Inhibition Effect of *Croton sparciflorus* stem on corrosion of mild steel in 1M HCl and 0.5M H_2SO_4 medium

By

Maheshwari.S

13PCH008

A dissertation submitted to

Avinashilingam Institute for Home Science and Higher

Education for Women, University

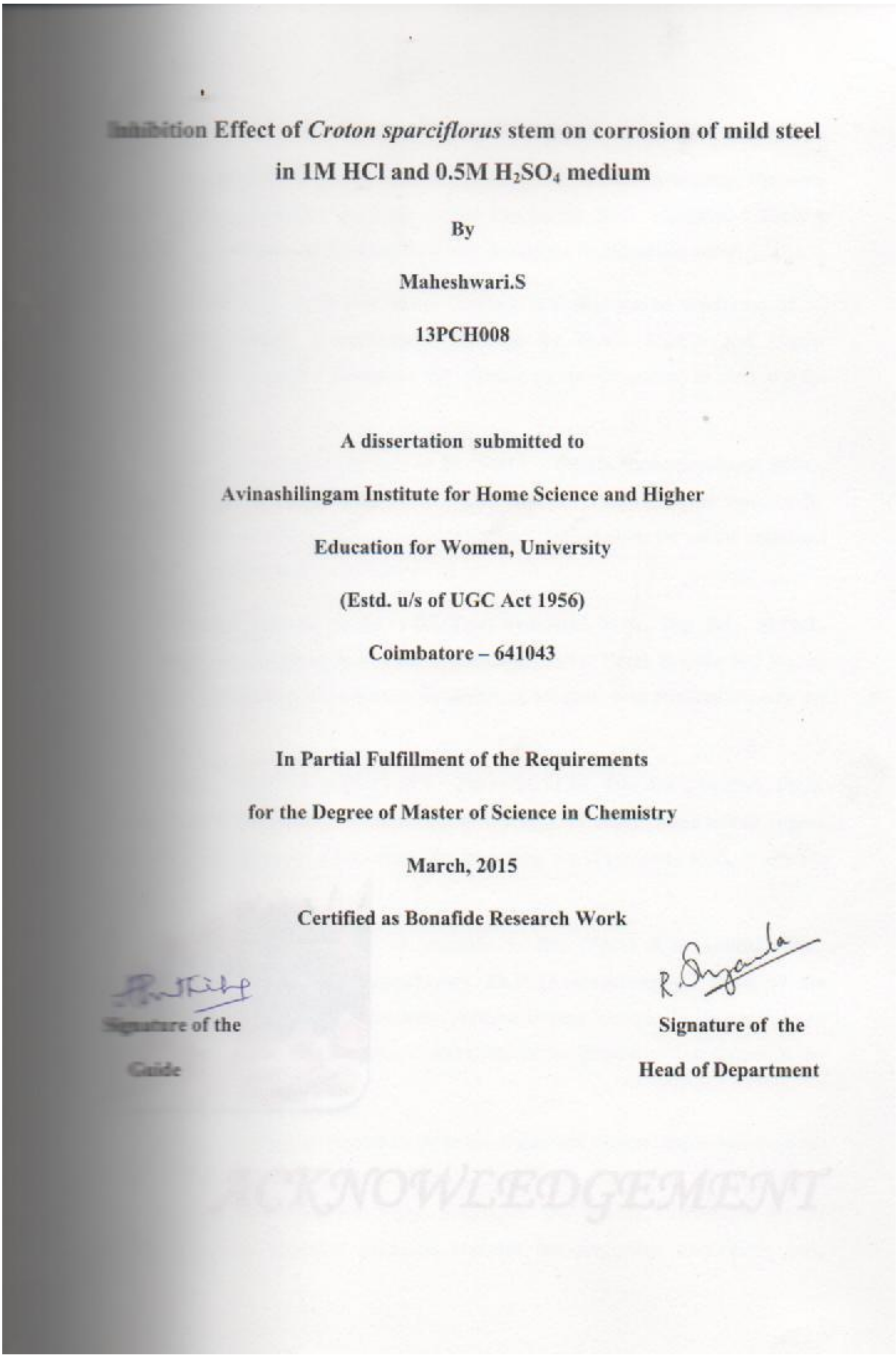
(Estd. u/s of UGC Act 1956)

Coimbatore – 641043

In Partial Fulfillment of the Requirements

for the Degree of Master of Science in Chemistry

March, 2015



Inhibition Effect of *Croton sparciflorus* stem on corrosion of mild steel in 1M HCl and 0.5M H_2SO_4 medium

By

Maheshwari.S

13PCH008

A dissertation submitted to

Avinashilingam Institute for Home Science and Higher
Education for Women, University
(Estd. u/s of UGC Act 1956)
Coimbatore – 641043

In Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemistry

March, 2015

Certified as Bonafide Research Work

Signature of the Guide	Signature of the Head of Department

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

Every work on its backdrop has the blessings of the **Lord Almighty**. Therefore submitting my reverential gratitude on the feet of the Lord Almighty, I deem it necessary to thank all who rendered their help during the course of this study.

I extend my heartfelt gratitude to **(Thiru.)T.S.K.Meenakshi Sundaram M.A., M.Phil., Chancellor**, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for offering an encouragement to carry out the study.

I express my sincere gratitude to **Dr.(Tmt.) Sheela Ramachandran, M.Sc., P.G.Dip., Ph.D(Avinashilingam), Vice –Chancellor**, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for all the amenities provided for the conduct of the study.

I extend my grateful thanks **to Dr.(Tmt) Venmathi, M.Sc., Dip .Ed ., M.Phil., Ph.D. Registrar (Incharge)**, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for rendering adequate help required to carry out the work.

I owe my gratitude to **Dr.(Tmt.) Parvathi, M.Sc., Dip .Ed ., M.Phil., Ph.D. Dean, Faculty of Science**, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for providing the opportunity to carry out the study.

I record my deep sense of gratitude to **Dr. (Tmt.) R.Shyamala M.Sc., Dip.Ed(Madras), M.Phil., (Bharathiyar), Ph.D.,(Avinashilingam), Head of the Department** ,Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for her inspiration and support in the completion of this work.

It is my privilege to express my heartfelt thanks and sincere appreciations to my **Guide (Mrs) A.Prithiba, M.Sc., M.phil., Assistant Professor,** Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, for her excellent support, inspiring guidance, constant encouragement ,meticulous care, valuable advice, timely suggestions and also co-operation for the successful completion of the study.

I extend my deep sense of gratitude to **Dr. (Tmt) R.Rajalakshmi, M.Sc., B.Ed.,(MaduraiKamaraj),M.Phil.,(Bharathiar),Ph.D.(Avinashilingam), Professor, Department of Chemistry**, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore, for her constant support and tremendous care rendered for carrying out of my thesis successfully.

My sincere and heartfelt thanks are due **to all the staff members** of chemistry department who rendered their help whenever required to complete this work.

My special thanks to my **beloved parents** for their help whenever required to complete this work.

I also thank **all my friends** for their continuous encouragement and support throughout the work.

Maheshwari.S

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

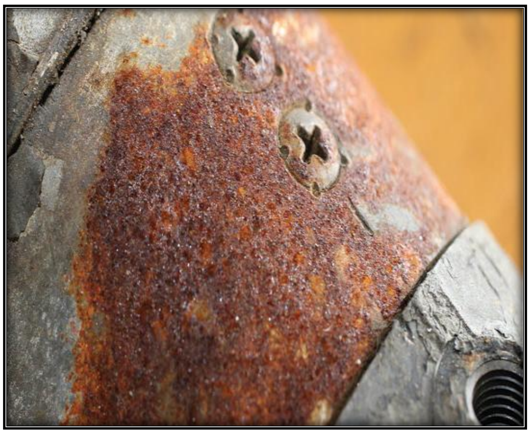
CS	*Croton sparciflorus*
CSS	*Croton sparciflorus* Stem
$\mathbf{H_2SO_4}$	Sulphuric acid
HCl	Hydrochloric acid
MS	Mild Steel
IE	Inhibitor Efficiency
CR	Corrosion Rate
Ppm	Parts per million
Mpy	Mils per year
$\boldsymbol{\Theta}$	Surface coverage
$\mathbf{I_{corr}}$	Corrosion current
$\mathbf{E_{corr}}$	Corrosion potential
$\mathbf{b_a}$	Anodic Tafel slope
$\mathbf{b_c}$	Cathodic Tafel slope
$\mathbf{C_{dl}}$	Double layer capacitance
$\mathbf{R_{ct}}$	Change transfer resistance
$\mathbf{R_p}$	Polarization resistance
mV	Milli Volt
LPR	Linear polarization resistance
EIS	Electrochemical Impedance Spectroscopy

INTRODUCTION

1. INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion.

Corrosion is a natural process. Just like water flows to the lowest level, all natural processes tend toward the lowest possible energy states. Thus, for example, iron and steel have a natural tendency to combine with other chemical elements to return to their lowest energy states. In order to return to lower energy states, iron and steel frequently combine with oxygen and water, both of which are present in most natural environments, to form hydrated iron oxides (rust), similar in chemical composition to the original iron ore.



Some definitions of corrosion are,

- Physicochemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part
- A chemical action that causes the gradual deterioration of the surface of a metal by oxidation or chemical reaction.
- The electrochemical degradation of metals/alloys or chemical degradation of materials (glass, concrete, etc.) due to a reaction with their environment; usually accelerated by the presence of acids or bases.

- A surface electrochemical phenomenon common to all base metals in aqueous or humid environments whereby metal ions are developed at an anodic site and the electrons associated with this dissolution accepted at a cathodic site.
- Degradation of the metal substrate by oxidation. That is the formation of an oxide layer on the metal surface. This process requires that the metal surface be exposed to oxygen, and is favored in the presence of water. In the case of iron and steel, corrosion is often referred to as rusting.

Degradation implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of cross-sectional area, it can be the shattering of a metal due to hydrogen Embrittlement, or it can be the cracking of a polymer due to sunlight exposure. Due to corrosion the useful properties of a metal such as malleability, ductility and electrical conductivity are lost. The most familiar example of corrosion is the rusting of iron when exposed to atmospheric conditions. During the process, a layer of oxide (Fe_3O_4) is formed and the iron becomes weak. It has been roughly assessed that the amount of iron wasted due to the corrosion is one fourth of world production. So it is better to control corrosion. Any process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted or unintentional chemical reaction starting at its surface is called corrosion. Thus, corrosion is a process, which is the exact reverse of extraction of metals (**Alm Otaibi *et al,* 2014**).

1.2 CONSEQUENCES OF CORROSION:

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small.

Some of the major harmful effects of corrosion can be summarized as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.

2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges,cars, aircraft).

3. Loss of time in availability of profile-making industrial equipment.

4. Reduced value of goods due to deterioration of appearance.

5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small Quantities of heavy metals are released by corrosion).

6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These couldinclude frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

8. Mechanical damage to valves, pumps, etc., or blockage of pipes by solid corrosion Products.

9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

1.3 CHEMISTRY OF CORROSION:

Common structural metals are obtained from their ores or naturally-occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states.

Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction.

Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a “mixed electrode” since simultaneous anodic and cathodic reactions are proceeding on its surface.

The mixed electrode is a complete electrochemical cell on one metal surface. The most common and important electrochemical reactions in the corrosion of iron are thus

Anodic Reaction (corrosion)

$Fe \longrightarrow Fe^{2+} + 2e$ (1)

Cathodic reaction (simplified)

$2H^+ + 2e^- \longrightarrow H_2$ (2a)

Or

$H_2O + ½ O2 + 2e \longrightarrow 2OH^-$(2b)

Reaction 2a is most common in acids and in the pH range 6.5 – 8.5, the most important reaction is oxygen reduction 2b. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$, Iron (II) hydroxide

Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish color due to partial oxidation in air.

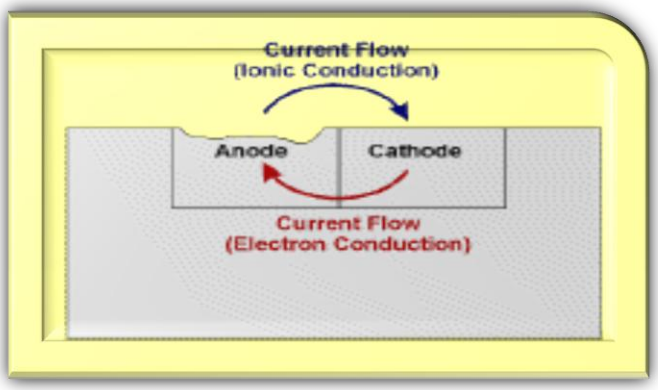
$2Fe(OH)_2 + H_2O + 1/2\ O_2 \longrightarrow 2Fe(OH)_3$, Hydrated iron(III) oxide

Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements which are present.

Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice which encourages further corrosion. For other metals or different environments different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film which retards further corrosion, the surface is then said to be “passive”.

An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidizing conditions or elevated temperatures.

$$2Fe + 3H_2O \longrightarrow Fe_2O_3 + 6H^+ + 6e$$



Schematic representation of current flow (conventional current direction in a simple corrosion cell.

1.4 FACTORS THAT CONTROL THE CORROSION RATE:

Certain factors can tend to accelerate the action of a corrosion cell.

These include:

(a) Establishment of well-defined locations on the surface for the anodic and cathodic reactions. This concentrates the damage on small areas where it may have more serious effects, this being described as "local cell action". Such effects can occur when metals of differing electrochemical properties are placed in contact, giving a "galvanic couple".

Galvanic effects may be predicted by means of a study of the Galvanic Series which is a list of metals and alloys placed in order of their potentials in the corrosive environment, such as sea water. Metals having a more positive (noble) potential will tend to extract electrons from a metal which is in a more negative (base) position in the series and hence accelerate its corrosion when in contact with it.

The Galvanic Series should not be confused with the Electrochemical Series, which lists the potentials only of pure metals in equilibrium with standard solutions of their ions.

Galvanic effects can occur on metallic surfaces which contain more than one phase, so that "local cells" are set up on the heterogeneous surface. Localized corrosion cells can also be set up on surfaces where the metal is in a varying condition of stress, where rust, dirt or crevices cause differential access of air, where temperature variations occur, or where fluid flow is not uniform.

(b) Stimulation of the anodic or cathodic reaction. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion. Sodium chloride is encountered in marine conditions and is spread on roads in winter for de-icing.

Quite small concentrations of sulphur dioxide released into the atmosphere by the combustion of fuels can dissolve in the invisibly thin surface film of moisture which is usually present on metallic surfaces when the relative humidity is over 60-70%. The acidic electrolyte that is formed under these conditions seems to be capable of stimulating both the anodic and the cathodic reactions.

In practical terms it is not usually possible to eliminate completely all corrosion damage to metals used for the construction of industrial plant. The rate at which attack is of prime importance is usually expressed in one of two ways:

(1) Weight loss per unit area per unit time, usually mdd (milligrams per square decimeter per day)

(2) A rate of penetration, i.e. the thickness of metal lost. This may be expressed in American units, mpy (mils per year, a mil being a thousandth of an inch) or in metric units, mmpy (millimetres per year).

1.5 TYPES OF CORROSION:

Corrosion comes in many different forms and can be classified by the cause of the chemical deterioration of a metal. Listed below are 10 common types of corrosion:

1.5.1 General Attack Corrosion:

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

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

1.5.2 **Localized Corrosion:**

Unlike general attack corrosion, localized corrosion specifically targets one area of the metal structure.

Localized corrosion is classified as one of three types:

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

The deterioration of this small area penetrates the metal and can lead to failure. This form of corrosion is often difficult to detect due to the fact that it is usually relatively small and may be covered and hidden by corrosion-produced compounds

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

iii)Filiform corrosion: Occurring under painted or plated surfaces when water breaches the coating, filiform corrosion begins at small defects in the coating and spreads to cause structural weakness.

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

Three conditions must exist for galvanic corrosion to occur:

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

1.5.4. Environmental Cracking:

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

- Stress Corrosion Cracking (SCC)
- Corrosion fatigue
- Hydrogen-induced cracking
- Liquid metal Embrittlement

1.5.5. Flow-Assisted Corrosion (FAC):

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

- Erosion-assisted corrosion
- Impingement
- Cavitation

1.5.6.Intergranular corrosion:

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

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

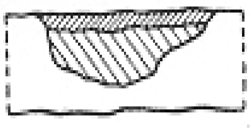
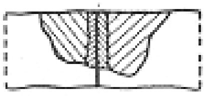
1.5.8.Fretting corrosion:

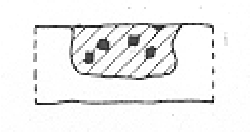
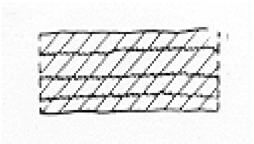
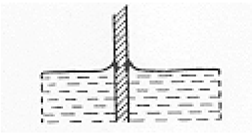
Fretting corrosion occurs as a result of repeated wearing, weight and/or vibration on an uneven, rough surface. Corrosion, resulting in pits and grooves, occurs on the surface. Fretting corrosion is often found in rotation and impact machinery, bolted assemblies and bearings, as well as to surfaces exposed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

1.5.9. High-Temperature Corrosion:

Fuels used in gas turbines, diesel engines and other machinery, which contain vanadium or sulfates can, during combustion, form compounds with a low melting point. These compounds are very corrosive towards metal alloys normally resistant to high temperatures and corrosion, including stainless steel. High temperature corrosion can also be caused by high temperature oxidization, sulfidation and carbonization

1.6.The various types of corrosion are listed in the following table:

 **Uniform corrosion** The reaction starts at the surface and proceeds uniformly.	 **Localized corrosion (pitting corrosion)** The basis metal is eaten away and perforated in places in the manner of holes, the rest of the surface being affected only slightly or not at all.	 **Wide pitting corrosion** The corrosion causes localized scarring.
 **Intergranular corrosion** Imperceptible or barely perceptible from outside, since the corrosion proceeds	 **Transgranular or intragranular corrosio** The grain boundary material is retained, since the corrosion proceeds preferentially within the	 **Galvanic corrosion** Increased corrosion in crevices or cracks or at contact surfaces

at the grain boundaries.	grain.	between two metal articles.
 **Selective corrosion** Corrosive attack on structural constituents	 **Exfoliation corrosion** Occurs in deformed articles. Corrosion follows "fiber orientation".	 **Interfacial corrosion** Frequently observed at water-air interfaces.

1.7.CORROSION PREVENTION:

By retarding either the anodic or cathodic reactions the rate of corrosion can be reduced. This can be achieved in several ways:

1.7.1 Conditioning the Metal

This can be sub-divided into two main groups:

(a) Coating the metal, in order to interpose a corrosion resistant coating between metal and environment. The coating may consist of:

(i) Another metal, e.g. zinc or tin coatings on steel,

(ii) A protective coating derived from the metal itself, e.g. Aluminium oxide on “Anodised” Aluminium,

(iii) Organic coatings, such as resins, plastics, paints, enamel, oils and greases.

The action of protective coatings is often more complex than simply providing a barrier between metal and environment. Paints may contain a corrosion inhibitor

(b) Alloying the metalto produce a more corrosion resistant alloy, e.g. stainless steel, in which ordinary steel is alloyed with chromium and nickel. Stainless steel is protected by an invisibly thin, naturally formed film of chromium sesquioxide Cr_2O_3.

1.7.2. Conditioning the Corrosive Environment

(a) Removal of Oxygen

By the removal of oxygen from water systems in the pH range 6.5-8.5 one of the components required for corrosion would be absent. The removal of oxygen could be achieved by the use of strong reducing agents e.g. sulphite.

However, for open evaporative cooling systems this approach to corrosion prevention is not practical since fresh oxygen from the atmosphere will have continual access.

(b) Corrosion Inhibitors

A corrosion inhibitor is a chemical additive, which, when added to a corrosive aqueous environment, reduces the rate of metal wastage. It can function in one of the following ways:

(i) Anodic inhibitors – as the name implies an anodic inhibitor interferes with the anodic process.

$$\mathbf{Fe \rightarrow Fe^{++} + 2e- \ (1)}$$

If an anodic inhibitor is not present at a concentration level sufficient to block off all the anodic sites, localised attack such as pitting corrosion can become a serious problem due to the oxidising nature of the inhibitor which raises the metal potential and encourages the anodic reaction (equation 1).

Anodic inhibitors are thus classified as “dangerous inhibitors”. Other examples of anodic inhibitors include orthophosphate, nitrite, ferricyanide and silicates.

(ii) Cathodic inhibitors – the major cathodic reaction in cooling systems is the reduction of oxygen.

$$\mathbf{½O2 + H_2O + 2e \rightarrow 2OH^- \ (2)b}$$

There are other cathodic reactions and additives that suppress these reactions called cathodic inhibitors. They function by reducing the available area for the cathodic reaction. This is often achieved by precipitating an insoluble species onto the cathodic sites. Zinc ions are used as cathodic inhibitors because of the precipitation of Zn(OH)2 at cathodic sites as a consequence of the localised high pH. (See reaction 2(b)). Cathodic inhibitors are classed as safe because they do not cause localised corrosion.

(iii) Adsorption type corrosion inhibitors– many organic inhibitors work by anadsorption mechanism. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of forming chemisorbed bonds with metal surfaces are amino ($-NH_2$), carboxyl

(-COOH), and Phosphonate (-PO_3H_2) although other functional groups or atoms can form co-ordinate bonds with metal surfaces.

(iv)Mixed inhibitors – because of the danger of pitting when using anodic inhibitors alone, it became common practice to incorporate a cathodic inhibitor into formulated performance was obtained by a combination of inhibitors than from the sum of the individual performances. This observation is generally referred to a ‘synergism’ and demonstrates the synergistic action which exists between zinc and chromate ions.

1.7.3. Electrochemical Control:

Since corrosion is an electrochemical process its progress may be studied by measuring the changes which occur in metal potential with time or with applied electrical currents.

Conversely, the rate of corrosion reactions may be controlled by passing anodic or cathodic currents into the metal.

