)** effectuated the corrosion inhibition effect of alkaloids extract from *Palicourea guianensis* plant (AEPG) on C38 steel in 1 M HCl medium by potentiodynamic polarization and electrochemical impedance spectroscopy. The polarization studies showed that AEPG acted 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. An efficiency of 89% was achieved with 100 mg L-1 of AEPG at 25 °C. The adsorption of AEPG was found to obey the Langmuir adsorption isotherm.

- **Al-Otaibi *et al.*, (2012)** studied the alcoholic extracts of eight plants namely *Lycium shawii*, *Teucrium oliverianum*, *Ochradenus baccatus*, *Anvillea garcinii*, *Cassia italica*, *Artemisia sieberi*, *Carthamus tinctorius*, and *Tripleurospermum auriculatum* grown in Saudi Arabia for their corrosion inhibitive effect on mild steel in 0.5 M HCl media using the open circuit potential (OCP), Tafel plots and A.C. impedance methods.

All the plant extracts inhibited the corrosion of mild steel in acidic media through adsorption and act as mixed-type inhibitors.

- **Shyamala *et al* ., (2012)** studied the inhibitive action of the extracts of *Adathoda vasica, Eclipta alba,* and *Centella asiatica* on the corrosion of mild steel in 1N HCl using weight loss method, electrochemical methods, and hydrogen permeation method. Polarization methods indicate that the plant extracts are under mixed controlled that is, promoting retardation of both anodic and cathodic reactions. The impedance method revealed that charge-transfer process controled the corrosion of mild steel. The plant extracts were found to obey Langmuir adsorption isotherm. The protective film formed on the surface was confirmed by SEM. Results obtained in all three methods were very much in good agreement in the order *Eclipta alba* > *Adathoda vasica* > *Centella asiatica*, and, among the three plant extracts studied, the maximum inhibition efficiency was found in *Eclipta alba* which showed 99.6% inhibition efficiency at 8.0% v/v concentration of the extract.
- The corrosion inhibition of *Ecbolium viride* plant extracts on the mild steel corrosion in 1 M HCl was investigated by weight loss, Tafel polarization and electrochemical impedance spectroscopy (EIS). The corrosion inhibition efficiency increased on increasing the plant extract concentration. Adsorption of inhibitor was found to follow the Langmuir`s adsorption isotherm. Thus, it can be classified as anionic inhibitor. Adsorption equilibrium constant (Kads) and free energy of adsorption (ΔG_0 *ads*) were calculted. Surface analysis (SEM) was also carried out to establish the corrosion inhibitive property of *Ecbolium viride* in 1 M HCl solution **(Ashok Kumar *et al.*, 2012).**
- **Mahima Srivastava *et al.*, (2012)** investigated the inhibitor efficiency of *Ipomoea carnea* and found that the mixtures of different proportions of HCl (4N) and H_2SO_4 (4N), showed 61% to 68% protection. The rate of dissolution increased with temperature. Results also show that inhibitor maintained its effectiveness over entire range of temperature. Electrochemical studies reveal that the inhibitor is predominately anodic in nature.
- **Behpoura *et al.*, (2012)** evaluated the effect of the extract of *Punica granatum* (PG) and their main constituents involve ellagic acid (EA) and tannic acid (TA), as mild

steel corrosion inhibitor in 2 M HCl and 1 M H_2SO_4 solutions by weight loss measurements. Potentiodynamic polarization curves indicated that PG and EA behave as mixed-type inhibitors. EIS measurements show an increase of the transfer resistance with increasing inhibitor concentration. The temperature effect on the corrosion behavior of steel without and with the PG extract was studied. The inhibition action of the extract was discussed in view of Langmuir adsorption isotherm.

- The inhibition of the corrosion of mild steel in 1 M HCl and 1 M H_2SO_4 by *Spirulina platensis* was studied at different temperatures viz., 303 K, 313 K and 323 K by weight loss method, potentiodynamic polarization method, electrochemical impedance spectroscopy measurements and SEM analysis. The inhibition efficiency increased with increasing concentration of the inhibitor in both HCl and H_2SO_4 media. The results of weight loss studies correlated well with those of impedance and polarization studies. From the results of weight loss studies at various temperatures, the mode of adsorption is confirmed to be physisorption. Further the adsorption was found to follow Temkin isotherm. From this isotherm, the free energy of adsorption (ΔG) and entropy (ΔS) are calculated **(Kamal *et al.*, 2012**).

- The corrosion inhibition effect of extracts of kola plant *(Cola acuminata)* and green tea *(Camellia sinensis)* in mixed form on the protection of mild steel specimens immersed in sulphuric acid solution was studied at ambient temperature by gravimetric and potential monitoring methods. The electrode potential monitoring was performed using a digital voltmeter and a saturated calomel electrode (SCE) as the reference electrode. Extracts of kola plant and green tea in different concentrations and combinations were used as ‘green’ inhibitors. There was significant reduction in the weight loss and in the corrosion rate of the test samples, particularly at the added extracts concentration of 100% and also at the concentrations of 50 and 25%. This behavior was attributed to the protective film provided on the steel’s surface by the complex chemical constituents of the plants extracts. **(Loto *et al.*, 2012).**

- **Maduabuchi A. Chidiebere *et al.*, (2012)** investigated the adsorption and corrosion inhibiting effect of aqueous extracts of Punica granatum (PNG) on mild steel in 1 M HCl and 0.5 M H_2SO_4 at 30 +/-1 ^{o}C using gravimetric, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization techniques. The experimental findings revealed that PNG inhibited the corrosion reaction in both acid environments. Impedance results indicate that the extract organic matter was adsorbed on the metal/solution interface, while polarization data show that the extract behaved mostly as a mixed-type inhibitor.

- **Emeka E *et al.,* (2005)** studied the inhibitive effect of ***Occimum viridis*** extract on the acid corrosion of mild steel in 2 M HCl and 1 M H_2SO_4 by using the gasometric technique at temperatures of 30 and 60 °C. The results indicated that the extracts inhibited the corrosion process in both acid media and inhibition efficiency increased with concentration.
- **Raja (2007)** studied the inhibitive effect of ***Datura stramonium*** extract on the acid corrosion of mild steel in HCl and H_2SO_4 media at different temperatures. The anticorrosion effect was evaluated by conventional weight loss studies, electrochemical studies. The studies reveal that the plant extract acts as a good inhibitor in both the acid media and better in H_2SO_4 medium and also the potential of D. stramonium for combating corrosion may be due to the adsorption of alkaloids and other phytoconstituents.
- **Maheswari *et al.,* (2001)** reported 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 effectiveness of the extract. An efficiency of 94.87% was found for 0.35% extract at 333K.
- **Prithiba *et al.,* (2002)** evaluated the effective inhibition of *E**rvatamia Coronaria*** leaves extract on the corrosion of mild steel in 1M HCl and 0.5M H_2SO_4 at ambient temperature. Mass loss and potential measurement techniques have been used. The inhibitor efficiency increased with the concentration of the extract and the system obeyed Langmuir adsorption isotherm.
- **Husnu Gerengi *et al.,* (2012)** observed the corrosion inhibition of low carbon steel in 1MHCl solution with different concentrations of *Schinopsis lorentzii* extract using Tafel extrapolation, linear polarization, and electrochemical impedance spectroscopy (EIS). It was found that *Schinopsis lorentzii* extract acted as slightly cathodic inhibitor and inhibition efficiencies increased with the increase of extract concentration. The adsorption of the molecules of the extract on the low carbon steel

surface was in accordance with the Temkin adsorption isotherm. The results showed that *Schinopsis lorentzii* extract could serve as a corrosion inhibitor of the low carbon steel in hydrochloric acid environment.

- **Okafor *et al.*, (2012)** investigated the action of ethanol (EEAA), acid (AEAA), and toluene (TEAA) extracts from *Artemisia annua* and Artemisinin (ATS) on mild steel corrosion in H_2SO_4 solutions using gravimetric and gasometric techniques. The extracts and ATS functioned as good inhibitors, and their inhibition efficiencies (%IE) followed the trend: EEAA > AEAA > TEAA > ATS. %IE increased with increase in inhibitors concentration and decreased with increase in temperature. The adsorption of the inhibitors was consistent with Langmuir isotherm.

2.2. Green corrosion inhibitors for other metals and alloys

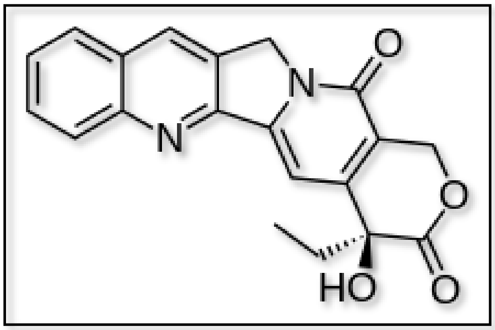
- **James *et al.*, (2009)** evaluated the inhibition efficiency of acetone extract of red onion skin on aluminium in hydrochloric acid solutions by weight loss techniques. Values of inhibition efficiency obtained are found to dependent upon the concentration of inhibitor and temperature. Generally, inhibition was found to increase with inhibitor concentration, half-life, activation energy but decrease with temperature and first-order rate constant at the temperatures studied. Physical adsorption mechanism has been proposed for the inhibition and Langmuir adsorption isotherm was obeyed. The compound responsible for the inhibitory action of red onion skin is Quercetin.
- **Ating *et al.*, (2010)** studied the inhibition of corrosion of aluminum in hydrochloric acid solutions by the ethanolic extract of the leaves of *Ananas sativum* using weight loss and hydrogen evolution methods. The plant extract retarded the acid induced corrosion of aluminum. Inhibition efficiency increased with increasing concentration of the extract and temperature. Adsorption studies revealed that Langmuir adsorption isotherm is the best adsorption model applicable to the adsorption of A. sativum on aluminum surface. Activation parameters such as activation energies (Ea), activation enthalpy (ΔH_o), and activation entropy (ΔS_o) were evaluated from the effect of temperature on the corrosion and inhibition processes.
- **Bouyanzer *et al.*, (2006)** analyzed the inhibition of the corrosion of mild steel in molar hydrochloric acid solution by natural oil extracted from ***Pennyroyal Mint*** (Mentha pulegium) using weight loss measurement, electrochemical polarization and EIS

methods. The inhibition efficiency was found to increase with oil content to attain 80% at 2.76g/L. Pennyroyal Mint oil acted as a cathodic inhibitor.

2.3. Phytochemical constituents of *Ixora Coccinea* :

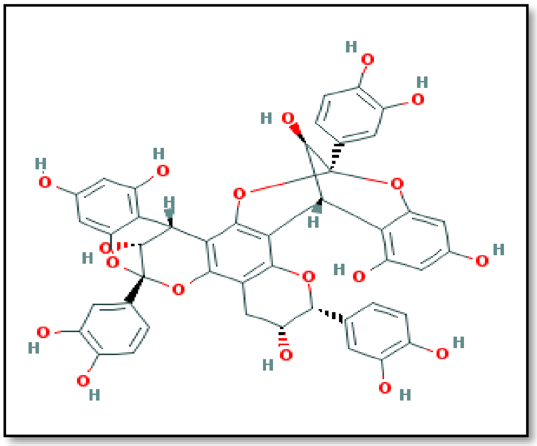
- The crude ethanolic extract of the leaves of ***Ixora Coccinea*** (Family- Rubiaceae) was evaluated for its possible phytochemical nature (group determination of plant constituents), anti-inflammatory activity and antinociceptive activity. Phytochemical analysis of the methanolic extract of ***I. Coccinea*** indicated the presence of tannin, steroid &alkaloid types of compounds.(**Kharat *et al.*,2013**)

- The major constituents of I. coccinea were reported to be lupeol, oleic acid, linolic acid, ursolic acid, oleanolic acid, stearicacid and β-sitosterol. The structures were elucidated by extensive 1D and 2D NMR spectroscopy and MS. The anticancer activity of the leaves of *I. coccinea* (Rubiaceae) was found to be due principally to the known alkaloid, camptothecin. The presence of camptothecin was confirmed by RP-HPLC analysis. **(Dontha *et al.*,2015)**