Cathodic protection may be achieved by using a DC power supply (impressed current) or by obtaining electrons from the anodic dissolution of a metal low in the galvanic series such as aluminium, zinc or magnesium (sacrificial anodes). Similar protection is obtained when steel is coated with a layer of zinc. Even at scratches or cut edges where some bare metal is exposed the zinc is able to pass protective current through the thin layer of surface moisture.

In certain chemical environments it is sometimes possible to achieve anodic protection, passing a current which takes electrons out of the metal and raises its potential. Initially this stimulates anodic corrosion, but in favourable circumstances this will be followed by the formation of a protective oxidised passive surface film.

1.8 IMPORTANCE OF NATURAL PRODUCTS AS CORROSION INHIBITORS:

The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency. 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.

Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency. Natural products are used as corrosion inhibitors for various metal and alloys in aggressive media.

1.9 PLANT DESCRIPTION

Croton sparsiflorus (Family- Euphorbiaceae) is a small annual herb, growing mainly road side up to 1-2 ft tall. Alternately arranged leaves, 3-5 cm long, are lance-shaped, with toothed margin. Small white flowers are borne in 3-8 cm long racemes at the end of branches. Flowers have 5 sepal and 5 petals and numerous long stemens producing out. Fruit is 5mm oblong capsule with warty surface. The plant is well known under vernacular as "**Ban Tulasi**" The powdered leaves are useful in controlling high blood pressure and used for treatment of skin disease, cuts & wounds as well as antiseptic and antidote. It contains broad spectrum antibiotic compounds in leaves of this species. This plant main chemical constituents i.e. **Glycoside, Saponins, Tannins, Flavonides, Terpenoids and Alkaloids. (Sanjay Kumar Yadav , Sanjib Das ,2013)**

1.9.1 **Scientific classification**

Kingdom:Plantae

Order: Malpighiales

Family: Euphorbiaceae

Subfamily: Crotonoideae

Tribe: Crotonae

Genus: Croton

Species: sparsiflorus

The results indicate that the plant contains numbers of secondary metabolites and significant against traditional uses. The aqueous extract of *Croton sparsiflorus* possesses significant antidiarrheal activity due to its inhibitory effect both on gastrointestinal propulsion and fluid secretion. The inhibitory effect of the extract justified the use of the plant as a non-specific antidiarrheal agent in folk medicine.

1.10 Objectives:

- To select an eco-friendly, cost effective, naturally occurring plant material as corrosion inhibitor for mild steel in acid medium.
- To utilize of the naturally occurring plant extracts such as *Croton sparciflorus* in 1M HCl and 0.5M H_2SO_4.
- To carry out phytochemical screening for the investigated inhibitor- *Croton sparciflorus* stem extract.
- To evaluate the corrosion studies of mild steel in 1M HCl and 0.5M H_2SO_4 in the presence of *Croton sparciflorus* stem extract at room temperature and higher temperature using the classical mass loss method.
- To calculate the activation energy and thermodynamic parameters 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.
- To evolve a suitable mechanism for the adsorption process. To correlate the results obtained by mass loss and electrochemical techniques.

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

Mild steel is one of the most widely used steel all over the World 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 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.

This thesis seeks to investigate effective and environmentally safe inhibitors such as *Croton Sparsiflorus* on corrosion of mild steel in 1 M Hydrochloric acid and 0.5M H_2SO_4 medium. In this direction a review of natural product as corrosion inhibitor has been carried out.

2.1 Natural products as corrosion inhibitors for Mild Steel

- **Farooqi *et al.*,(1997)** reported the inhibitive effects of aqueous extracts of *Jasminum auriculatum*(leaves), *Monocardia charantia*(fruits) &*Hibiscus***(**flower) on the corrosion of mild steel for cooling water system, using 3% NaCl water. The inhibition efficiencies of the extracts were compared with that of HEDP. All the extracts were found to inhibit corrosion and their inhibition efficiencies were HEDP(93%), *Jasminumauriculatum*(80%),*Monocardicacharantia*(79%) and Hibiscus(76%).Polarization measurements shows that extract of jasmine was anodic while *Monocardia charantia* and Hibiscus were found to be cathodic.
- **Smita and Mehta *et al.*,(1998)** suggested that the acid extracts of *Calotropis giganta*latex inhibited the acid corrosion of mild steel effectively at 0.08% and the inhibition decreased with decrease in concentration. Electrochemical studies showed that inhibitor was mixed type and effective one.
- **Minhaj *et al.*,(1999)** investigated the inhibitive effects of aqueous extracts of *Eucalyptus*(leaves),*Hibiscus*(flowers),*Agarius*on the corrosion of mild steel for cooling systems using tap water by weight loss and polarization methods.The results showed that all the plant extract inhibit corrosion of mild steel and their

inhibitive efficiencies were in the order:Agaricus(85%) > Hibiscus > Eucalyptus(74%).

- The effect of *cashew juice* extract on corrosion inhibition of mild steel in HCl was investigated by **Loto and Mohammed *et al,*(2000).** Weight loss and potential measurement techniques were used. The extracts from bark provided no inhibition while nut-juice extract accelerated corrosion. Apple juice extracts at a concentration of 2ml/100ml of 0.1M HCl gave good results of corrosion inhibition.
- **Sethuraman *et al.,*(2001)** observed the effect of *Solanum trilobatum*extract on the corrosion of mild steel in 5% HCl by weight loss measurement. It was found that inhibition efficiency increased with increase in concentration.
- **Maheswari *et al.*, (2001)** investigated the inhibitive effect of acid extracts of flowers and leaves of *Thespesia populnea*on the corrosion of mild steel in 1M HCl. The mass loss method and potentiostatic studies revealed the effectiveness of the extract. An efficiency of 94.87% was found for 0.35% extract at 333K.
- **Manohari and Rajalakshmi *et al.*,(2001)** determined the effective performance of extracts of *Psidium gujava*(bark) and *Callistemon*(leaves) for mild steel in 1M HCl. The extracts were effective at high concentration and at room temperature. The polarization curves showed mixed type behaviour.
- **Rajalakshmi *et al.*, (2002)** investigated of the performance of acid extract of *Ficus banghalensis*bark on the corrosion inhibition of mild steel in 1M HCl and 0.5 M H_2SO_4 at room temperature. Mass loss, electrochemical polarization and impedence measurements were used. It was found that the inhibitor increased with increase in concentration of the extract.
- **Maheswari *et al.*,(2003)** observed the performance of *Cajanus cajan*seed extract on the corrosion inhibition of mild steel in 1M HCl. A maximum efficiency of 95.59% was observed at 0.7concentration at 65°C and the efficiency of 92.84% at 0.7 concentration of 5% extract.
- **Parikh & Joshik (2004)** utilized extracts ofMehndi‟(Henna;*Lawsonia inermis*) and Babul(*Acacia arabica*) for mild steel.Variable experimentalparameters like effect of inhibitor concentration,temperature, immersion period and stirring rate were studied, 1% inhibitor concentration in 5% HCl environment gave 83% and 85% inhibition efficiency respectively.

- The efficacy of *Telfaria occidentals*extract as a corrosion inhibitor for mild steel in 2M HCl and 1M H_2SO_4 solutions, and the effect of temperature and the halide additives on the inhibition efficiency were investigated by **Oguzie *et al* ., (2005)** . Corrosion rate was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. The inhibition efficiency increased with increase in concentration of inhibitor but decreased with an increase in temperature. Synergistic effects increased the efficiency of the extract in the presence of halide additives in the order KCl<KBr<KI. Protonated species in the extract composition played a vital role in the inhibiting action.
- The inhibitive effect of the extract of *khillah (Ammi visnaga)*seeds, on the corrosion of SX 316 steel in HCl solution was determined using weight loss measurements as well as potentiostatic technique. The inhibitive effect of khillah extract was discussed on the basis of adsorption of its components on the metal surface. Negative values of free energy of adsorption indicating the spontaneity of the adsorption process. Khillah extract was found to afford an efficiency of 99.3% at 300 ppm **(El-Etre *et al*.,(2005)**.
- **Yan Li *et al.*,(2005)** explained the inhibition efficiency of Berberine extracted from *Coptis chinensis* on corrosion of mild steel in 1M H_2SO_4 studied by Weight loss, electrochemical techniques,surface analysis in the presence of inhibitor was done by scanning electron microscope(SEM) with energy disperse spectrometer(EDS). The weight loss results showed that berberine is an excellent corrosion inhibitor for mild steel immersed in 1M H_2SO_4.
- **Sheyreese *et al.*,(2005)** analysed the effective environmentally safe inhibitors such as green tea.Green tea extracts contain significant amount of water soluble electrochemically active compounds as well as high concentration of alkaloids,fatty acids and N and O containing compounds. The studies were carried out by rapid and convenient zero resistance Ammeter(ZRA) technique. They inferred that both the leaf as well as plant wastes are excellent sources of corrosion inhibitors and can replace a wide variety of current toxic and polluting industrial inhibitors including tobacco.
- **Adbel-Gaber *et al.*,(2005)** observed that the effects of extracts of Chamomile (*Chamaemelum Mixtum.L),*Halfabar(*Cymbopogonproximus*), Black cumin (*Nigella sativa L*.), and kidney bean plants on the corrosion of steel in aqueous 1M H_2SO_4 using EIS and potentiodynamic polarization technique. Potentiodynamic

polarization curves indicated that the plant extract up to a critical concentration. The adsorption of the extracts inhibited corrosion obeyed Langmuir,Florry – Hugins,and the Kinetic Thermodynamic model,were tested to clarify the nature of adsorption.

- Corrosion inhibition of mild steel 2M HCl and 1M H_2SO_4 by leaf extracts of *Occimum viridus*was studied using gasometric technique at temperatures of 30°C and 60°C and EIS,weight loss.The results indicated that the extract inhibited the corrosion process in both acid media and the inhibition efficiency increases with increase in concentration of inhibitor.Temperature studies revealed a decrease in efficiency with rise in temperature**(Emeka Oguzie *et al* ., 2005).**
- **Lakshmi *et al.*,(2006),** investigated the inhibitive action of seed powder extract of *Brassica jencea*(mustard seed) on the corrosion of mild steel in HCl and H_2SO_4 by weight loss technique. It was shown that the mustard seed powder acted as a better inhibitor in H_2SO_4 medium than HCl medium.
- ***Quinine,*** a natural product, was investigated as a corrosion inhibitor for low carbon steel in 1M HCl solution. EIS, potentiodynamic polarization methods were used to study the inhibition action in the temperature range 20-50°C.The result proved the inhibition efficiency was found to increase up to 96% at 20°C**. (Mohamed Ismail *et al*,2006).**
- The inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in 5% and 15% aqueous hydrochloric acid solution has been investigated by weight loss and electrochemical impedance spectroscopy by **Chauhan *et al.*,(2007).**The effect of temperature on the corrosion behavior of mild steel in5% and 15%HCl with addition of plant extract was studied in the temperature range 50-80^0 C. Inhibition efficiency was found to increase with increase in extract concentration till 2400 ppm. The adsorption of the inhibitor on the metal surface was found to obey the Langmuir adsorption isotherm.
- The inhibition of the corrosion of mild steel by ethanol extract of *Musa sapientum peels* in H_2SO_4 was studied by gasometric and thermometric methods. The results of the study revealed that different concentrations of ethanol extract of *M. sapientum* peels inhibited mild steel corrosion. ***Eddy et al.,(2008).***
- **Ebenso *et al.,(2008)*** observed the corrosion inhibition of mild steel by ethanol extract of *Piper guinensis*(EEPG) using gravimetric, gasometric and thermometric

methods. The results of the study reveals that the different concentrations of ethanol extract of *Piper guinensis* (EEPG) inhibit mild steel corrosion.

- Estimation of the effective performance of acid extracts of poultry waste (Hen feather) on the corrosion inhibition of mild steel in 0.5M H_2SO_4 at ambient temperature was made by **Subhashini *et al,* (2008).** Conventional weight loss and electrochemical measurement techniques were used for evaluation. The maximum efficiency was found to be 95.5% for a period of 6 hours with 0.5% concentration of the hen feather extract. Experimental results were fitted to Langmuir adsorption isotherm. Electrochemical studies confirm the inhibitive nature of the hen feather extract and also the mixed nature of the inhibitor.
- Evaluation of the performance of acid extract of *Ficus Benghalensis*bark on the corrosion inhibition of mild steel in 2N, 3N, and 4N HCl medium at different temperature were studied by **Subhashini *et al.*, (2008).** Weight loss, electrochemical polarization and impedance measurement techniques were conducted. The efficiency of the inhibitor was noticed to increase with increase in concentration of the inhibitor.
- **Rajalakshmi *et al.*, (2008)** studied the role of extracts of *Phaseolus aureus*on corrosion of mild steel in 1M HCl by weight loss method and potentiodynamic polarization technique. The potentiodynamic polarization results reveal that the seed extract behaved like mixed type inhibitor. Maximum inhibition efficiency of Phaseolus aureus in 1M HCl was found to be 93%.
- **Subhashini *et al*.,(2008)** studied the use of aquatic waste – fish scale extract as corrosion inhibitor for mild steel in 0.5M H_2SO_4 by the classical weight loss measurements and electrochemical polarization measurements. The acid extract could bring out a maximum of 96.5% inhibition of mild steel corrosion in 0.5M H_2SO_4.The extract was temperature resistant. Thermodynamic parameters of the corrosion process were calculated from temperature study. The absorptive behaviour of fish extract in acid solution may be approximated by Langmuir isotherm. Values of Tafel constant ba and bc confirmed that the fish scale extract acted like mixed type inhibitor.
- **Saratha *et al.*,(2009)** investigated the inhibition efficiency of acid extract of leaves of ***Citrus aurantiifolia*** [CAL] plant on the corrosion of mild steel in 1 M HCl by weight loss measurements and electrochemical studies. The corrosion rate of mild steel and the inhibition efficiencies of the extract were calculated. The results

obtained show that the extract could serve as an effective inhibitor for the corrosion of mild steel in HCl media. Inhibition was found to increase with increasing concentration of the plant extract. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich, Frumkin, Flory-Huggins and the kinetic thermodynamic model, were tested to clarify the nature of adsorption. Polarisation curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 97.51% can be obtained. The surface analysis study confirmed the corrosion of mild steel and its inhibition by the inhibitor CAL.

- **Christy Ezhilarasi *et al*.,(2009)** studied the influence of the addition of the extract of naturally occuring *Hibiscus syriacus linn* and the flavonoid component Rutin on the corrosion of mild steel in 1M hydrochloric acid by weight loss measurement, gasometric and polarization study in the presence and absence of quaternary ammonium salt. It was observed that the extract of the plant and Rutin reduced the corrosion rate and it was reported that the inhibition efficiency increases with increase in inhibitor concentration.
- **Umoren *et al.,(2009)*** studiedthe corrosion inhibition of aluminium in HCl solution in the presence of exudate gum from *Raphiahookeri* at the temperature range of 30-60^{0}C using weight loss and thermometric techniques. It was found that the inhibition efficiency increases with increase in temperature. The exudate gum was found to obey Temkin adsorption isotherm.
- **Quraishi *et al*.,(2009)**studied the corrosion inhibition of mild steel in hydrochloric solution by black pepper extract ***(Piper nigrum)***. The techniques employed for study were mass loss measurements, potentiodynamic polarisation, linear polarization resistance and electrochemical impedance spectroscopy (EIS). The results obtained revealed that Black pepper extract was a good corrosion inhibitor for mild steel in hydrochloric acid medium and maximum inhibition efficiency (98%) was found at 120 ppm at 35 ºC. Potentiodynamic polarization curves showed that black pepper extract is a mixed-type inhibitor. EIS showed that the charge transfer controls the corrosion process in inhibited solutions Adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm. The value of the free energy of adsorption, ΔGads, indicated that the adsorption of inhibitor molecules was typical of chemisorption. The results obtained show that

the Black pepper extract which mainly contains alkaloid ‘Piperine’ could serve as an excellent green inhibitor for corrosion of mild steel in acid solutions.

- **Nnabuk Eddy *et al.*,(2009)** investigated the inhibitive and adsorption properties of ethanol extract of *Terminalia catappa* for the corrosion of mild steel in H_2SO_4 using weight loss, hydrogen evolution, and infrared methods of monitoring corrosion. The studies revealed that the inhibition efficiency of the inhibitor increased with increasing concentration but decreased with increasing temperature and it obeyed the Langmuir adsorption isotherm. The inhibition potential of ethanol extract of *T.catappa* was attributed to the presence of saponin, tannin, phlobatin, antharaquinone, cardiac glycosides, flavonoid, terpene, and alkaloids in the extract.
- **Aisha *et al*.,(2010)** studied the corrosion and corrosion inhibition of mild steel in 1.0 M H_2SO_4 containing 10% ethyl alcohol(EtOH) by ***Zizyphus Spina-Christi*(*ZSC*)** extracts (aqueous extract and alcoholic extract) has been studied using chemical techniques (hydrogen evolution(HE) and mass loss(ML)) and electrochemical techniques(electrochemical impedance spectroscopy(EIS) and potentiodynamic polarization(PDP)). The effect of acid concentration on the corrosion rate of mild steel increases with acid concentration (0.25-1.5) M showing first order corrosion reaction without changing the reaction mechanism, and the results showed that when the concentration of ***ZSC*** extracts (aqueous extract and alcoholic extract) increased the rate of steel corrosion is decreased, which indicates that the inhibition of the corrosion process is produced. Electrochemical impedance spectroscopy results showed that the corrosion and corrosion inhibition of steel occurred mainly by charge transfer. The electrochemical results of polarization also showed that the extracts of ***ZSC*** plant act as mixed type inhibitors, they retarded both cathodic and anodic reaction. The experimental results from chemical and electrochemical studies were found to fit Langmuir isotherm.
- **Sivaraju &Kannan.,(2010)** The inhibition effect of alcoholic extract on mild steel corrosion in 1N phosphoric acid has been studied*Acalypha indica L.* by mass loss and polarization techniques between 303 K and 333K.The inhibition efficiency increased with increase in concentration of plant extract. The corrosion rate increased with increase in temperature and decreased with increase in

concentration of inhibitor compared to blank. The adsorption of inhibitor on mild steel surface was found to obey Temkin's adsorption isotherm.

- **Mohd. Hazwan Hussinand Mohd. Jain Kassim.,(2010)** investigated inhibition of the corrosion of mild steel in aqueous solutions by ethyl acetate extract of *Uncaria gambir* containing catechin using weight loss, Potentiodynamic polarisation measurements, electrochemical impedance spectroscopy (EIS) and scanning electron microscope technology with energy dispersive X-ray spectroscopy (SEM-EDX). Inhibition was found to be highest at a concentration of 150 ppm in solutions with a pH of 5. The results obtained showed that the ethyl acetate extract of U.Gambir acted as a mixed-type inhibitor and could serve as an effective corrosion inhibitor of mild steel in aqueous solution.
- **Okafor *et al*.**,(2010) investigated the inhibitive action of leaves (LV), root (RT) and seeds (SD) extracts of *Azadirachta indica* on mild steel corrosion in H_2SO_4 solutions using weight loss and gasometric techniques. The results obtained indicated that the extracts functioned as good inhibitors in H_2SO_4 solutions. Inhibition efficiency was found to increase with extracts concentration and temperature, and followed the trend: SD > RT > LV.
- **Vivek Sharma *et al.,(*2010)** investigated the effect of extract of *Musa paradisiaca* on corrosion inhibition of mild steel in aqueous 0.5 M sulphuric acid by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency was found to increase with increase in concentration of the extract. Polarization measurement indicates that *Musa paradisiaca* acts as a mixed type inhibitor and the inhibition efficiency decreases with rise in temperature. The inhibition was assumed to occur via adsorption of inhibitor molecules on metal surface, which obeys Langmuir adsorption isotherm. The activation energy (Ea) and other thermodynamic parameters for inhibition process were calculated. These thermodynamic parameters indicate a strong interaction between the inhibitor and the mild steel surface. SEM and AFM studies confirmed the adsorption of inhibitor molecules on mild steel surface.
- **Vinod kumar *et al.*,(2010)** analysed the corrosion inhibition effect of acid extract of the pericarp of the fruit ***Garcinia mangostana*** on mild steel in hydrochloric acid medium. Using weight-loss data, corrosion rate (CR) and thermodynamic parameters such as energy of activation for corrosion of mild steel (E), heat of

adsorption of the inhibitors on the metal surface (Q) and change in free energy (ΔG) were calculated. The study revealed that the pericarp extract of the fruit G. mangostana is a non-toxic, cost-effective corrosion inhibitor for mild steel in acid medium.

- **Tedjani Yahia Namoussa *et al*.,(2010)**The inhibitive action of aqueous extract of ***Tamarix gallica*** on the corrosion of mild steel in 1m sulphuric acid was assessed by weight-loss method and polarization technique. Polarization curves revealed that the plant extract behave as mixed-type inhibitors. inhibition efficiency increased with extract concentration up to a critical value. the results show that the extract solution of the plant could serve as an effective inhibitor for the corrosion of steel in sulphuric acid medium.
- **Rajiv Prakash *et al*.,(2011)** investigated the effect of plant extract of Papaveraceae family ***Argemone mexicana*** for use as a low cost and efficient corrosion inhibitor for mild steel in acidic environment. Weight loss and electrochemical methods were used to study the corrosion. Nearly 80% corrosion inhibition was observed at around 200 mg L^{-1} inhibitor concentration and maximum (92.5%) for 500 mg L^{-1} extract concentration in 1 M HCl. Inhibition mechanism is studied using UV–vis, electrochemical, and surface imaging techniques.
- **Anozie *et al*.,(2011)**studied the inhibitive effect of leaf extracts of ***Euphorbia hirta*** and ***Dialum guineense*** on aluminium alloy (AA8011) in 0.5M HCl solution using gravimetric technique at 30° and 60°C. The results indicated that both extracts functioned as good inhibitors and inhibition efficiency improved with concentration. The leaf extracts inhibited corrosion process in the medium by virtue of adsorption. Inhibition mechanisms were deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. Adsorption of both leaf extracts on the aluminium alloy was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption was proposed from the obtained thermodynamic parameters.
- **Sangeetha *et al*.,(2011)** studied the inhibition efficiency (IE) of ***Phyllanthus amarus*** extract (PAE)-Zn^{2+}system, in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of Cl-, has been evaluated by weight loss method. Weight loss study reveals that the formulation consisting of 2 mL of PAE and 25 ppm of Zn^{2+} has 98% inhibition efficiency in controlling corrosion of

carbon steel immersed in an aqueous solution containing 60 ppm of Cl-. Synergistic parameters suggest that a synergistic effect exists between PAE and Zn^{2+}. Polarization study reveals that this system functions as mixed type of inhibitor controlling the cathodic reaction and anodic reaction to an equal extend. AC impedance spectra reveal that a protective film is formed on the metal surface. The FTIR spectra reveal that the protective film consists of Fe^{2+}-phyllanthus complex.