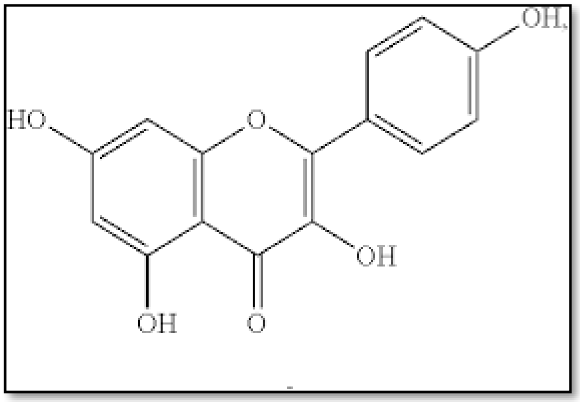


camptothecin

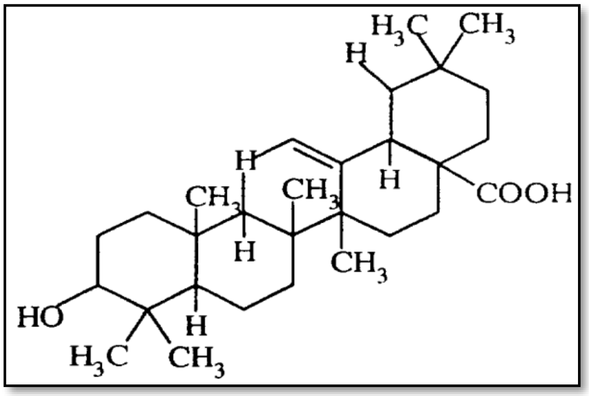
The methanol extract of the leaves of I. coccinea yielded ixoratannin A-2, kaempferol. I.coccinea leaves afforded quercetin which exhibited high antioxidant activity **(Bose *et al.*, 2013).**



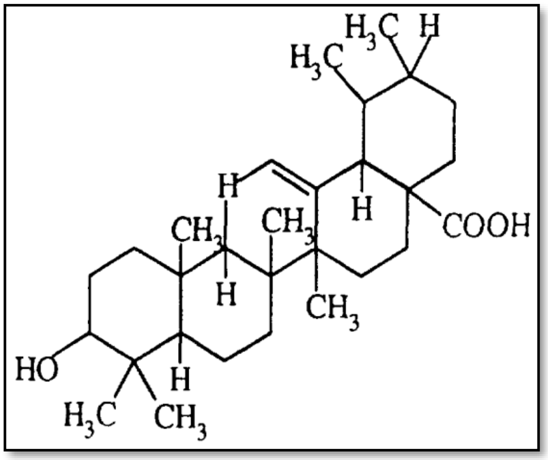
Ixoratannin A-2



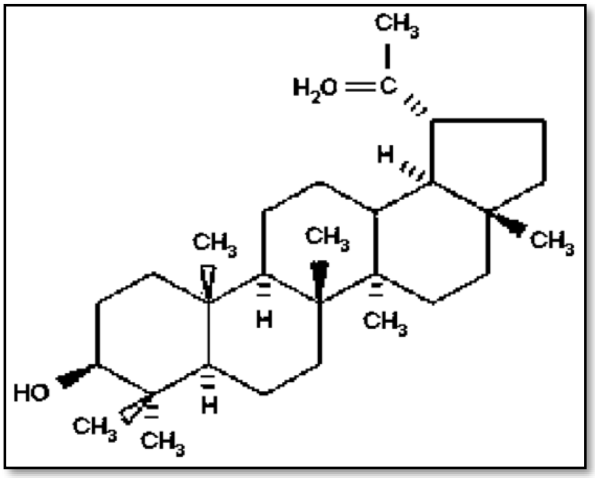
Kaempferol



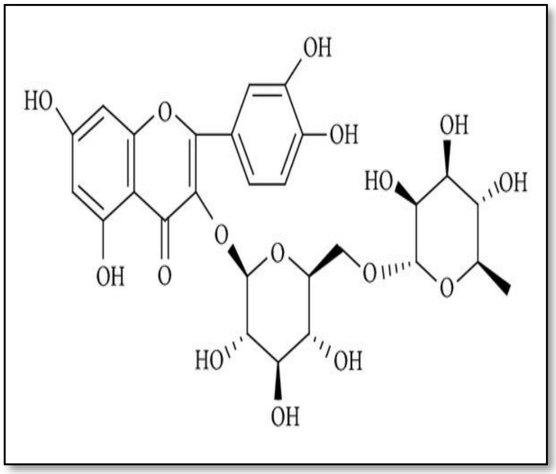
Oleanolic acid



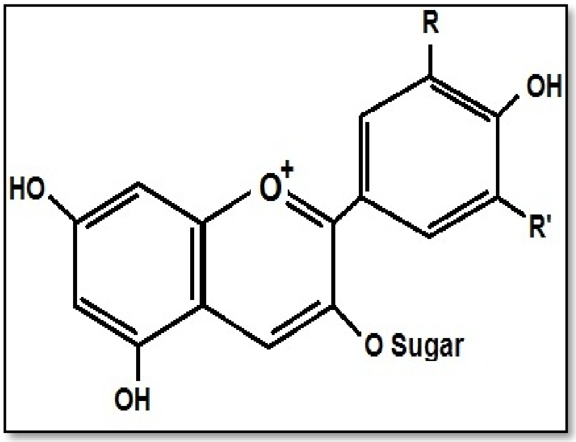
Ursolic acid



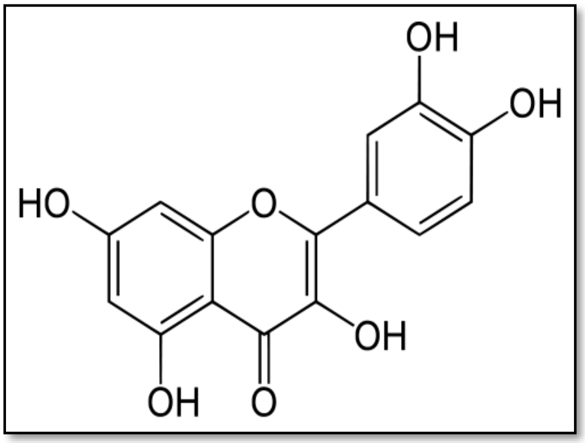
Lupeol



Rutin



Anthocyanin



Quercetin

Thus from the review, it can be seen that the plant selected had abundant phyto constituents which will aid as corrosion inhibitor for metals. The effectiveness of the inhibitor will also be due to the large size of the phytochemical constituents present in the plant extract which will cover a wider area of the metal surface thereby minimising the corrosion. Thus this overview justifies the choice of the plant source selected as an inhibitor for mild steel. Further investigations are warranted to prove its role in the corrosion inhibition of mild steel in acid media.

Methods and Materials

MATERIALS AND METHODS

In any research work the materials and methods adopted are the aspects, which decide and determine qualitatively and quantitatively the outcome of the research. In the present investigation, efforts have been taken to study the inhibitive action of the ***Ixora coccinea*** leaves extract as corrosion inhibitor for mild steel (MS) in 1M HCl and 0.5 M H_2SO_4. The design of the present investigation consisted of the following steps.

3.1. SELECTION OF SAMPLE

Mild steel is one of the most important widely used engineering materials particularly for the structure and automobile applications due to low cost and easy availability. MS suffers from severe corrosion in aggressive environment, which needs to be protected. Hence the study of corrosion inhibitor of MS in aqueous aggressive media is the subject of pronounced technological significance. Thus the investigation was carried out using mild steel.

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 then thoroughly dried and kept in desiccators for weight loss tests. The mild steel specimens used in the following percentage elemental of composition as shown in table .

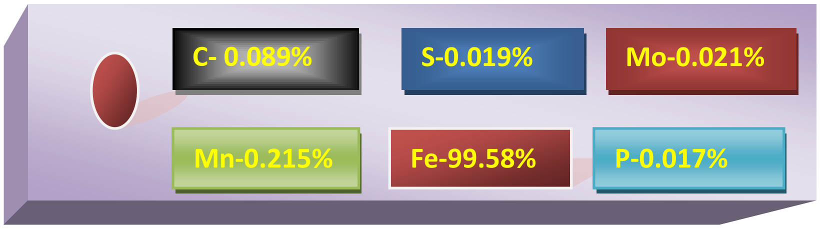


Figure 3.1Elemental composition of MS

3.3. TEST MEDIUM

Acid solutions are widely used in chemical laboratories and in several industrial processes such as pickling, acid cleaning, acid de-scaling and oil wet cleaning etc. among the commercially available acids hydrochloric acid and sulphuric acid are used in nearly all industries and is vital commodity in our national economy. Experiments were performed in 1M HCl. The acid used was of LR grade.

3.4. SELECTION OF INHIBITOR

The choice of the inhibitor is based on the following consideration,

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

3.5. PREPARATION OF THE INHIBITOR

The extract was prepared by refluxing 25g of ***Ixora Coccinea*** 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.

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. **(Prashant Tiwari ,et al, Jan-March 2011)**

3.7.TECHNIQUES EMPLOYED

- Mass loss methods
- Electrochemical measurement

3.7.1. 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 (313K-353K)

3.7.1.1. 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,

$$\mathbf{C.R\ (mpy) = 543 \times W/ D \times A \times T}$$

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

3.7.1.2. Determination of percentage of inhibition and surface coverage

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

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

$$\boldsymbol{\theta = w_o - w/w_o \times 100}$$

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**)

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

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

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

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

3.7.1.3. 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)

3.7.1.4. 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

3.7.1.5. Activation Parameters

An alternative formulation of Arrhenius equation is

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

Where,

h is Planck’s constant

N is Avagadro 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.

3.7.2. ELECTROCHEMICAL METHOD

3.7.2.1. 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 10.23.

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. 1 sq.cm.of polished mild steel surface was exposed and the electrochemical studies are carried out at 303K.

3.7.2.2. 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,

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

I.E from LPR technique

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

Where,

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

3.7.2.3. 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,

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

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,

$$\mathbf{\theta = 1 - \frac{C_{dl}\ (inhibited)}{C_{dl}\ (blank)}}$$

Where,

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

3.8. SURFACE ANALYTICAL TECHNIQUES

3.8.1. FTIR 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 ICL extract with a frequency ranging from 4000 to 400 cm^{-1} using **Perkin Elmer FT-IR spectrophotometer** with the **SOFTWARE – OPUS version 6.5**.

FTIR Spectral Analysis

FTIR was recorded using **Nexus 670/ Thermo Electron Corporation Spectrometer** which extended from 4000 and 400 cm^{-1}**.** The interaction between the organic molecules and the metal surface has been studied by FTIR spectra.

3.8.2. UV analysis

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% inhibitor for 3h.

3.8.3. SEM 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% inhibitor .

3.8.4. 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 ICL extract for 3h were examined by Zeta 3D Profiler.

Result and Discussion

RESULT AND DISCUSSION

Corrosion of metals is one of the most important and challenging problems in industry. Nowadays the study of mild steel corrosion phenomena has become an important industrial and academic topic.

Acid solutions are widely used for the removal of oxide from the metallic parts before coating (acid pickling), removal of undesirable scales and rust (acid cleaning) and in several other industrial processes .

Hydrochloric acid and Sulphuric acids are the most important pickling acids used for steel and ferrous alloys in industry. Inhibitors are commonly used in these processes to control the metal dissolution and acid consumption. The use of corrosion inhibitors is one of the most effective methods to protect metal surfaces against corrosion, especially in acid media**.** The cost, toxicity, availability etc, are of considerable importance in the selection and the utilization of the inhibitors.

The aim of the present investigation is to evaluate the effectiveness of ICL extract on the corrosion of mild steel in 1M HCl medium and 0.5 M H_2SO_4.

Results of the present investigation are discussed under following headings:

MASS LOSS STUDIES:

1. Variation of inhibition efficiency with
    - ➢ Concentration
    - ➢ Immersion time and
    - ➢ Temperature
2. Nature of adsorption and thermodynamic parameter
3. Change in kinetic parameters

ELECTROCHEMICAL MEASUREMENT

1.Polarization techniques

2.Impedance Spectroscopy

3.Surface Analytical Techniques

- ➢ FT-IR
- ➢ UV
- ➢ SEM
- ➢ 3D Laser Profilometer

4.1. CHARACTERISATION OF ICL EXTRACT

4.1.1 Phytochemical Screening

The investigated plant extract was screened for the presence of various phyto chemicals namely, flavonoids, alkaloids, terpenoids, saponins, tannins, reducing sugar, polyphenols, and anthraquinones using standard procedure (**Harborne .,1973**).

Table 4.1

Phyto chemical screening of ICL crude extract

Phytochemicals							
Alkaloid	**Reducing sugars**	**Flavonoids**	**Saponins**	**Steroids**	**Gums**	**Tannins**	**Carbohydrates**
+	+	-	+	+	-	+	+

+ present; - absent

The results confirm the presence of constituents which are known to exhibit medicinal as well as physiological activities. The results indicated the presence of phytoconstituents like flavonoid, tannins, terpenoids , steroids in the extract.