- **Rosaline Vimala *et al*., (2011)** reported the inhibition efficiency of acid extract of flowers of ***Cassia auriculata*** (CAF) plant on the corrosion of mild steel in 1 M HCl was investigated by weight loss measurements and electrochemical studies. The corrosion rate of mild steel and the inhibition efficiencies of the extract were calculated. The results obtained showed that the extract could serve as an effective inhibitor for the corrosion of mild steel in HCl media. Inhibition was found to increase with increasing concentration of the plant extract. The inhibitive action of plant extract is discussed on the basis of adsorption of stable complex at the mild steel surface. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich and the thermodynamic model, were tested to clarify the nature of adsorption. Potentiodynamic Polarisation curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 74.7% can be obtained.
- Corrosion inhibition effect of alkaloids extract from ***Palicourea guianensis*** plant (AEPG) on C38 steel in 1 M HCl medium has been investigated by potentiodynamic polarization and electrochemical impedance spectroscopy. The polarization studies showed that AEPG acts as mixed-type inhibitor. The electrochemical impedance spectroscopy showed that the charge transfer resistance increases and the double layer capacitance decreases on increasing plant extract concentration. The inhibition efficiency of the extract obtained from impedance and polarization measurements was in a good agreement and was found to increase with increasing concentration of the extract. Inhibition efficiency of 89% was achieved with 100 mg L-1 of AEPG at 25 °C. The obtained results showed that, the *Palicourea guianensis* extract could serve as an effective inhibitor for the corrosion of steel in acid media. The adsorption of AEPG obeys the Langmuir adsorption isotherm. **Lebrini *et al*., (2011)**

- **Sribarathy *et al*.,(2011**) evaluated the effect of aqueous extract of the leaves of ***Daucus carota*** (Beta carotene) on the corrosion inhibition of Carbon steel solution containing sea water, using the polarization technique. It was found that the extract acted as a good corrosion inhibitor for the three tested electrodes in all tested media. The inhibition efficiency increased as the added concentration of the extract increased. The extract was found to act as a anodic inhibitor. The protective film has been analyzed using Fourier transform infrared (FTIR) spectroscopy and fluorescence spectroscopy.
- **Shuduan Deng *et al.,(*2011)** investigated the inhibition effect of *Ginkgo* leaves extract (GLE) on the corrosion of cold rolled steel (CRS) in 1.0–5.0 M HCl and 0.5–2.5 M H_2SO_4 solutions by weight loss, potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) methods. The results showed that GLE is a good inhibitor, and exhibits more efficient in 1.0 M HCl than 0.5 M H_2SO_4. The adsorption of GLE on CRS surface obeyed Langmuir adsorption isotherm. GLE acts as a mixed-type inhibitor in 1.0 M HCl, while a cathodic inhibitor in 0.5 M H_2SO_4.
- **Khalid Hasan *et al*.,(2011)** investigated the inhibition of corrosion of mild steel using *Paniala* ***(Flacourtia jangomas)*** extract in 1M HCl and 0.5M H_2SO_4 solutions was investigated by weight loss method at 30 degree C. The result showed that corrosion rate significantly decreased in presence of the extract and inhibition efficiency increased with increasing concentration of the extract. In case of HCl maximum inhibition efficiency (98%) was noticed at 5% v/v inhibitor concentration and no considerable change in inhibition efficiency was observed after this concentration and in 0.5M H_2SO_4, it was found 95% efficiency at the same concentration of inhibitor. At lower concentration of inhibitor, better inhibition was observed in HCl medium as compared to H_2SO_4. The decreased corrosion rate was due to adsorption of plant extract which was discussed on the basis of Langmuir and Freundlich adsorption isotherm. Adsorption of ***Flacourtia jangomas*** depends on its chemical composition which showed the presence of various compounds like flavonoids, steroids, tannins and phenolic compounds etc. which has oxygen atoms with lone pair electrons for co-ordinate bonding with metal.
- Corrosion inhibition effect of ***Vernonia amygdalina*** extract on aluminium in 0.5 M HCl solution was studied using gravimetric method at 40°C temperature.

Aluminium coupons of dimension 3x1.5 cm were immersed in test solutions of uninhibited acid and those containing extract concentrations of 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 g/L concentration at intervals of 30 minutes progressively for 150 minutes. The results revealed that *V.Amygdalina* could be used as an ecofriendly corrosion inhibitor for Aluminium in HCl solution. The corrosion inhibition efficiency of the extract increases with concentrations in the corrosion media. The surface coverage of the extract obeyed Langmuir adsorption isotherm. Hence, the corrosion inhibition effect of the extract was rationalized via adsorption mechanism. **Ajanaku Kolawole Oluseyi *et al*.,(2012)**

- **Ben Hmamou et al., (2012)** studied the effectiveness of *Chamomile* extract (CE) as corrosion inhibitor for C38 steel in 1 M HCl using Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM) studies. The effect of temperature on the corrosion behavior of C38 steel in 1 M HCl with addition of plant extracts was studied in the temperature range of 298–328 K. Inhibition efficiency of 88% was achieved with 7g/L CE at 298 K. It is evident from the results of this study that CE inhibits the corrosion in 1 M HCl through adsorption process following Langmuir adsorption isotherm. The protection efficiency increased with increase in inhibitor concentration but decreases with temperatures. The Nyquist plots showed that on increasing CE concentration, increases charge transfer resistance and decreases double layer capacitance. The mixed mode of action exhibited by the inhibitor was confirmed by the polarization studies while SEM analysis substantiated the formation of protective layer over the C38steel surface. The values of inhibition efficiency obtained from different techniques measurements are in good agreement.
- **Hemalatha *et al*., (2013)** investigated the corrosion inhibitive action of flower extracts of ***Nelumbo nucifera*** *flower* on mild steel corrosion in 1 N H_2SO_4 solution was studied using weight loss method, Potentiodynamic polarization and EIS measurements. The results obtained indicate that the extracts functioned as good inhibitors in 1 N H_2SO_4 solution. Inhibition efficiency was found to increase with extract concentration. The adsorption of constituents in the plant extract on the surface of the metal is proposed for the inhibition behavior.
- **Aisha *et al*., (2012)** ***Plectranthus tenuiflorus*** *(Shara)* plant was investigated as safe (green) inhibitor on the corrosion of mild steel in 2.0 M H_2SO_4 solution using

weight loss and hydrogen gas evolution technique. The results showed that Shara plant aqueous extract is good inhibitor for mild steel in this medium. The inhibition efficiency increases with the inhibitor concentration and decreases with rising temperature. The inhibition is attributed to adsorption of the inhibitor molecules on mild steel surface. Adsorption characteristics of the aqueous extract of Shara plant were approximated by Langmuir adsorption isotherm.

- **Babatunde *et al*.,(2012)** reported the inhibitive effect of leaf extract of ***Irvingia gabonensis*** on the corrosion of aluminum in 1M HCl solution was investigated using chemical method at 30, 35 and 40°C respectively. The inhibition efficiency for the extract increased with increasing concentration of the extract and decreased with increase in temperature. The adsorption of the inhibitor molecules on Aluminium surface was found to obey Langmuir adsorption isotherm. The phenomenonof physical adsorption is proposed based on the thermodynamic parameters that govern the inhibition process.
- **Olusegun Sunday *et al*.,(2013)** investigated the inhibitive effect of the acid extract of ***Jatropha curcas*** leaves on the corrosion inhibition of mild steel using mass loss method . The study was carried out at different concentration of the extract and temperature. Inhibition efficiency of 93.69% was obtained and this show that ***Jatropha curcas*** leaves extract could inhibit mild steel corrosion in acidic medium. The inhibition efficiency of the extract was found to increase as both the concentration of the extract and temperature increased. Langmuir isotherm was best fitted into the results. The activation energy values of the inhibited corrosion reaction of mild steel are lesser than the value obtained for the blank. The adsorption mechanism was found to be chemiosorption.
- The inhibitive effect of the extract of ***Salvia judica*** on aluminum corrosion in 1 M NaOH solutions was investigated by using the weight loss method at different temperatures. It was found that the extract play as corrosion inhibitor for aluminum corrosion in 1 M NaOH solution. The inhibition action of the extract was discussed in view of Langmuir and Temkin adsorption isotherms. It was found that the adsorption of the extract on aluminum surface is a spontaneous process. The efficiency was found to increase with increasing concentration of the extract and decreased with increasing temperature. **Eyad Nawafleh *et al*., (2013)**

- **Ananth Kumar *et al*.,(2013)** investigated the ***Oxystelma esculentum*** leaves inhibition effects on the corrosion of steel in 0.5M H_2SO_4 solution were using polarization and electrochemical impendence techniques. The results revealed that ***Oxystelma esculentum*** leaves acts as a corrosion inhibitor in 0.5M H_2SO_4 solution. The inhibition efficiency increased with an increase in inhibitor concentration. The inhibition is attributed to adsorption of the inhibitor on the steel surface.
- Leaves of ***Punica granatum*** extract (LPGE) as green inhibitor for the corrosion of mild steel in 1M HCl solution was studied using weight-loss and potentiodynamic polarization measurements. The results obtained revealed that LPGE has fairly good inhibiting properties for mild steel corrosion in 1M HCl solution, with efficiency of around 94 % at a concentration of 1 g/l. The inhibition was of a mixed anodic–cathodic nature. The film which is formed over the metal surface was analysed by FT-IR spectroscopy. Further examination using X-ray diffraction confirms the role of LPGE as an effective corrosion inhibitor for mild steel in acid media. **Abboud *et al*.,(2013)**
- The extract of ***Adhatoda vasica*** in aqueous 0.5 M H_2SO_4 was systematically investigated by **Ramananda Singh (2013)** to ascertain its inhibitory effect on corrosion of mild steel and its mechanism of the inhibition by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency of ***Adhatoda vasica*** on corrosion of mild steel in 0.5 M H_2SO_4 solution increases on increasing in its concentration and decreases with rise in temperature. Potentiodynamic Polarization measurements show that ***Adhatoda vasica*** act as mixed type inhibitor. The increase in activation energies of corrosion process in presence of the extract indicates that ***Adhatoa vasica*** extract retarded the rate of corrosion of mild steel in 0.5M H_2SO_4 solution. The nature of adsorption of the extract on mild steel surface was in conformity with Langmuir isotherm. The result of EIS was correlating with the result of polarization measurement. Scanning electron microscopy (SEM) study confirmed that the inhibition of corrosion of mild steel is through adsorption of the extract molecules on surface of metal.
- **Chauhan *et al*.,(2013)** studied the Corrosion inhibition of Zn in HCL by *Nictanthes* plant extract The natural plant product used as a medicine namely marigold were tested as corrosion inhibitor of Zn in 0.5M HCl. The Cyclic-

Voltameter, potentiometry technique data suggested that the inhibition efficiency increases with the concentration of extract.

- **Ananth Kumar *et al.*,(2013)** The corrosion inhibitive action of flower extracts of *Magnolia champaca flower* on mild steel corrosion in 0.5 M H_2SO_4 solution was studied using weight loss method, potentiodynamic polarization and EIS measurements. The results obtained indicate that the extracts functioned as good inhibitors in 0.5 M H_2SO_4 solution. Inhibition efficiency was found to increase with extract concentration. The adsorption of constituents in the plant extract on the surface of the metal is proposed for the inhibition behavior.
- **Ananth Kumar *et al.*,(2013)** studied the corrosion inhibitive action of ***Oxystelma esculentum*** *stem* on mild steel corrosion in 0.5 M H_2SO_4 solution using weight loss method, potentiodynamic polarization and EIS measurements. The results obtained indicate that the extracts functioned as good inhibitors in 0.5 M H_2SO_4 solution. Inhibition efficiency was found to increase with extract concentration. The adsorption of constituents in the plant extract on the surface of the metal is proposed for the inhibition behavior.
- Extract of ***Clerodendrum phlomidis*** leaves was investigated as corrosion inhibitor of mild steel in 0.5M HCl using conventional weight loss method and scanning electron microscopic studies. The weight loss results showed that all the plant extracts are excellent corrosion inhibitors, Scanning electron microscopic studies provided the confirmatory evidence of improved surface condition, due to the adsorption, for the corrosion protection. **Pruthviraj *et al.*, (2013)**
- The inhibition property of ***Ruta graveolens*** extract (RGE) on the corrosion of carbon steel in 1M HCl solution was investigated using potentiodynamic polarization and weight loss techniques. The percentage inhibition increased with the increase of the concentration of the extract. At a concentration of 2.0g/l, the percentage inhibition reached about 94.34% at 25℃ and 6 hours. The inhibition efficiency decreased with the increase of temperature. The results showed that the adsorption of the extract on the carbon steel surface obeys Langmuir isotherm. **Mahir Majeed *et al.*,(2014)**
- **Krishnaveni and Ravichandran.,(2014)** studied the effect of ***Morinda tinctoria*** *(MT)* ***leaves*** extract on the corrosion inhibition of Al in acid medium. The inhibition studies were carried out on Al in 0.5 mol/L HCl using mass loss and electrochemical techniques. Parameters, such as concentration of the inhibitor,

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

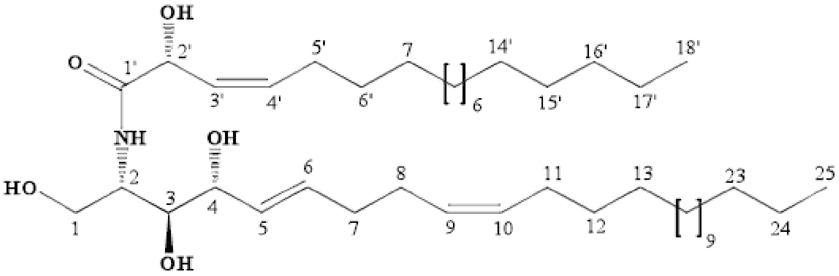
- **Pasupathy *et al*.,(2014)** investigated the extract of the leaves and berries of ***Solanum nigrum*** as a green corrosion inhibitor for zinc in 0.5N HCl by using weight loss, gasometric and thermometric methods. Results obtained showed that the extract of ***Solanum nigrum*** offered good protection against corrosion of zinc metal and exhibited high inhibition efficiencies. The inhibition efficiency was found to increase with increase in the extract concentration. The adsorption of the inhibitor molecules on the zinc metal surface obeyed Temkin adsorption isotherm.
- The corrosion inhibition of mild steel in H_2SO_4 solution in presence of ***Juniperus*** plant at a temperature range of 30 to 60°C was studied using chemical (Hand WL) and electrochemical (PDP and EIS) methods. The ***Juniperus*** plant acts as an inhibitor in the acid environment. The inhibition efficiency increases with increase in inhibitor concentration but decreases with an increase in temperature. The inhibitive effect of the ***Juniperus*** plant could be attributed to the presence of some compound in the plant which is adsorbed on the surface of the mild steel. The ***Juniperus*** plant was found to conform to the Frumkin adsorption isotherm and Temkin adsorption isotherm at all the concentration levels and temperature studied. The phenomenon of physical adsorption is proposed from the activation parameters obtained. Thermodynamic parameters revealed that the adsorption process was spontaneous. **Saedah Al-Mhyawi(2014)**
- **James and Akaranta ., (2014)** studied the results of corrosion inhibition of aluminium 3SR alloy in 2M sulphuric acid solution using acetone extract of *Red onion skin*. Hydrogen gas evolution and weight loss techniques were used to determine the amount of aluminium dissolved from the alloy in the aggressive solution were and. The experiments were carried out at the temperatures of 30^oC, 40^oC & 50^oC. Inhibition was found to increase with increasing inhibitor concentration and decreasing temperature. The inhibition is attributed to the adsorption of red onion skin extract on the surface of the aluminium coupon and conforms to Langmuir adsorption isotherm. The results from the hydrogen evolution and weight loss techniques confirmed that acetone extract of red onion is

effective in reducing the corrosion of aluminium in sulphuric acid medium. The active component in red onion skin is quercetin**.**

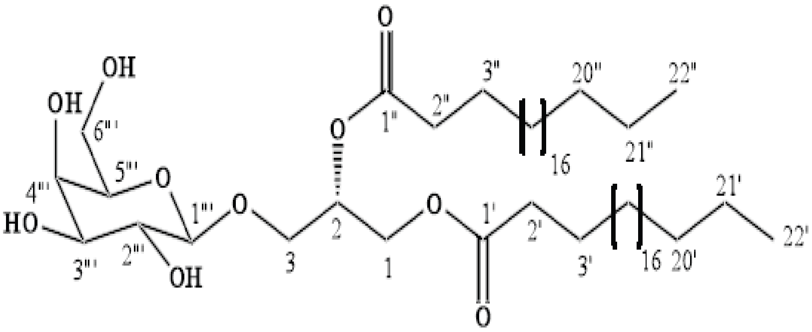
- **Anbarasi and Vasudha (2014)** investigated the inhibitive action of PCM (*peel of **Cucurbita maxima***) on mild steel corrosion in 1N HCl using weight loss method and FT IR techniques. The calculated results of corrosion rates of steel and the inhibition efficiency of plant extract show that the extract functions as a good corrosion inhibitor and IE increased with extract concentration. Maximum IE of 93 % was obtained at 2 % v/v concentration of the plant extract. Temperature studies revealed an increase in IE with rise in temperature. The adsorption of PCM extract was found to follow Langmuir's adsorption model at all concentrations and temperatures studied.
- **Onuegbu *et al*.,(2013)** reported the use of ***Eupatorium odoratum*** (E.O) as corrosion inhibitor of mild steel in 1M H_2SO_4 acid. The effects of temperatures on the inhibition efficiency of ***Eupatorium odoratum*** were also tested at temperature of 30^0C and 60^0C respectively. The weight losses of the mild steel were taken for complete four days, for the two temperatures. The rates of corrosion of the mild steels were found to increase with increase in concentration of the acid and also decrease with increase in concentration of the ***Eupatorium odoratum***. The ***Eupatorium odoratum*** gave an inhibition efficiency of 71% at the concentration of 0.5g/l, which shows that it is a good corrosion inhibitor of mild steel in acidic medium. This efficiency was found to decrease as the temperature increases and also the activation energy value calculated showed that the extract was physically adsorbed on the mild steel coupons.
- **Kamaraj *et al*.,(2014)** investigated the effect of ***Podophyllum hexandrum*** fruit extract as an inhibitor for mild steel in 1N HCl using weight loss method. The corrosion coupons were immersed in 1N HCl solution containing varying inhibitor concentrations (1%, 2%, 3%, 4% and 5% v/v) within a period of 1-4 hours. From the result, it was found that the adsorption of ***Podophyllum hexandrum*** fruit extract reduced the corrosion rate in acid medium. The inhibitive action of this plant extract has been found to be significant. The most suitable inhibitor concentration was found to be 5% for an inhibition efficiency of 89%. The inhibition is attributed to physical adsorption. The adsorbed molecules of the inhibitor lie on the surface of the mild steel blocking the active corrosion sites on the alloy.

2.2 Phytochemical constituents of *Croton sparsiflorus*

- The crude ethanolic extract of the root of ***Croton sparsiflorus*** Lin. (Family-Euphorbiaceae) was evaluated for its possible phytochemical nature (group determination of plant constituents) and antinociceptive activity. Phytochemical analysis of the ethanolic extract of C. sparsiflorus indicated the presence of tannin, steroid &alkaloid types of compounds [6].
- Sparsioamide (1), a new sphingolipid, and sparsioside (2), a new diglyceride galactoside, have been isolated from the ethyl acetate soluble fraction of the 80% ethanolic extract of the whole plant of Croton sparsiorus Morong [7]. Their structures were assigned by 1 H- and 13C-NMR spectra and DEPT, COSY, NOESY, HMQC, HMBC, and ESI-MS experiments.

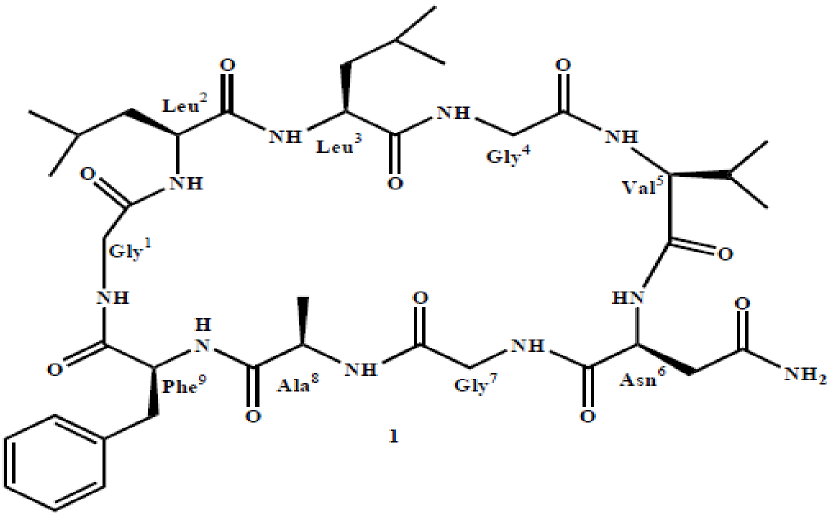


- **Sparsifloamide - sphingolipid**



Sparsifloside- diglyceride galactoside

- Crotosparsamide (1), a new cyclic nonapeptide, has been isolated from the n-butanol soluble sub-fraction of Croton sparsiflorus along with p-hydroxy methylcinnamate and kaempferol, which are reported for the first time from this species. Their structures were determined by chemical and spectral studies including ESIMS, and 1D and 2D NMR spectroscopic data[11]



1

Crotosparsamide – cyclic nona peptide

Thus from the review, it was 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.