4.1.2 FT –IR

Figure 4.1

FT- IR spectral peak of crude ICL extract

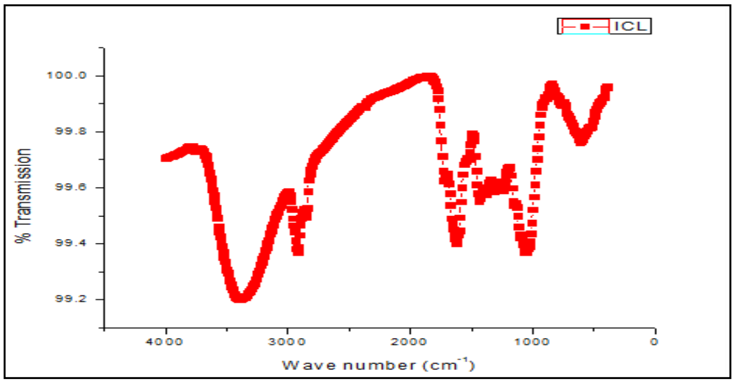


Figure.4.1 shows the FT-IR spectrum of crude extract. A very strong broad band at 3394.72 cm^{-1} is attributed to O–H stretching. The absorption band at 2924 cm^{-1} is related

to –CH asymmetrical stretching vibration **(Li *et al*, 2009)**, and a strong band at 1627 cm^{-1} corresponds to the C=O stretching vibration. Hence, it can be inferred that contains oxygen and nitrogen atoms in functional groups (O–H, N–H, C=O, C–O, C=C), aromatic ring, which meets the general structural consideration of the corrosion inhibitors.

4.2. MASS LOSS MEASUREMENTS OF *Ixora coccinea* LEAF EXTRACT IN 1M HCl

4.2.1. EFFECT OF CONCENTRATION

The IE of mild steel exposed to 1M HCl at room temperature (30 ± 2°C) as a function of concentration of different inhibitor is shown in **Figure 4.2 & Table 4.1**. It is observed that the inhibition efficiency of mild steel increased with increasing concentrations of inhibitors. This behavior could be attributed to the increase in adsorption of inhibitors on the metal or at the solution interface on increasing its concentration. The highest % IE was **93.9** at **0.7%** concentration of the extract.

The effect of different concentrations of ICL extract on corrosion rates in 1M HCl solution are illustrated in **Figure 4.2**. The plant extract was seen to reduce the corrosion rate at all studied concentrations indicating inhibition of the corrosion reaction. The effect becomes more pronounced with increasing extract concentration, which suggested that the inhibition process is sensitive to the amount of the additive present. (**Obot and Obi-Egbedi, 2010**).

4.2.2. EFFECT OF IMMERSION TIME ON CORROSION INHIBITION

The immersion time is another important parameter in assessing the stability of inhibitive behavior. So it is necessary to evaluate the IE for a long immersion time. In this study, effect of immersion time (1/2- 24 h) on corrosion inhibition of ICL extract in 1M HCl at room temperature was investigated using mass loss method.

Figure 4.3 depicted the corrosion rates obtained in the absence & presence of ICL extract act as a function of time. As the immersion period increased the IE was also found to increase with 93.9% to 96% for 1/2 -3 h. But it slightly decreased in 6h. And then the IE stabilized at 24h to yield efficiency 97%.

This behaviour can be discussed on the basis that prolonged immersion of mild steel in acid solution (**Zakvi and Mehta, 1987**).

- allows the cathodic or hydrogen evolution kinetics to increase presumably or more cathodic or carbon containing sites are exposed by the corrosion process.

- increase the concentration of ferrous ions which decrease the corrosive nature of the acid.

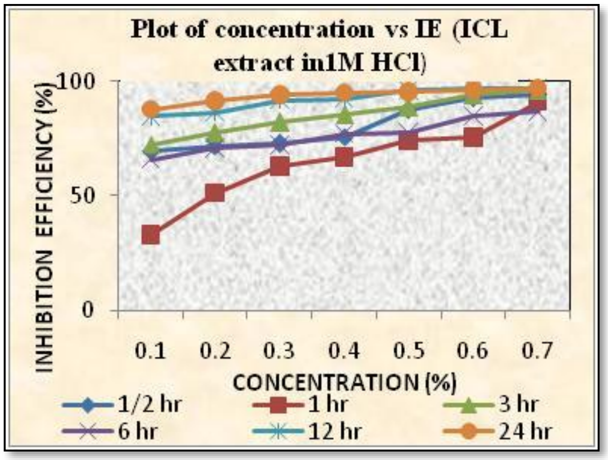


Figure 4.2

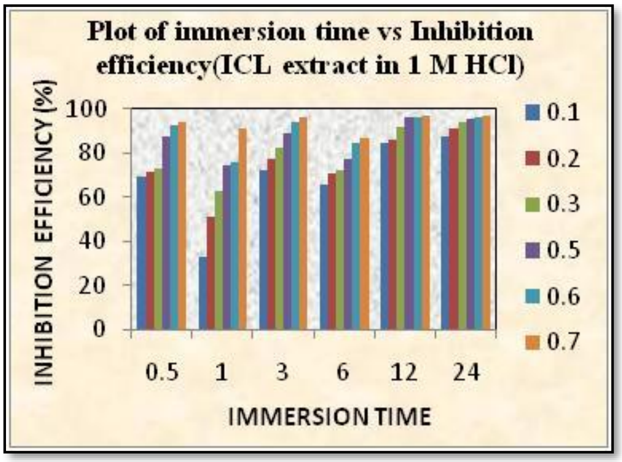


Figure 4.3

TABLE 4.2: Role of concentration and immersion time of ICL extract on MS in 1M HCl

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	844	-	332	-	864	-	253	-	532	-	379	-
2.	0.1	255	69.6	221	33	237	72.5	86	65.8	81	84.7	46	87.7
3.	0.2	243	71.7	162	51.2	196	77.3	73	70.8	72	86.3	33	91.3
4.	0.3	230	72.7	123	62.8	154	82.1	70	72.2	44	91.6	23	93.9
5.	0.4	204	75.7	102	66.6	127	85.2	58	77.0	40	92.4	18	95.1
6.	0.5	102	87.8	85	74.3	98	88.7	56	77.5	20	96.1	18	95.1
7.	0.6	59	92.9	81	75.6	51	94.1	38	84.8	18	96.5	13	96.4
8.	0.7	34	93.9	29	91.0	34	96.1	33	86.8	17	96.7	11	**97.0**

4.2.3. ROLE OF TEMPERATURE

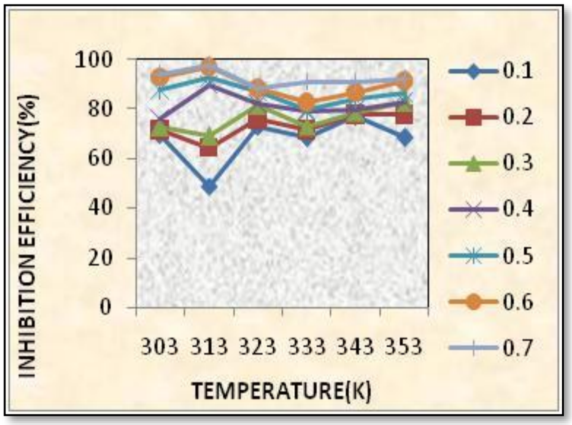
The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition (**Bentiss *et al.*, 2005**). It shows that an increase in temperature decreases the inhibition efficiency of the extract. But the corrosion rate will be easily increased at higher temperature. This can be explained on the fact that an increase in temperature usually assists corrosion processes, particularly in media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal.

The influence of temperature on ICL extract was tested in 1M HCl solution at different temperatures (303K- 353K). It has been found that the corrosion rate increased with the increase in temperature for the inhibitor. The corrosion rate of MS in the absence of inhibitor increased steeply from 303K-353K. But in the presence of inhibitor the corrosion rate increased slowly. The inhibition efficiency was found to increase upto 313K and then decrease . A maximum efficiency of 97.4% was obtained at 313K. After 313K a slight decrease in IE was noted . Inhibition efficiency was found to stabilize at 353K and a maximum efficiency of 92.3% was obtained.

The decrease in efficiency might be attributed to the desorption of the adsorbed inhibitor molecules from the surface of MS at elevated temperatures (Quraishi *et al*, 2010)

Table 4.3: Role of temperature on corrosion of MS in the presence of various concentration of ICL extract in 1M HCl

S .No	Conc (%)			Corrosion rate and inhibition efficiency									
		303K		313K		323K		333K		343K		353K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	844	-	2021	-	3997	-	5416	-	12401	-	33862	-
2.	0.1	255	69.6	1032	48.9	989	73.0	1705	68.5	2840	77.0	10721	68.3
3.	0.2	243	71.7	716	64.5	887	75.8	1535	71.6	2729	77.9	7565	77.6
4.	0.3	230	72.7	622	69.1	673	81.6	1458	73.0	2644	78.6	5885	82.6
5.	0.4	204	75.7	204	89.8	656	82.0	1134	79.0	2490	79.9	5697	83.1
6.	0.5	102	87.8	145	92.8	469	87.2	1100	79.6	1970	84.1	4546	86.5
7.	0.6	59	92.9	59	97.0	435	88.1	938	82.6	1629	86.8	2942	91.3
8.	0.7	34	93.9	51	**97.4**	417	88.6	477	91.1	1134	90.8	2601	92.3



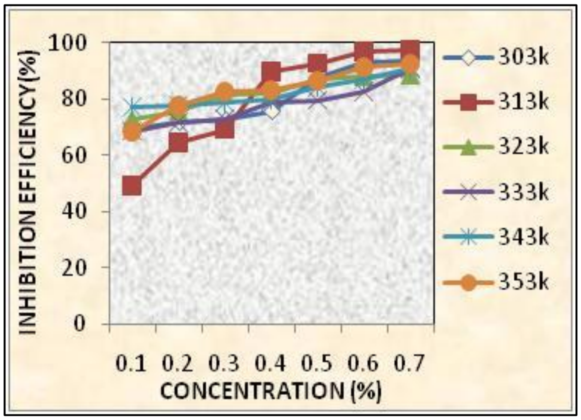


FIGURE 4.4

Variation of IE as a function of Temperature (ICL extract in 1M HCl)

FIGURE 4.5

Variation of IE as a function of concentration (ICL extract in 1M HCl)

4.3. MASS LOSS MEASUREMENTS OF *Ixora coccinea* LEAF EXTRACT IN 0.5M H_2SO_4

4.3.1EFFECT OF CONCENTRATION

Table 4.4 and **Figure 4.6** reflect the corrosion rate of MS and inhibition efficiency of ICL extract on the MS sample with various concentrations of the extract in 0.5M H_2SO_4 acid. The corrosion rate was found to decrease with the increase in concentration of the inhibitor for all the periods of immersion. The inhibitor efficiency was found to increase with concentration, at all the periods of exposure.

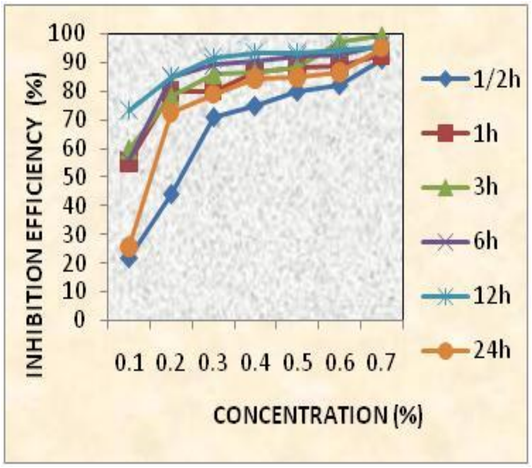
A maximum of 91 % inhibition efficiency was noted with 0.7% concentration of the inhibitor. The increase in IE with concentration may be explained due to the increase in the surface area of the adsorbed molecules of the inhibitor on MS surface.

4.3.2. EFFECT OF IMMERSION TIME ON CORROSION INHIBITION

The influence of duration of immersion on the IE of MS system is given in **Table 4.4**. From the table, it may be noticed that as the immersion period increased the inhibition efficiency decreased and the corrosion rate increased. This indicated that the protective film formed on the metal surface, was broken by the corrosive environment and the film was dissolved. But in this mass loss study, results revealed that IE increased in immersion time till 3 h **(Table 4.4, Figure 4.7)**. At 3h, the efficiency was maximum 99.6% and then decreased to 95.1% at 24 h. The best performance of the ICL extract was perceived at 3 and 6 h of immersion period with the entire concentration of the inhibitor.