MATERIALS & METHODS

3.MATERIALS AND METHODS

In any research work the materials and the 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 CSS extract as corrosion inhibitor for mild steel (MS) in 1 M Hydrochloric acid. 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 structural 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

Rectangular 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 had the following percentage elemental of composition as shown in table.

3.3 TEST MEDIUM

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. 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 1 M HCl. The acid used was LR grade.

3.4 ELEMENTAL ANALYSIS

C -0.089%
S-0.019%
Mo-0.021%
Mn- 0.215%
Fe-99.58%
P-0.017%

3.5 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

3.6 PREPARATION OF INHIBITOR

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

3.7 PHYTOCHEMICAL SCREENING OF THE INHIBITOR

Phytochemical examinations were carried out for the extract 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-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 glycosides: Extracts were hydrolysed with dil. HCl, and then subjected to test for glycosides.

a) Modified Borntrager's Test: Extracts were treated with Ferric Chloride solution and immersed in boiling water for about 5 minutes. The mixture was cooled and extracted with equal volumes of benzene. The benzene layer was separated and treated with ammonia solution. Formation of rose-pink colour in the ammonical layer indicates the presence of anthranol glycosides.

4. Legal's Test: Extracts were treated with sodium nitropruside in pyridine and sodium hydroxide. Formation of pink to blood red colour indicates the presence of cardiac glycosides.

5. 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.

6. 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.

7. 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.

8. 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.

9. 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.

10. 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.

11. Detection of diterpenes:

Copper acetate Test: Extracts were dissolved in water and treated with 3-4 drops of copper acetate solution. Formation of emerald green colour indicates the presence of diterpenes.

3.8 TECHNIQUES EMPLOYED

1.Physio - chemical method

2.Electrochemical measurements

3.8.1 Physico chemical method (Mass loss method)

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 predetermined period of time. It is then removed and weighed. The mass 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 100 ml of acid with and with out inhibitor for a particular period of time. The coupons are then washed, dried and reweighed. The average mass loss of the 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, 1 h, 3 h,12h& 24 h)
- Temperature (303 K – 353 K)

3.8.2 Determination of corrosion rate

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

$$\text{C.R (mpy)} = \frac{534 \text{x} W}{D \text{x} A \text{x} T}$$

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

3.8.3 Determination of percentage of inhibition and surface coverage

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

$$\text{I.E (\%)} = \frac{w_0 - w}{w_0} \text{ x } 100$$

Where,

w_0- Corrosion rate without inhibitor in g

w- Corrosion rate with inhibitor in g

3.8.4 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)

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

Where,

$$\Delta G = (-1.74 - \log B) \times (2.303\ RT)$$

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

θ is the surface coverage

C is the concentration the inhibitor

R is the gas constant 8.314 J/mol

T is the temperature in K

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

$$\Delta G = \Delta H - T\ \Delta S$$

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

3.8.5Adsorption 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 terms of adsorption isotherm. The knowledge of the adsorption behaviour of the inhibitor is important for definition of its active mechanism. The dependence of surface coverage on concentration is studied through the following adsorption isotherms.

Langmuir [log (θ /1 – θ) Vs log C]

Temkin (θ Vs log C)

3.8.6 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-gas constant 8.314 J/mole

3.9 ELECTROCHEMICAL METHODS

3.9.1 Polarization techniques

Electrochemical studies were carried out using conventional three electrode cell with large area of platinum foil as counter electrode saturated calomel electrode (SCE) as reference electrode and sample as working electrode. Solartron 1280B interfaced with an IBM computer was used for the polarization study.

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 starting from -0.1 to -1mV with respect to the corrosion potential in the presence and absence of the inhibitor. 1sq.cm. of polished mild steel surface was exposed and the electrochemical studies are carried out at 303 K.

3.9.2 Tafel plot

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

The inhibitor efficiency was calculated using the following equation,

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

I.E from LPR technique

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

Where,

$R_{p\ (inhibited)}$ and $R_{p(blank)}$ are linear polarization resistance in the presence and absence of the inhibitor respectively.

3.9.3 Impedance spectroscopy

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

The I.E can be calculated using the equation,

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

Where,

$R_{ct\ (inhibited)}$ and $R_{ct\ (blank)}$ are charge transfer resistance in the presence and absence of the inhibitor respectively.

With the help of the double layer capacitance C_{dl}, θ can be calculated using the equation,

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

Where,

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

3.10 SURFACE ANALYTICAL TECHNIQUES

3.10.1. FTIR TECHNIQUE

The qualitative aspects of infrared spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. In order to identify the presence of plant constituents in the extract and that adsorbed on the metal surface, FTIR technique was followed. The metal specimens were immersed in 100 ml of the test solution with optimum 0.45% concentration of the both the inhibitors for 24 hrs. It was then dried with acetone and the adsorbed materials were carefully scratched and the powder was taken for FT-IR analysis. The powder obtained by evaporating the extract on a water bath was also subjected to FT-IR analysis.

FT-IR stands for Fourier Transform Infra-Red, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample and is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FT-IR studies are carried out to characterize the functional group present on the mild steel.

3.10.2 OPTICAL ELECTRON MICROSCOPE:

Surface morphology of the specimens with and without inhibitors was studied using an optical electron microscopic method. The specimens were immersed in 100ml of test solution containing 0.45% concentration of the inhibitor and blank solution for 3 hours. Then they were removed and quickly rinsed with water, well dried and finally analyzed through Carl Zeiss optical electron microscope.

Optical electron microscope deals with the examination of materials by optical microscopy are essential in order to understand the relationship between properties and microstructure. Metallography is the study of metals by optical examination. This is most commonly done using a conventional light microscope. Structures which are coarse enough to be discernible be the naked eye is termed macrostructures. Those which require magnification to be visible are termed microstructures.

RESULTS & DISCUSSION

4. RESULT AND DISCUSSION

Results pertaining to the current investigation on "**Inhibition Effect of *Croton sparciflorus* stem on corrosion of mild steel in 1M HCl and 0.5M H_2SO_4medium**" are discussed under the following headings on the basis of the objectives set forth.

To control corrosion process on the mild steel, many methods are available. Among this, one of the most appropriate method is to use of inhibitors. In this direction the present study has been conducted to explore the inhibition efficiency that can be afforded by *Croton sparciflorus* extract in acid medium.

The inhibitive action of *Croton sparciflorus* Stem extract was measured at room temperature and at higher temperature for various concentration of the extract and for different period of immersion. Results of the findings are discussed under the following headings.

a) Mass loss measurements

1. Effect of concentration of *Croton sparciflorus Stem* extract and time of immersion on the corrosion of mild steel in acid medium at room temperature.
2. Influence of temperature in the presence of the extract on the corrosion of mild steel.
3. Adsorption isotherms.
4. Activation energy and thermodynamic parameter.

b) Electro chemical measurements

1. Tafel intercepts method and linear polarization method.
2. Electrochemical impedance measurements.
3. Mechanism for inhibition process.

c) Surface Analytical Techniques

1. FT-IR
2. Optical electron microscope

4.1 Characterisation of *Croton sparciflorus Stem* extract

4.1.1 Phytochemical Screening

The investigated plant extract was screened for the presence of flavonoids, alkaloids, terpenoids, saponins, tannins, reducing sugar, polyphenols, and anthraquinones using standard procedure

Table 1

Phyto chemical screening of crude CSS extract

Phyto constituents	**Results**
Alkaloids	+
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 CSS extract.

4.1.2 FT –IR

Figure 1

FT- IR spectral peak of crude CSS extract

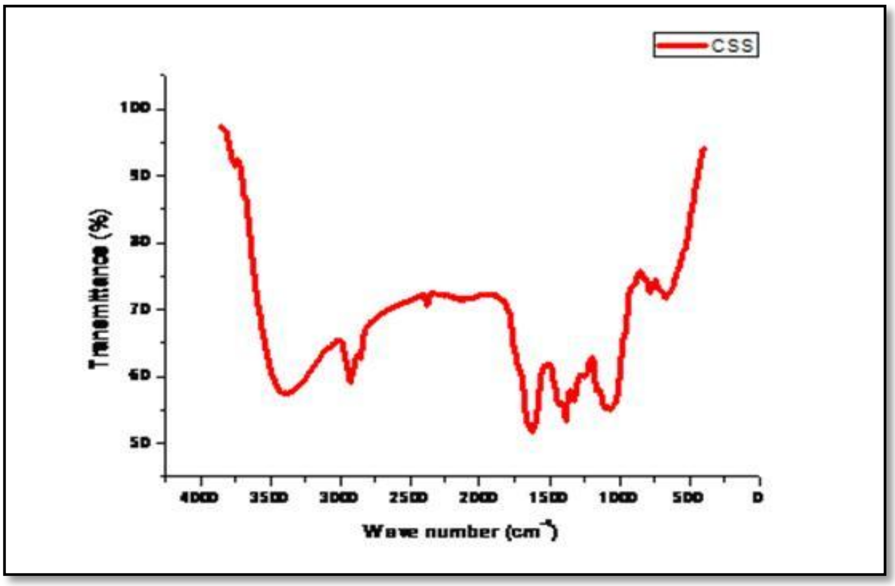


Figure. 1 shows the FT-IR spectrum of CSS crude extract. A very strong broad band at 3356 cm^{-1} is attributed to O–H stretching. The absorption band at 2924 cm^{-1} is related to –CH asymmetrical stretching vibration **(Li *et al*, 2009)**, and a strong band at 1627 cm^{-1} corresponds to the C=O stretching vibration. Hence, it can be inferred that CSS 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 METHOD

Mass loss measurements were carried out for mild steel both in the absence and presence of acid extracts of *Croton sparciflorus stem.* The experimental results have been evaluated on the following parameter,

- Effect of concentration of inhibitor
- Impact of period of immersion
- Role of temperature

4.2.1 MASS LOSS METHOD OF *Croton sparciflorus* STEM EXTRACT IN 1M HCl

4.2.1.1 Effect of Concentration

The concentration of the inhibitor plays an important role to fix an effective concentration for the extract under study. The effect of CSS on the dissolution of mild steel in 1M HCl was investigated by conducting the test with various concentrations of the extract (0.1%-0.7%). The results are illustrated in the **Table 2** and **Figure 2.** It was obvious from the result that CSS inhibited the corrosion of mild steel at all concentrations used in this study. It was observed from **Table 2**, that the corrosion rate of mild steel decreased while the protection efficiency increased as the concentration of CSS increased in acid media. A maximum efficiency of 94 % was achieved at 0.7% of CSS in 1M HCl respectively. Increase in IE with increase in concentration of the extract inferred that there is an increased surface area of the adsorbed molecule of the extract resulting in decrease in dissolution of mild steel.