Table 4.4: Role of concentration of ICL extract on MS 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	1142	-	1345	-	1390	-	1806	-	2137	-	1134	-
2.	0.1	895	21.6	605	55.2	562	59.5	796	55.8	568	73.3	842	25.7
3.	0.2	639	44.0	272	79.8	301	78.3	272	84.9	324	84.8	312	72.4
4.	0.3	332	70.8	268	80.1	196	85.8	191	89.3	177	91.6	239	78.9
5.	0.4	290	74.6	183	86.4	183	86.8	174	90.3	146	93.1	179	84.1
6.	0.5	230	79.8	157	88.3	164	88.1	145	91.9	142	93.3	172	84.7
7.	0.6	204	82.0	153	88.6	41	97.0	135	92.5	124	94.1	152	86.5
8.	0.7	102	91.0	102	92.4	4	**99.6**	73	95.9	96	95.4	55	95.1



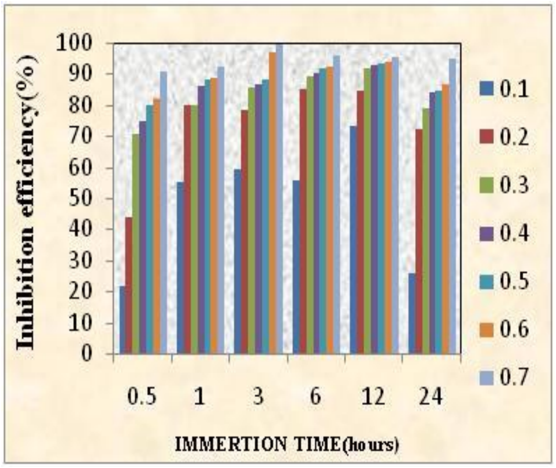


FIGURE 4.6

Plot of concentration Vs inhibition efficiency(ICL extract 0.5 M H_2SO_4)

FIGURE 4.7

Plot of immersion time Vs inhibition efficiency (ICL extract in 0.5M H_2SO_4)

4.3.3. ROLE OF TEMPERATURE

Temperature can influence the interaction of mild steel with acid in the absence and presence of the extract. The effect of temperature on the inhibition of corrosion of mild steel in 0.5M H_2SO_4 by ICL extract are listed in **Table 4.5** and depicted in **Figures 4.8, 4.9.** From the results, it can be seen that the Inhibition efficiency decreased with increase in temperature for all the investigated temperatures. A maximum IE of 95.8 % was obtained for 313K at 0.7 % ICL concentration. However the IE stabilized at 353 K to yield an efficiency of 69.2% This decrease in IE was noted due to desorption of the adsorbed inhibitor molecules from the surface of MS. (Umoren *et al*, 2011)

TABLE 4.5: Role of temperature of ICL extract on MS in 0.5 M H_2SO_4 medium

S. No	Conc (%)	Corrosion rate and inhibition efficiency											
		303K		313K		323K		333K		343K		353K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	blank	1142	-	5143	-	12273	-	20249	-	29742	-	48754	-
2.	0.1	895	21.6	895	82.5	3010	75.4	10346	48.9	18568	37.5	38118	21.8
3.	0.2	639	44	665	87.0	2848	76.7	5783	71.4	13186	55.6	30561	37.3
4.	0.3	332	70.8	520	89.8	1740	85.8	3437	83.0	10056	66.1	27439	43.7
5.	0.4	290	74.6	503	90.2	1458	88.1	3027	85.0	6311	78.7	23012	52.7
6.	0.5	230	79.8	290	94.3	1407	88.5	2550	87.4	4981	83.2	19302	60.4
7.	0.6	204	82	238	95.3	1134	90.7	2302	88.6	4930	83.4	19285	60.4
8.	0.7	102	91	213	**95.8**	622	94.9	2081	89.7	4034	86.4	15003	69.2

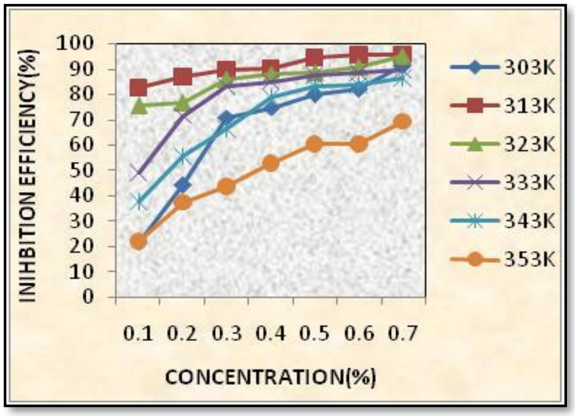


FIGURE 4.8

Variation of IE as a function of Conc. (ICL extract on 0.5M H_2SO_4)

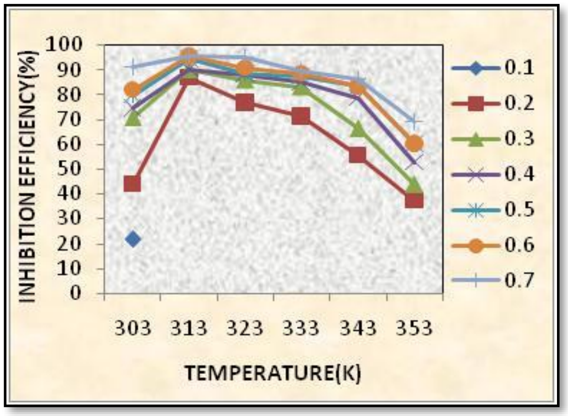


FIGURE 4.9

Variation of IE as a function of temp. (ICL extract on 0.5M H_2SO_4)

4.4. ADSORPTION ISOTHERMS

Adsorption isotherms are very important in understanding the mechanism of organo electrochemical reactions. Adsorption isotherms were employed in this study to investigate which of two main types of interaction - chemisorption (or) physisorption describes the interaction between the mild steel and ICL extract molecules. Basic information on the interaction between the inhibitor and the MS surface can be provided by the adsorption isotherm.

The establishment of isotherms that describe the adsorptive behavior of a corrosion inhibitor is an important part of its study, as they can provide important clues to the nature of the metal- inhibitor interaction.

In order to obtain the isotherm, the surface coverage values (θ) (θ=% IE/100) were evaluated by using the %IE values obtained from mass loss studies. The θ values increased with increasing inhibitor concentration as a result of more inhibitor molecules adsorption on the metal surface. The inhibitor best fitted with Langmuir isotherm. This isotherm assumed that the adsorbed molecules occupied only on the one site and there was no interaction with other molecules adsorbed.

Under these circumstances the proportionality between (θ) and concentration (c) of the adsorbing inhibitor may be given as follows,

$$\mathbf{KC = \theta/1-\theta}$$

(Or)

$$\mathbf{C/\theta = C_{inhibitor} + 1/K_{adsorption}} \longrightarrow \mathbf{(4.1)}$$

Where, $\mathbf{K_{adsorption}}$ is the equilibrium constant of the inhibitor adsorption process

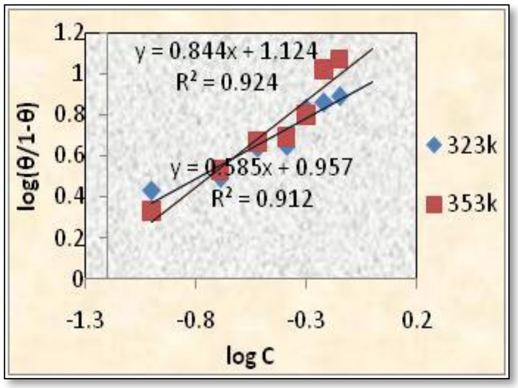
$\mathbf{C_{inhibitor}}$ is the inhibitor concentration

$\boldsymbol{\theta}$ is the fraction of metal surface covered with the inhibitor as a result of adsorption.

4.4.1. LANGMUIR ADSORPTION ISOTHERM

Linear plots of **log θ/1-θ** against the **log C** were obtained with the slope in the range of which is close to unity (**Figure 4.10, 4.11)**. These results suggest that the inhibitor occupies the adsorption sites on the metal surface.

Besides, the results show that all the linear correlation coefficients ($\mathbf{R^2}$) were almost equal to **unity**. Thus the adsorption phenomenon of inhibitors into the mild steel surface obeyed the Langmuir isotherm. It further confirmed the validity of Langmuir adsorption isotherm.



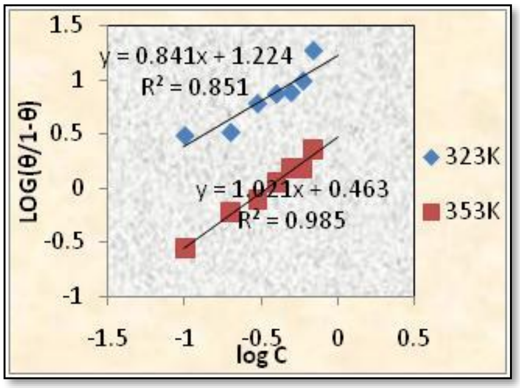


Figure 4.10

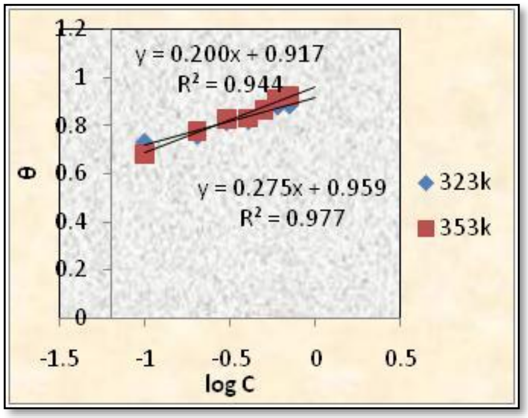
Langmuir adsorption isotherm for MS/HCl/ICL extract

Figure 4.11

Langmuir adsorption isotherm for $MS/H_2SO_4/ICL$ extract

4.4.2. TEMKIN ADSORPTION ISOTHERM

A straight line was obtained on plotting **θ** against **log C,** suggesting that the adsorption of the compound on the MS followed Temkin adsorption isotherm model. The best fit was estimated with the Temkin isotherm. **Figure 4.12, 4.13** gave **θ** values as a function of **log C** obtained for MS immersed in 1M HCl and 0.5 M H_2SO_4 presence and absence of various concentration of ICL extract. A straight line with a relatively high co-efficient constant (**R^2**) was obtained. This indicated that the adsorption of ICL extract molecules on MS surface obeyed temkin isotherm.



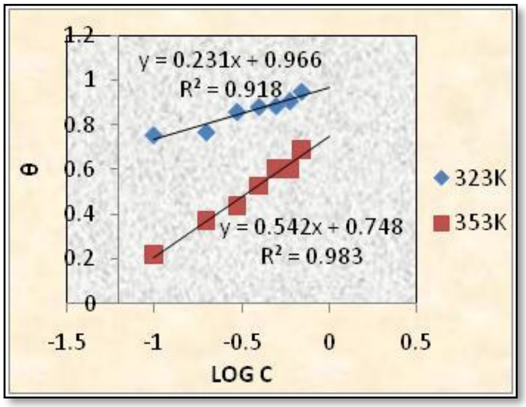


FIGURE 4.12

Temkin adsorption isotherm for -MS/ HCl /ICL extract

FIGURE 4.13

Temkin adsorption isotherm for $-MS/H_2SO_4/ICL$ extract

4.4.3. STATISTICAL ANALYSIS OF ADSORPTION ISOTHERM

Comparing the linearity of Langmuir and temkin adsorption isotherm, the correlation co-efficient values were calculated. The correlation obtained for the fitness of the data to adsorption models were furnished in the **Table 4.6.** From these findings, it can be inferred that ICL was adsorbed on MS surface obeying Langmuir and temkin isotherms. This confirms that adsorption behavior of the inhbitor is strongly influenced by temperature. The correlation values are significant at 1% level. Hence Langmuir and temkin adsorption isotherm were both appreciable at all temperatures in the presence of investigated inhibitor in both acid media.

TABLE 4.6: Values of correlation obtained for Langmuir and temkin adsorption isotherm

Temperature (K)	**Correlation Values (R^2)**			
	1M HCl Extract		**0.5 M H_2SO_4 Extract**	
	Langmuir	**Temkin**	**Langmuir**	**Temkin**
303	0.702	0.759	0.970	0.966
313	0.896	0.952	0.911	0.971
323	0.923	0.949	0.851	0.918
333	0.702	0.818	0.970	0.917
343	0.668	0.730	0.983	0.980
353	0.926	0.977	0.985	0.983

4.4.4. ACTIVATION ENERGY

The activation energy (E_a) of the corrosion process was calculated using the Arrhenius equation (**Putilova *et al.*, 1960**).

$$\mathbf{LOG\ CR = -Ea/2.303\ RT+CONSTANT} \longrightarrow \mathbf{(4.2)}$$

Where,

CR= Corrosion rate
Ea=Activation energy
T= Temperature

The value of apparent activation energy (Ea) for the corrosion process were calculated from Arrhenius plot of **log CR vs 1/T** in the absence and presence of inhibitor as shown in **Figure 4.14, 4.15**. The values of E_a obtained from the slopes of these straight lines were recorded in **Table 4.7**. The values of E_a were higher for inhibited solutions indicating physical adsorption of the inhibitor on the metal surface. This was also observed and discussed by **Sitashree Banerjee *et al*.,(2012).**

It is well known that stabilization of the surface film formed due to the treatment with inhibitors on MS surface cause corrosion inhibition. The effect of chemically stable surface active inhibitors increases the Ea of iron dissolution reaction and to diminution of surface available for corrosion.

Analysis of temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of inhibitors gave some insight into the possible mechanism of inhibitor adsorption.

A decrease in IE % with rise in temperature with analogues increase in Ea in presence of inhibitor compared to its absence is frequently interpreted as being suggestive of formation of an adsorption film of physical electrostatic nature. The reverse effect, corresponding to an increase in IE % with rise in temperature and lower Ea in presence of inhibitor suggests a chemisorption mechanism. From the foregoing, the trend for crude ICL extract adsorption onto the MS surface in 1M HCl suggest physisorption.

4.4.5. Activation parameters of MS in the presence of ICL extract in acid medium

The values of standard enthalpy of activation (ΔHa) and standard entropy of activation (ΔSa) were calculated using the following equation.

$$\mathbf{CR=RT/Nh\ exp\ (\Delta Sa/R)\ exp\ (\Delta Ha/R)} \longrightarrow \mathbf{(4.3)}$$

Where,

h is a plank’s constant

N is Avagadro number

ΔSa is entropy of activation

ΔHa is enthalpy of activation

The plot of log CR/T against 1/T yielded straight line **figure 4.16, 4.17** with a slope of (-ΔHa/2.303R) and an intercept of (log (R/Nh) + (ΔSa/2.303R)).The values thus obtained are recorded are in **Table 4.7**.

Enthalpy of activation

The values of Ea & ΔHa were close to each other as expected from the concept of transition state theory and vary in the same manner on the addition of different concentrations of inhibitor. So all values were of endothermic nature due to iron dissolution. The positive sign of ΔHa may be contributed to the endothermic nature of the MS dissolutions process.

Entropy of activation

The higher values of ΔSa for inhibited solutions may contribute to the increase in solvent entropy. The negative value of ΔSa for ICL in HCl indicated that activated complex in the rate determining step represented an association compared to dissociation step. That means, a decrease in disorderliness i.e. (entropy) takes place during the transition from reactants to the activated complex (**Saliyan & Adhikari, 2008**).

TABLE 4.7: Values of Ea, ΔHa and ΔSa of MS in various concentration of ICL extract in 1M HCl and 0.5M H_2SO_4 medium

S.No	**Conc V/V (%)**	**Activation energy -Ea kJ/mol**		**ΔHa kJ/mol**		**ΔSa J/mol**	
		HCl	**H_2SO_4**	**HCl**	**H_2SO_4**	**HCl**	**H_2SO_4**
1.	Blank	61.02	62.91	58.37	60.19	3.27	15.77
2.	0.1	56.36	73.29	53.45	70.57	-21.46	40.60
3.	0.2	54.79	73.08	52.19	70.38	-26.73	37.54
4.	0.3	53.61	79.69	51.08	76.99	-31.21	54.58
5.	0.4	62.26	75.99	59.37	73.29	-8.12	41.75
6.	0.5	69.86	78.77	74.06	76.07	30.84	48.26
7.	0.6	76.55	81.87	67.16	79.17	13.03	56.88
8.	0.7	78.92	88.23	76.32	85.53	35.05	73.54

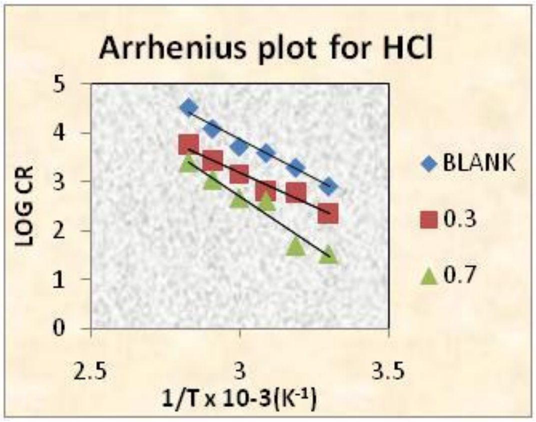


Figure 4.14

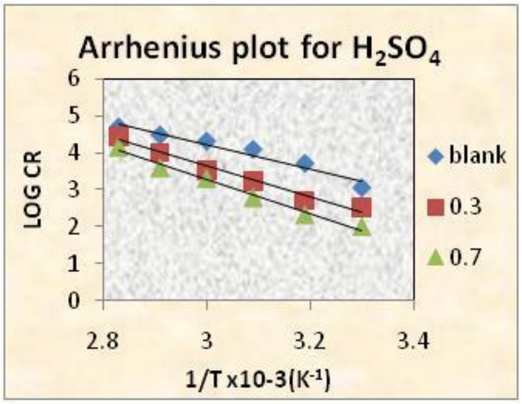


Figure 4.15

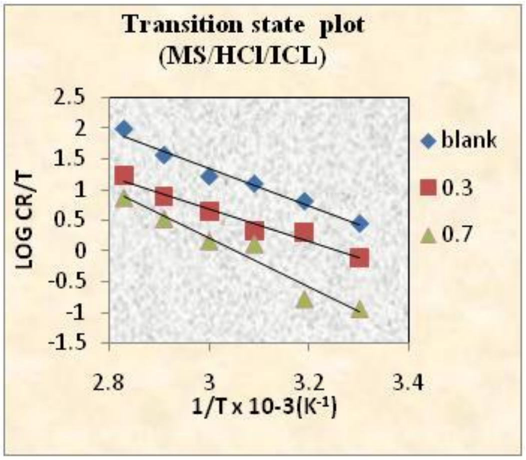


Figure 4.16

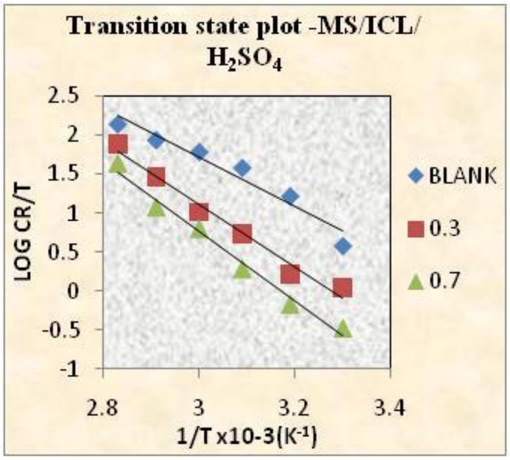


Figure 4.17

4.4.6. THERMODYNAMIC PARAMETERS

Thermodynamic parameters are useful tool to find out the strength of adsorption of the inhibitor on the electrode surface. In the current study, the values of thermodynamic parameters suggested that, in the system, there exists a favorable condition for adsorption of inhibitors on the metal surface.

The thermodynamic functions, free energy of adsorption, entropy and enthalpy of the present system can be calculated by using the standard equation

$$\log C = \log (\theta / 1 - \theta) - \log B \longrightarrow (4.4)$$

Where log **B**=-1.74-(-ΔG/2.303RT) and **C**=inhibitor concentration.

Results of temperature study helps in the calculation of thermodynamic parameters viz. change in free energy, entropy and enthalpy. The results of thermodynamic parameters studied in the present systems, were reported in **Table 4.8** and represented in **Figure**

4.18, 4.19. Analysis of the **Table 4.8** and **Figure 4.18, 4.19** infer that the ΔG_{ads} values ranges from -14KJ/ mol to – 21 KJ/mol from 303K to 353K. For all the systems studied in 1M HCl medium and 0.5 M H_2SO_4 the value of ΔG increased with increase in concentration and increases with increase in temperature. Thermodynamic parameters ΔH_{ads} and ΔS_{ads} could be arrived at, from the temperature studies and using a plot of -ΔG Vs T. The negative values of ΔH_{ads} also show that the adsorption of inhibitor is an exothermic process. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of a physisorption process lower than 40 kJ mol^{-1} while the adsorption heat of a chemisorption process approaches 100 kJ mol^{-1}. The adsorption of inhibitor molecules was accompanied by positive values of ΔS_{ads}.

TABLE 4.8: VALUES OF -ΔG, ΔH AND ΔS OF MS IN VARIOUS CONCENTRATION OF ICL EXTRACT IN 1M HCl AND 0.5M H_2SO_4 MEDIUM

S.NO	Concentration of inhibitor V/V(%)	Free energy of adsorption -ΔG (kJ/mol)						ΔS (J/mol)	ΔH (kJ/mol)
		303K	313K	323K	333K	343K	353K		
1M HCl									
1.	0.1	17.98	16.30	19.61	19.62	21.44	20.77	8.38	-8.21
2.	0.2	16.49	16.17	18.15	18.11	19.61	20.13	8.13	-8.57
3.	0.3	15.59	15.65	17.99	17.18	18.57	19.86	8.36	-9.96
4.	0.4	15.26	18.47	17.29	17.30	17.97	19.12	5.08	0.88
5.	0.5	16.81	18.88	17.77	16.78	18.15	19.24	2.56	9.52
6.	0.6	17.86	20.80	17.51	16.82	18.25	20.16	9.04	15.60
7.	0.7	17.88	20.78	17.22	18.52	18.97	20.09	1.98	12.40
0.5M H_2SO_4									
1.	0.1	12.64	20.45	19.95	17.34	16.53	14.77	1.07	-20.47
2.	0.2	13.54	19.56	18.28	18.08	16.65	14.96	5.21	-18.56
3.	0.3	15.35	19.22	18.82	18.81	16.76	14.55	3.26	-27.96
4.	0.4	15.11	18.59	18.59	18.43	17.76	14.76	1.25	-21.31
5.	0.5	15.30	19.53	18.10	18.37	17.96	15.03	1.64	-22.79
6.	0.6	15.20	19.59	18.25	18.18	17.48	14.49	2.82	-26.46
7.	0.7	16.82	19.49	19.57	18.07	17.71	15.18	4.29	-31.89

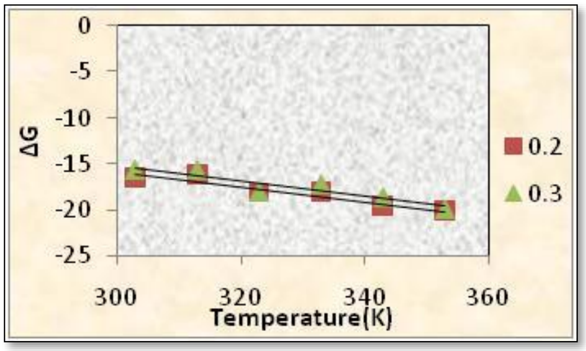


FIGURE 4.18

Plot of ΔG Vs Temperature for ICL extract in 1M HCl

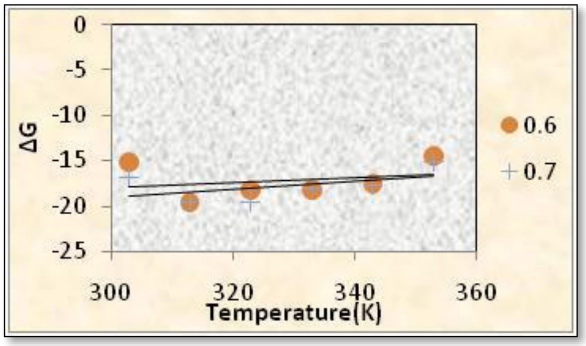


FIGURE 4.19

Plot of ΔG Vs Temperature for ICL extract in 0.5M H_2SO_4

4.5. ELECTROCHEMICAL MEASUREMENTS:

Electrochemical measurements were carried out using Biologic EC software version 10.23. Linear polarization measurements, Tafel intercept method and electrochemical impedance measurements were carried out for mild steel acid corrosion in the presence of ICL extract. Electrochemical studies predict the nature of inhibitor whether anodic, cathodic or mixed type and also predict a suitable mechanism for inhibition process. The values of corrosion kinetic parameters - corrosion current (E_{corr}), current density (I_{corr}), Tafel slope constants (b_a and b_c) , Linear polarization resistance (R_p) were recorded in **Table 4.9**.

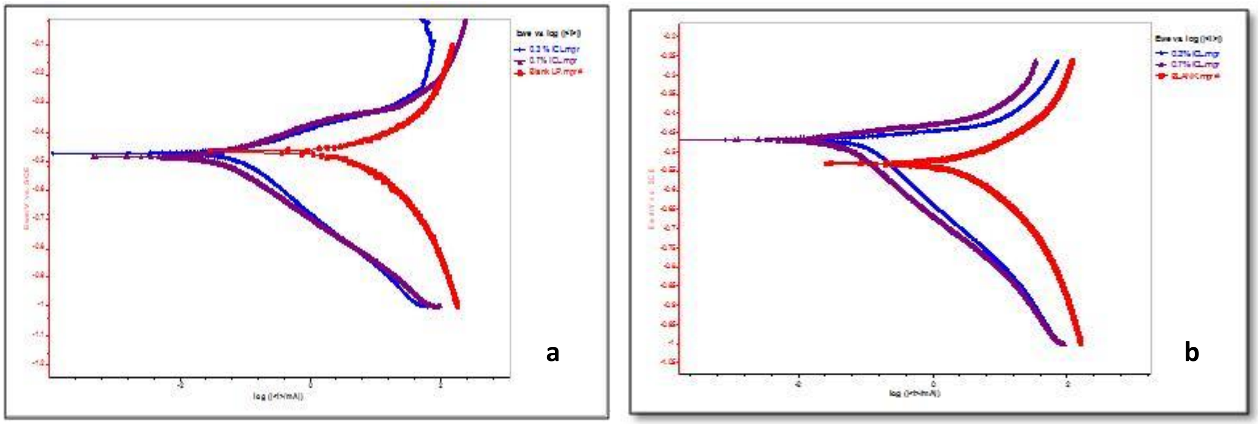


FIGURE 4.20: Potentiodynamic polarization plots for MS in a) 1M HCl b) 0.5M H_2SO_4 in the presence and absence of ICL extract

Table 4.9: Electrochemical polarization parameters for the corrosion of MS in the presence of ICL extract in 1M HCl / 0.5M H_2SO_4

S.NO	Conc v/v(%)	$-E_{corr}$ mV/SCE	I_{corr} μA/cm^2	b_a mV/dec	b_c mV/dec	IE (%)	R_p (Ω/cm^2)	IE (%)
1M HCl								
1	Blank	-479.7	530.7	93.8	150.5	-	55.4	-
2	0.3	-478.0	85.2	74.6	190.3	83.9	269	79.4
3	0.7	-456.7	28.3	52.9	153.6	94.6	491	88.7
0.5M H_2SO_4								
4	Blank	-557.7	4973.2	171.7	185.8	-	10.2	-
5	0.3	-632.0	1242.3	212.9	160.6	75.0	106	90.3
6	0.7	-625.1	512.0	187.5	148.3	89.7	311	96.7

From **Table 4.9**, it can be inferred that the values of corrosion current density I_{corr} decreased with increasing concentration of the inhibitor. Noticeable change was not observed in E_{corr} values. The values of Tafel slopes (b_a and b_c) changed with increasing concentration of the ICL extract. Potentiodynamic curves of mild steel in 1M HCl & 0.5M H_2SO_4in the presence of ICL extract was recorded and depicted in **Figure 4.20**. The potentiodynamic polarization parameters including corrosion current densities (i_{corr}), corrosion potential (E_{corr}) , cathodic Tafel slope (b_c), anodic Tafel slope (b_a), and IE% were presented in **Table 4.9**.

From the above experimental results the following conclusions were drawn.

- Values of b_a and b_c indicate, the extract acted mixed type by controlling the cathodic hydrogen evolution as well as anodic metallic dissolution.
- Polarization parameters for MS/1MHCl, 0.5M H_2SO_4/ICL reflected decrease in I_{corr} values with increase in concentration of extract. This revealed that the inhibition process was taking place by adsorption of the extract on mild steel. Inhibition efficiency calculated using I_{corr} and R_p indicate that inhibition efficiency increased with increase in concentration of the extract and maximum inhibition efficiency was found to be 94.6% for HCl & 89.7% for H_2SO_4 using I_{corr} values.
- Values of Ecorr indicated that the ICL extract behaved as a mixed type inhibitor. According to literature (**Quaraishi *et al.*,2010**) it was reported that if the shift in Ecorr

values with that of Ecorr of blank is < 85 mV the inhibitor may be called as mixed type inhibitor. In the current investigation as the shift is less than 85 mV in both 1M HCl & 0.5M H_2SO_4, the inhibitors can be said to act through mixed mode.

- The results reflect that the values of R_p increased with increase in concentration of the ICL extract for both 1M HCl and 0.5M H_2SO_4. This indicated that IE increased with increasing concentration of the inhibitors. A maximum efficiency of 88.7% (for HCl) & 96.7% (for H_2SO_4) was observed.
- In the case of H_2SO_4 medium, the corrosion current density (I_{corr}) of uninhibited 0.5M H_2SO_4 was higher than that of uninhibited 1M HCl. The polarization curves show that the higher current in H_2SO_4 was observed in the anodic branch, and not in the cathodic branch, so the effect was in the kinetics of anodic dissolution. The acid anions (Cl^-, SO_4^{2-}) were firstly adsorbed on the steel surface to form the surface complexes in the anodic process, and the complexes desorbed from the surface. **Table 4.9** show that (i_{corr}) decreased considerably in the presence of ICL extract. A maximum of 89.7% (for) IE was noticed at 0.7% concentration.

4.5.1. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Nyquist representation of the impedance with and without the addition of ICL is given in **Figure 4.21(a-c, d-f)**. The Nyquist plots were depressed semi circles with centers below the real axis. This indicated that the corrosion process was charge transfer controlled. The corrosion parameters obtained were presented in **Table 4.10**. The charge transfer resistance (R_{ct}) increased with inhibitor concentration. The inhibition efficiency was calculated using the relationship

$$\text{Inhibition Efficiency (\%)} \quad = \quad \left(\frac{1 - R_{ct}}{(R_{ct})_i} \right) x\,100$$

R_{ct} and $(R_{ct})_i$ are the charge transfer resistances without and with addition of ICL inhibitors.

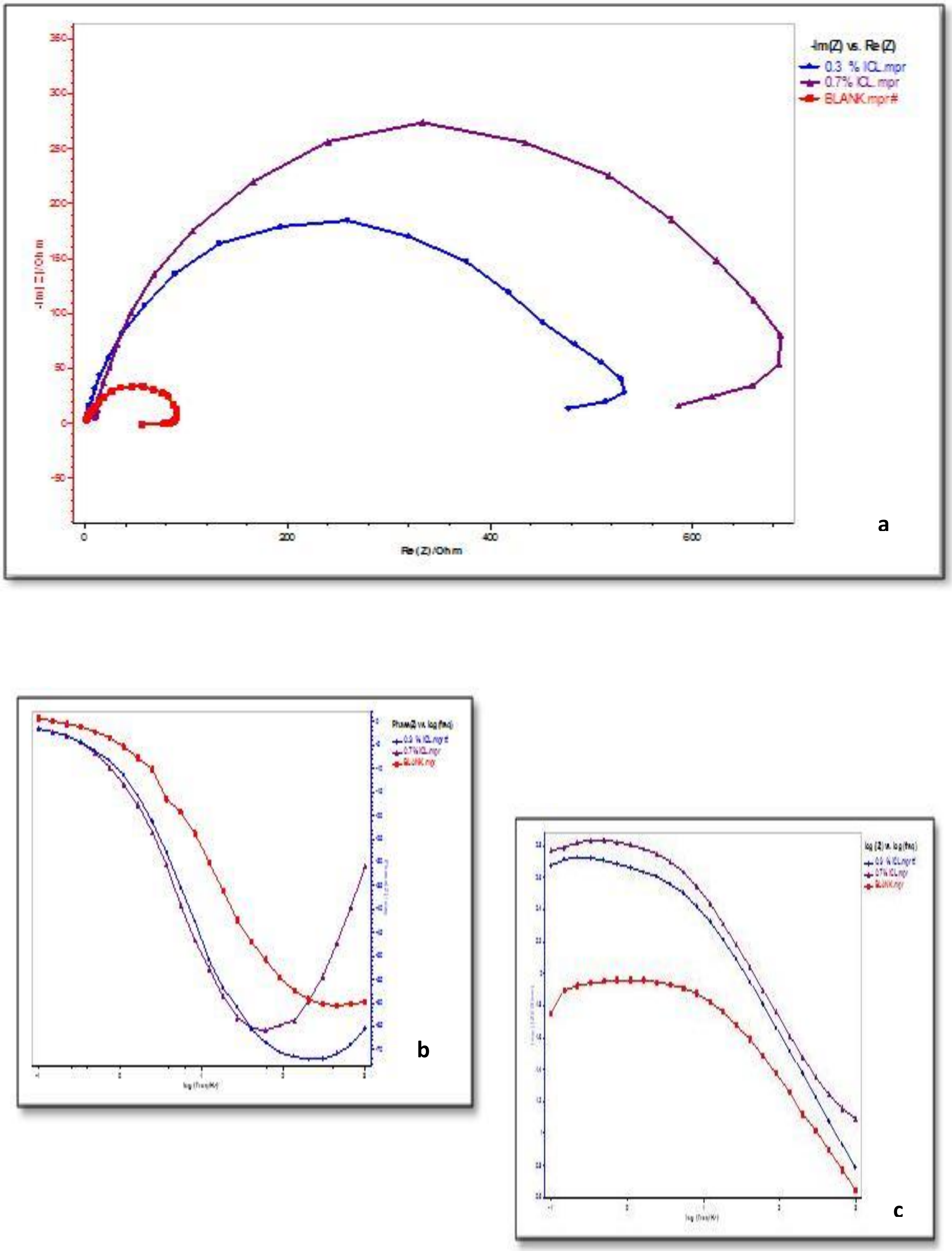


Figure 4.21 (a- c): Impedance plots in Nyquist and Bode format for MS in 1M HCl in the presence and absence of ICL extract

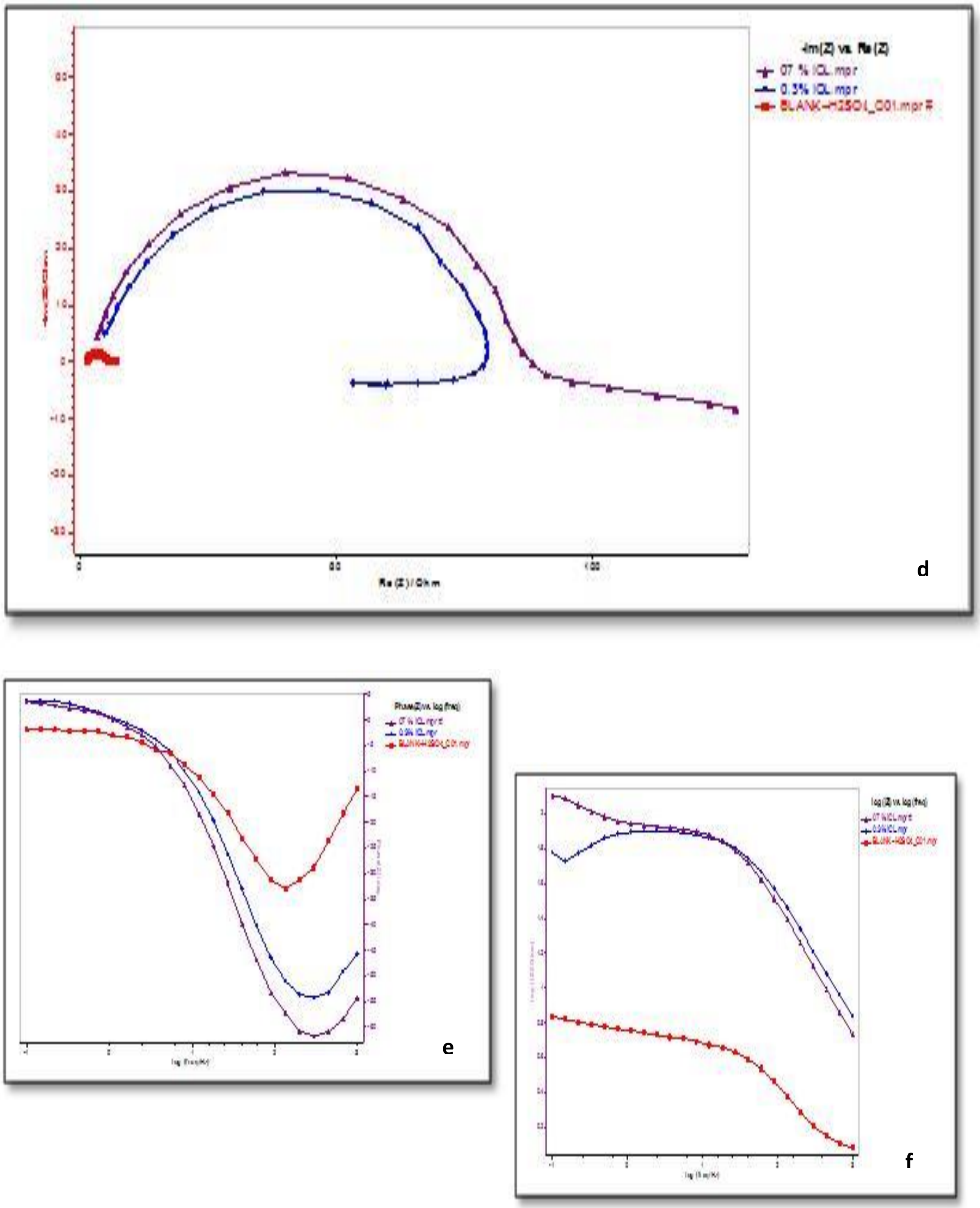


Figure 4.22. (d-f): Impedance plots in Nyquist and Bode format for MS in 0.5M H_2SO_4 in the presence and absence of ICL extract

Maximum inhibition efficiency using R_{ct} values was found to be 87.6% at 0.7%. concentration. The large charge transfer resistance could be due to a decrease in the active surface necessary for the corrosion reaction.**(M.Lebrini *et al.*, 2008).**

The recorded EIS spectrum of mild steel in 1M HCl and 0.5M H_2SO_4 solutions without and with 0.7% ICL extract showed one depressed capacitive loop at low frequencies. The high frequency semicircle was attributed to the time constant of charge-transfer and double-layer capacitance.

The low frequency inductive loop may be attributed to the relaxation process obtained by adsorption species such as Cl^-_{ads} and H^-_{ads}. As can be seen from the curves only one time constant was detected on the Bode plot for mild steel in 1M HCl and 0.5M H_2SO_4 solutions without and with 0.7% ICL extract .

The value of C_{dl} decreased with increase in inhibitor concentration thus the thickness of protective layer increased. This may be attributed to the decrease in local dielectric constant and an increase in the thickness of the electrical double layer suggesting that ICL inhibited 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. It can be found that the charge transfer resistance values increased and the capacitance value decreased with increasing inhibitor concentration.

Table 4.10: Rs , Rct, C_{dl} , & IE of MS in presence of ICL extract in 1M HCl / 0.5 M H_2SO_4

S.NO	**Conc(%)**	**Rs**	**Rct(Ω cm^2)**	**IE(%)**	**Cdl(F/cm^2)**	**ϴ**
1M HCl						
1	Blank	6.28	81.1	-	107	-
2	0.3	-3.29	526	84.5	55.15	0.4845
3	0.7	14.72	654.3	87.6	44.34	0.5856
0.5M H_2SO_4						
4	Blank	0.90	5.26	-	498	-
5	0.3	10.57	62.98	91.6	62.2	0.87
6	0.7	1.79	84.15	93.7	46.6	0.90

4.6. PERFORMANCE EVALUATION OF ICL EXTRACTS USING CONVENTIONAL MASS LOSS METHOD AND ELECTROCHEMICAL MEASUREMENTS

Performance evaluation of ICL extract using mass loss and electrochemical methods are pictorially represented in **Figure 4.23**. Inhibition efficiency values obtained from electrochemical studies for different concentration of extract under investigation do not show an absolute agreement with those obtained from mass loss measurements. These observations can be explained in the following ways.

The values of inhibition efficiency calculated from electrochemical measurements are lower than those obtained from mass loss data. Nevertheless, in general, the polarization data confirms the results of steel dissolution measurements. The difference in inhibition efficiency by different techniques can be attributed to the fact that mass loss method gives average corrosion rates, while electrochemical measurements gives instantaneous corrosion rate. The difference may be expected to arise because of the difference in time required to form an adsorbed layer, which brings down corrosion.

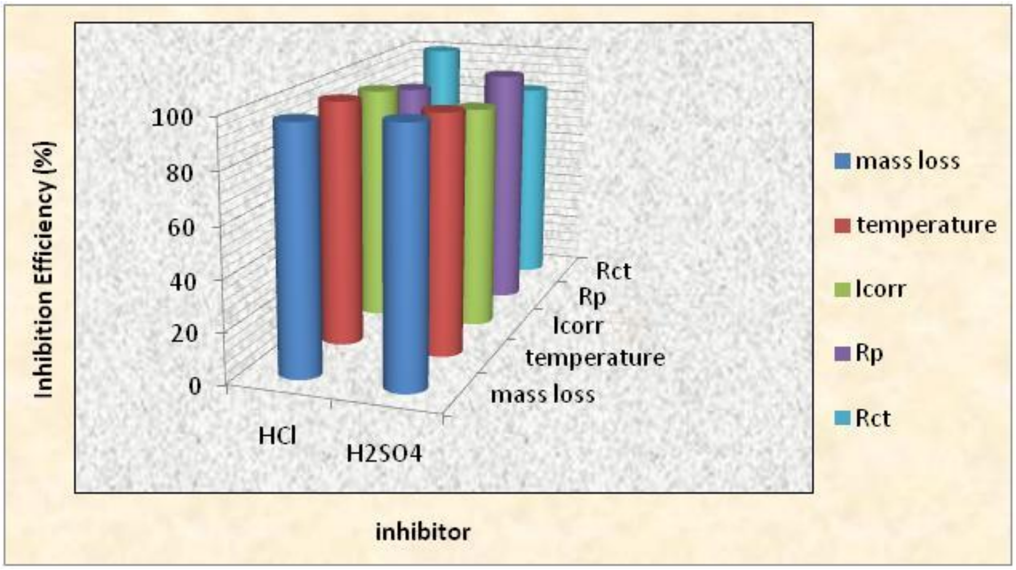


Figure 4.23.Performance evaluation of ICL extracts using conventional mass loss method and electrochemical measurements

4.7. SURFACE ANALYSIS

4.7.1 FT- IR SPECTRAL ANALYSIS

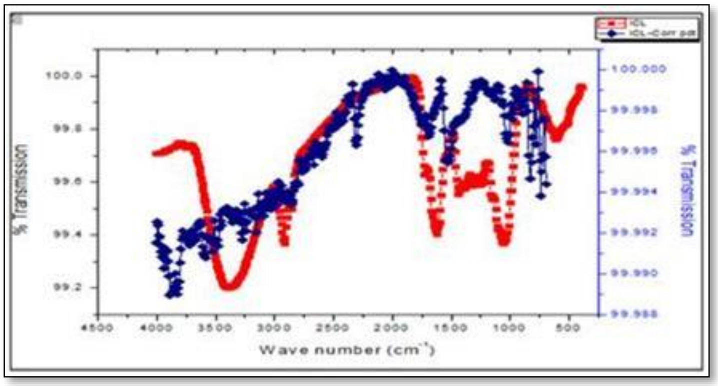


Figure 4.24. IR spectrums of ICL extract and corrosion products in 1M HCl

Table 4.11 IR spectrum of (a) acid extract of concentrates (b) adsorbed material of MS in the presence of HCl extract of ICL as an inhibitor

Powdered Plant material			**Corrosion product of**		
Frequency cm^{-1}	**Assignment**	**Functional Groups**	**Frequency** cm^{-1}	**Assignment**	**Functional Groups**
3394.72	OH stretch	Alcohol	3479.58	O–H stretch, H–bonded	1°, 2° amines, amides
2924.09	C–H stretch	Alkanes	2985.81	C–H stretch	Alkanes
-	-	-	-	-	-
2376.30	-C ≡ N stretch	Aliphatic amines	2306.86	–C ≡ N stretch	Aliphatic amine
1627.92	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers	1689.64	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers
1442.75	C–H bend	Aliphatic amines	1527.62	C-C in ring	Aromatics
1327.03	C–O-C stretch	Ethers	1427.32	C–H bend	Aliphatic amines
1249.87	C-O stretch	carboxylic acids	-	-	-
1064.71	C-O stretch	carboxylic acids	1018.41	C-O stretch	carboxylic acids
771.53	O–H bend	Alcohols	779.24	O–H bend	Alcohols
			740.67	- γ -Fe2O3	-

In the presence of the inhibitor, IR spectrum of the corrosion product **Figure 4.24** revealed that the –OH stretch (3394.72 cm^{-1}) shifted from 3479.58 cm^{-1}. From the spectra, it is observed that the C–H stretch of alkanes and C–C stretch (in–ring) of aromatics from the absorption bands at 2924.09 cm^{-1} and 2985.81 cm^{-1}. From the **Figure 4.24** 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 1627.92cm^{-1} and 1689.64cm^{-1}. From the crude plant extract to the corrosion product of ICL absorption shifts of –C ≡ N stretch (2376.30 cm^{-1} to 2306 cm^{-1}), C-H bend (1442.75 cm^{-1} to 1527.62cm^{-1}) and C-O stretch (1064.71cm^{-1} to 1018.41 cm^{-1}) were noticed. The shift in the absorption frequencies of the inhibitor on the metal surface strongly supported the interaction between the phytochemical compounds of the inhibitor and metal surface. The band at 450 $cm^{-1}$to 800 cm^{-1}probably originates mainly from γ - Fe_2O_3 (740.67cm^{-1}). Some missing bonds are there in corrosion products indicating the interaction (Fe-complex formation) between the leaves extract of and the surface of mild steel.

4.7.2. 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 ICL extract before and after the mild steel immersion are shown in **Figure 4.25**. The electronic absorption spectra of ICL before immersion have absorption maximum at 282, 389 and 342 nm which may be attributed to π- π* and n- π* transitions. After 3 hrs immersion of mild steel, the change in the position of absorption maximum or the change in the absorbance values to 284 and 318 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.

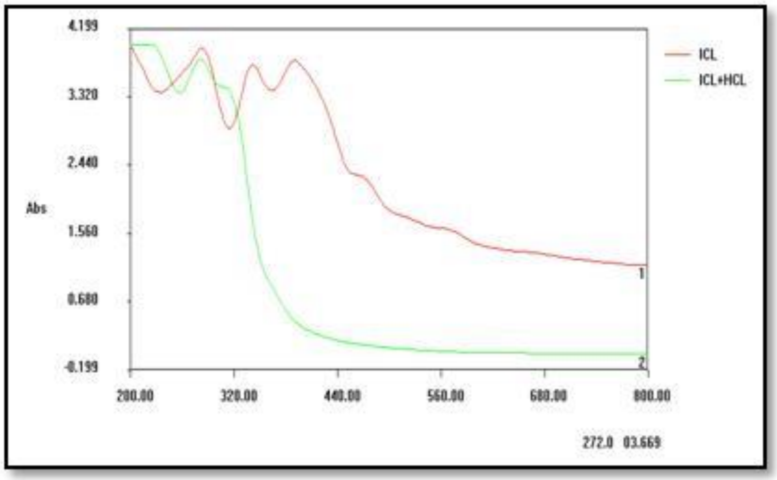


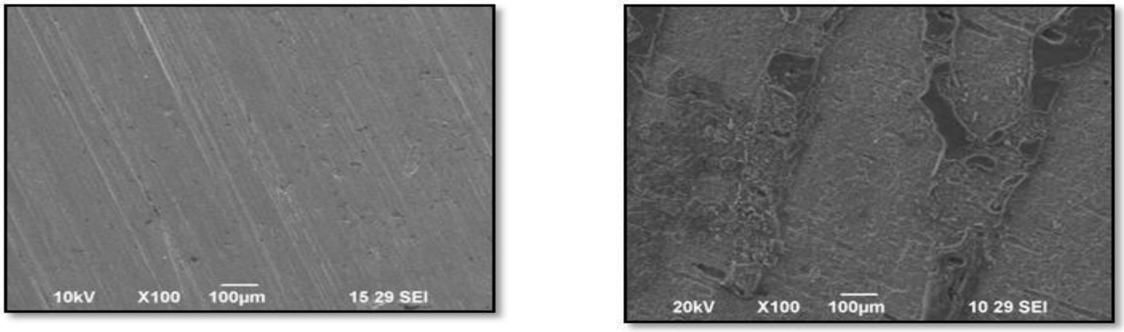
Figure 4.25 UV spectrum of ICL extract in 1M HCl

Table 4.12 UV visible spectral details of ICL extract and 1M HCl+0.7%ICL

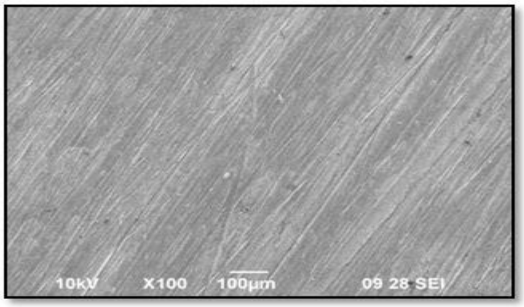
Inhibitor	Absorption bands (nm)	
	Crude plant extract	Mild steel+1M HCl+ inhibitor
ICL	342	318

4.7.3. SEM ANALYSIS

Surface morphology of MS was studied by scanning electron microscopy after 3h immersion in 1M HCl before and after addition of 0.7% ICL **Figure 4.26a** represent the micrograph obtained of polished MS without being exposed to the corrosive environment while **Figure 4.26b** showed strongly damaged MS surface due to the formation of corrosion produces after immersion in 1M HCl solution. SEM images of MS surface after immersion in 1M HCl solution are shown in **Figures 4.26b, 4.26c**. It could be seen that no pits and cracks were observed in the micrographs after immersion of MS in 1M HCl in the presence of 0.7% ICL except polishing lines (**Figure 4.26c).** Thus, it revealed the presence of a good protective film upon adsorption of inhibitor molecules onto the MS surface, which was responsible for the inhibition of corrosion.



a) Plain MS **b) MS in 1M HCl**



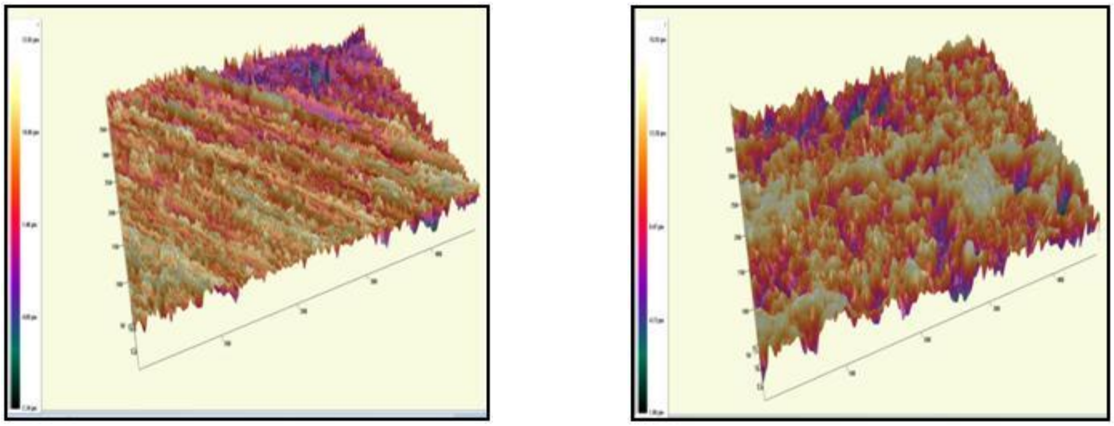
c) 1M HCl + 0.7% ICL

Figure 4.26: SEM images of a) plain MS b) MS in 1M HCl c) 1M HCl + 0.7% ICL

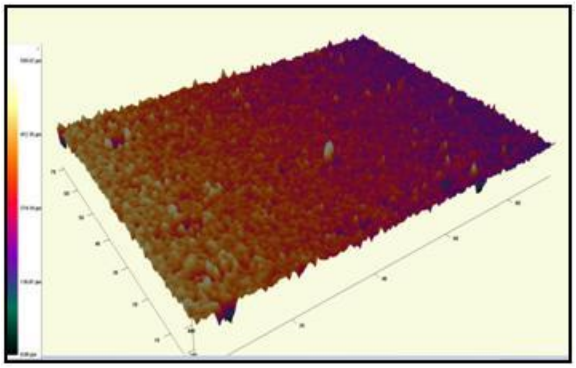
4.7.4. LASER PROFILOMETER

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. **Figure 4.27** displayed the three-dimensional image of mild steel surface immersed in 1M HCl solution without and with addition of 0.7% ICL for 3 h. **Table 4.13** gives the corresponding average roughness Ra and RMS roughness (Rq) values. From **Figure 4.27b**, 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 4.27b** that mild steel sample was badly damaged due to the acid attack on surface. By contrast, the corrosion morphology of mild steel in inhibited 1M HCl solution containing the inhibitor was smooth **Figure 4.27c**. The average roughness of the mild steel surface in uninhibited 1M HCl solution was about 17.28 µm and Rq is 22.35 µm as a result of the acid attack, while in the presence of ICL, Ra and Rq decreased to 8.48 and 12.14µm respectively. This indicated that the addition of the extract reduced the surface roughness. 3D Laser profilometer images and the roughness quantification were also consistent with SEM studies. This confirmed that the corrosion inhibition on mild steel occurs through adsorption of the extract on it.



Plain MS **MS in 1M HCl**



MS in 1M HCl + 0.7% ICL

Figure 4.27: Three-dimensional image of a) plain MS b) MS in 1M HCl c) MS IN 1M HCl + 0.7% ICL

Table 4.13: Ra and Rq values for MS/1M HCl /ICL

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% ICL	9.20	12.57

4.8. 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.*, 2012**). ICL 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 ICL molecules **(lupeol, ursolic acid, oleanolic acid, anthocyanin, quercitin, kaempferol, ixoratannin)** may adsorb through protonated heteroatoms (N, O, and S) and already adsorbed anions on the mild steel surface. Initially the protonated forms of ICL 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 ICL molecules and in turn strengthen their adsorption on the mild steel surface (**Olivares *et al.*, 2008**).

A schematic representation of the adsorption behavior of ICL extract on mild steel in acid solution shown in **Figure 4.28**. 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.*, 1982**). 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.

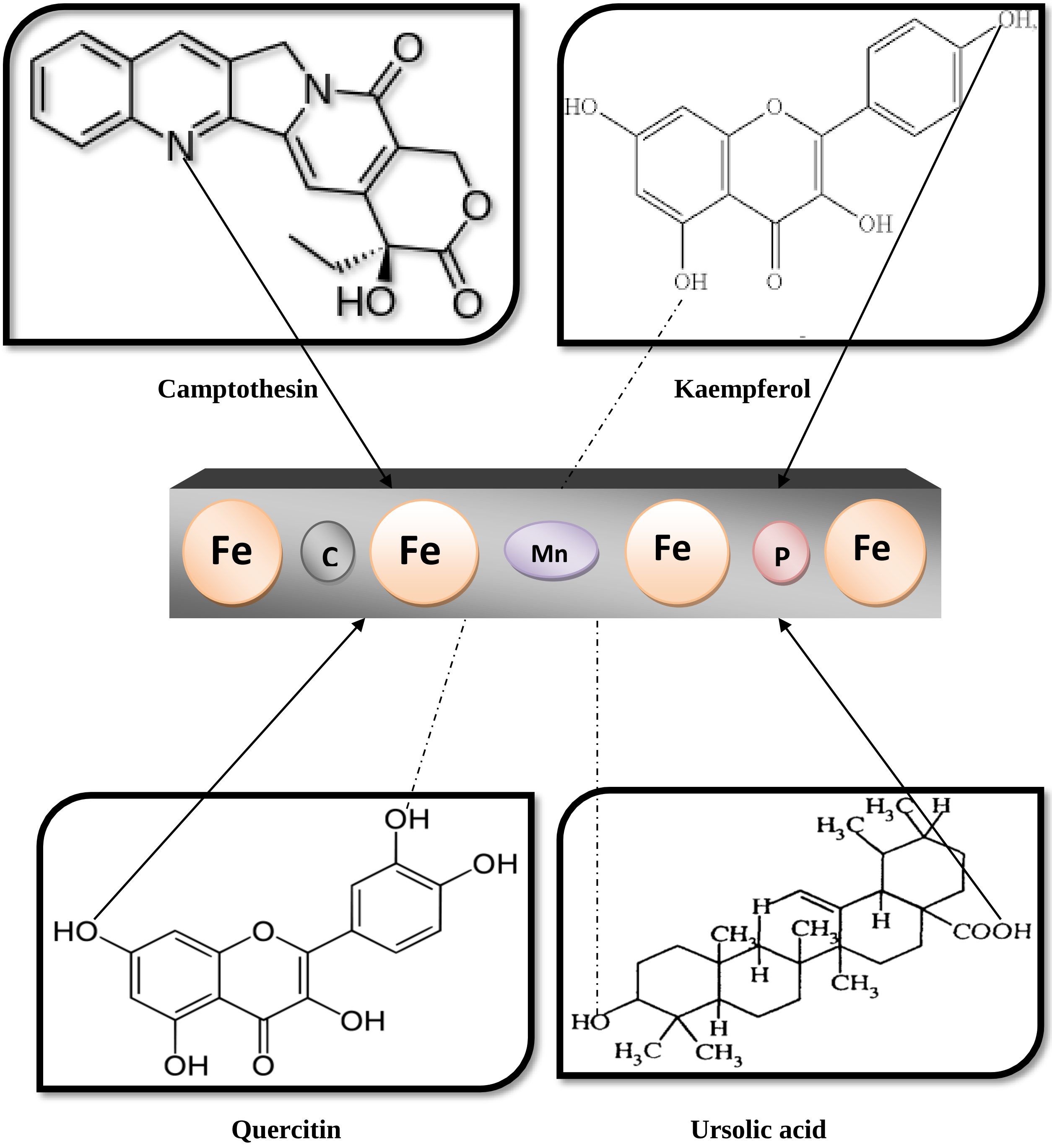


Figure 4.28 Adsorption of inhibitor molecules of ICL on the surface of MS

Summary and Conclusion

SUMMARY AND CONCLUSION

Corrosion inhibitors for acid cleaning process are used to restrict dissolution of the base metal and decrease acid consumption and hydrogen gas evolution. Because of the toxic nature and high cost of some chemicals currently in use, it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose.

Hence an evaluation of the effective performance of acid extract of ICL on the corrosion inhibition of mild steel in 1M HCl and 0.5 M H_2SO_4 at ambient temperature was made.

Conventional mass loss and electrochemical measurement techniques were used for the experimental purpose. Experiments were carried out by varying the concentration of the extract in different period of immersion and at different temperatures. Suitable adsorption isotherm was obtained. Thermodynamic and kinetic parameters were evaluated. Electrochemical measurements were made using Biologic EC software version 10.23. Results of the current investigation are summarized below.

- Inhibition efficiency increased with increase in concentration both at room temperature and at higher temperature in 1M HCl and 0.5M H_2SO_4 medium.
- Maximum inhibition efficiency of the ICL extract was found to be 97% and 99.6% for the concentration of 0.7 %.
- Optimum time of immersion for the ICL extract was found to be 24 h with 97 % efficiency in 1M HCl.
- A maximum of 95.1% efficiency in 0.5M H_2SO_4 was observed for ICL extract at 24 h of immersion.
- Inhibition efficiency was found to be increasing with increase in temperature up to 313 K for both acid medium.
- Experimental results fitted well into Langmuir and Temkin isotherm.
- Values of activation energy infer the strong adsorption of inhibitor molecules on mild steel surface.
- Thermodynamic parameters showed that the inhibition was spontaneous physical adsorption of inhibitors on mild steel surface.

- Polarization curves obtained in the presence of ICL extract indicate that it controls both anodic and cathodic reactions.
- Increase in R_p and R_{ct} values and decrease in I_{corr} and C_{dl} values confirm that the extract gets adsorbed on the mild steel surface and the inhibition process is followed by monolayer adsorption.
- A maximum inhibition efficiency of 94.6% for HCl & 89.7% for H_2SO_4 was obtained using I_{corr} values.
- A maximum IE of 88.7% (for HCl) & 96.7% (for H_2SO_4)for 0.7% ICL extract was noticed using Rp values.
- Inhibition efficiency obtained by mass loss method was found to be quite comparable with electrochemical measurements.

The present study on corrosion inhibition of mild steel in the presence of ICL extract could reduce the pollution problems and the inhibitor could act definitely as environmentally friendly corrosion inhibitor.

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