The increase in inhibitive action with the increase in concentration of the inhibitor can be ascribed to the blocking of active sites on metal surface. The active polar sites form a monolayer on the surface of mild steel. At any instant a fraction of θ of the metal surface is covered by the inhibitor molecules and uncovered fraction (1- θ) reacts with acid as it does in the absence of the inhibitor. At all test durations 0.7% extract showed maximum efficiency. This behaviour may be attributed to the increase of the surface coverage (θ) by the adsorption of the extract on the mild steel surface.

4.2.1.2 Impact of period of immersion

Analysing the data presented in **Table 2**, as the concentration of CSS extract increases, the corrosion rate decreased for all periods of immersion. Maximum I.E was found to be 99% at 6 hours immersion time. For **MS/CSS/HCl** system the time of immersion increased as ½ h to 6h then inhibition efficiency increased from 94% to 99% at 0.7% concentration and it was denoted in **Table 2 and Figure 3** . After 6h there was a slight decrease in inhibition efficiency (IE) at 12h (95.4%). After 12h there was slight increase in the inhibition efficiency (IE) at 24h (96.3). It can be concluded that the inhibitor molecule was effectively adsorbed on the mild steel surface till 6h immersion, after that slight decrease in IE at 12 hours immersion period.

This can be attributed to the formation of a protective film being time dependent on MS surface. In this present investigation it is also observed that the inhibitor function very well at higher concentration at all period of immersion in acid media.

However the I.E is stabilized at 12 hours and 24 hours furnishing around 96.3%. This result indicates that the studied extract functioned well at longer period of immersion.

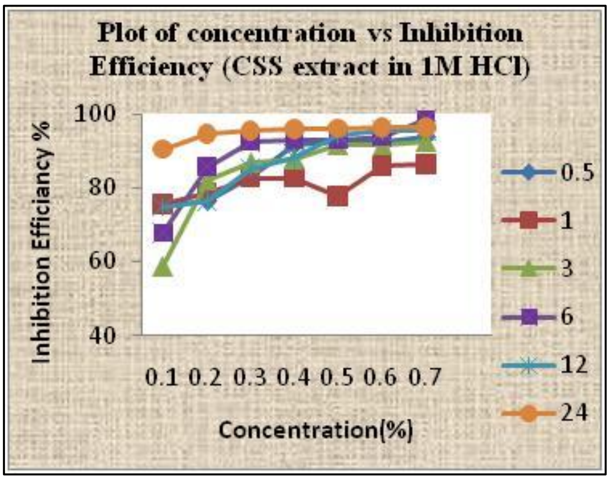


Figure 2

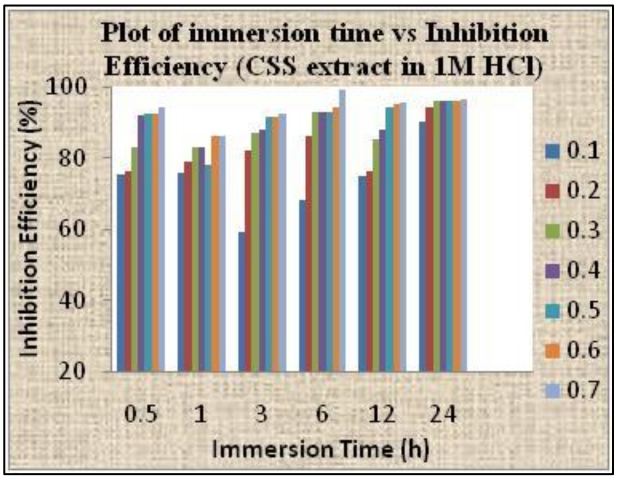


Figure 3

These finding also highlighted the stability of the extract at longer period of immersion in 1M HCl medium. The corrosion inhibition can be attributed to the adsorption of the inhibitor at the steel/HCl solution interface.

Table 2 Role of concentration of CSS 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.	0.1	384	75	265	76	361	59	242	68	146	75	163	91
2.	0.2	367	76	230	79	158	82	108	86	138	76	95	95
3.	0.3	266	83	188	83	115	87	56	93	85	85	77	96
4.	0.4	128	92	188	83	107	88	53	93	69	88	70	96
5.	0.5	120	92	243	78	75	92	52	93	33	94	68	96
6.	0.6	115	93	154	86	75	92	46	94	27	95	64	96
7.	0.7	94	94	149	86	67	92	11	99	26	96	63	96

4.2.1.3 ROLE OF TEMPERATURE

Temperature is an important parameter in studies on metal dissolution process.The corrosion rate in acid solutions increases exponentially with a temperature increase because the hydrogen evolution over potential decreases (**Popova *et al*, 2003**). The mild steel samples were exposed to 1M HCl at specific temperatures (303K, 313K, 323K, 333K, 343K, and 353K) for 30 minutes. The performance of the extract increased at all concentrations in all studied temperatures.

Taking a critical look on the Table 3 and Figures 4 and 5 the result indicated that a maximum IE of 94% was obtained with 0.7% concentration at 303K. Decrease in IE with temperature can be explained due to increase in the adsorption of inhibitor molecule on mild steel surface up to 323K. The maximum IE was observed at a temperature 303K (94%). After 303K, the IE was found to be stabilised at 323K, and after that there is decrease in IE at 333K (92.1) and enhancement in IE at 353K (91%). These finding confirmed that the inhibitor formed a stable layer at higher temperatures and it could be used as pickling inhibitor up to 333K. The decrease in IE at higher temperature can be ascribed due to the following reasons: The adsorption and desorption of inhibitive molecules continuously occur at the metal surface and equilibrium exists between these two molecules processed at particular temperature.

With the increase in temperature the equilibrium between the adsorption and desorption processes are shifted, leading to higher desorption rate than adsorption. The desorption at elevated temperature thus exposes the metal surface to further attack.

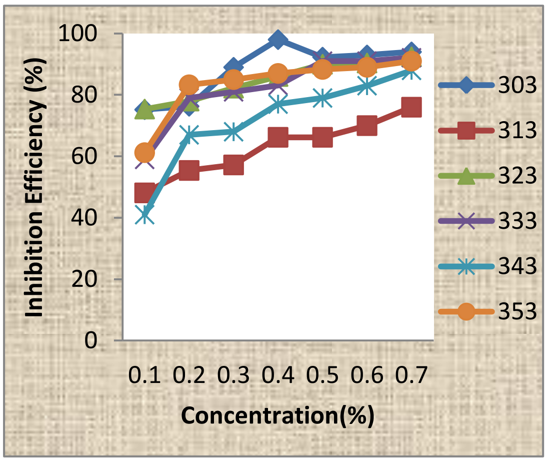


Figure 4

Variation of inhibition efficiency as a function of Concentration (CSS extract in 1M HCl)

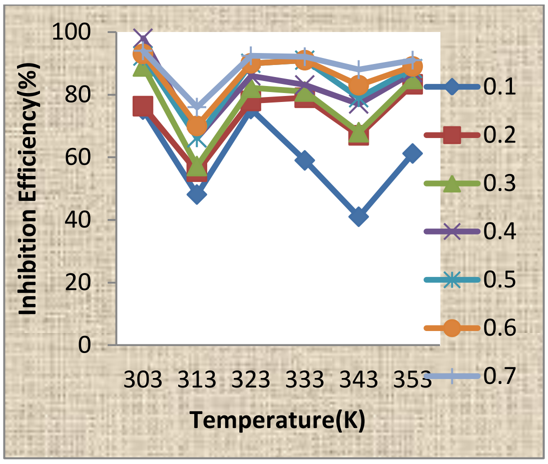


Figure 5

Variation of inhibition efficiency as a function of Temperature (CSS extract in 1M HCl)

Table 3

Role of temperature on Corrosion of MS in the presence of various concentration of CSS 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.	0.1	384	75	734	48	1356	76	7574	59	5331	41	5220	61
2.	0.2	367	76	631	55	1237	78	2269	79	2968	67	2243	83
3.	0.3	266	89	606	57	981	82	2030	81	2900	68	2081	85
4.	0.4	128	98	478	66	785	86	1800	83	2064	77	1817	87
5.	0.5	120	92	478	66	554	90	1006	91	1885	79	1570	88
6.	0.6	115	93	426	70	529	91	972	91	1561	83	1527	89
7.	0.7	94	94	341	76	418	93	836	92	1135	88	1211	91

4.2.2 MASS LOSS METHOD OF *Croton Sparciflorus* EXTRACT IN 0.5M H_2SO_4

4.2.2.1 Effect of concentration

Dissolution rate of mild steel was studied for different concentration of the CSS in H_2SO_4 at various period of immersion at room temperature and the results are presented in the **Table 4.**Results indicated a significant decrease in the corrosion rate with increase in concentration of extract of *Croton sparciflorus*. Analysis of the table revealed that the inhibition efficiency increased with increase in concentration of the extract. The results are represented in the **Figure 6.** A maximum I.E of 91% was observed at 0.7% concentration of the extract. At all test durations 0.7% extract showed maximum efficiency. This behaviour may be attributed to the increase of the surface coverage (θ) by the adsorption of the extract on the mild steel surface.

4.2.2.2 IMPACT OF PERIOD OF IMMERSION

Considering the technical process for an inhibitor, the optimum period of immersion has to be observed. To investigate the effect of inhibition with exposure time experiments were carried out at various time intervals (1/2 hr, 1 hr, 3hr, 6hr, 12 hr, 24hr) with and without CSS extract by mass loss method.

As the time of immersion increases from ½ h to 3 h the IE also increases from 90.7% to 93% at 0.7% concentration and was denoted in **Table 4**. After 3h there was slight decrease in IE at 6 h. After 6h there was slight increase in the IE at 12h .

From the experimental results it can be concluded that the inhibitor molecule was being adsorbed on the MS surface effectively up to 6 hrs after that there is a slight decrease in IE at 24h . In this present investigation it was also observed that the inhibitors function very well at higher concentration at all period of immersion. It is graphically represented in the **Figure 7.**

Hence it is suggested that higher concentration of the inhibitor might be used in the pickling bath. Stability of CSS extract on MS/0.5M H_2SO_4 is a remarkable point and this appreciable stability of CSS extract at longer time duration may be due to the strong adsorption of phytochemical constituents on MS surface.

Table 4

Role of concentration of CSS extract on MS in 0.5M 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.	0.1	1194	48	738	53	340	83	505	50	766	62	658	52
2.	0.2	802	65	392	75	338	83	285	72	346	83	393	71
3.	0.3	478	79	371	77	215	89	269	73	252	88	297	78
4.	0.4	452	81	341	78	205	90	262	74	209	90	211	85
5.	0.5	230	90	320	80	188	91	211	79	166	92	188	86
6.	0.6	230	90	286	82	172	91	154	85	147	93	157	89
7.	0.7	213	91	277	83	149	93	121	88	129	94	149	89

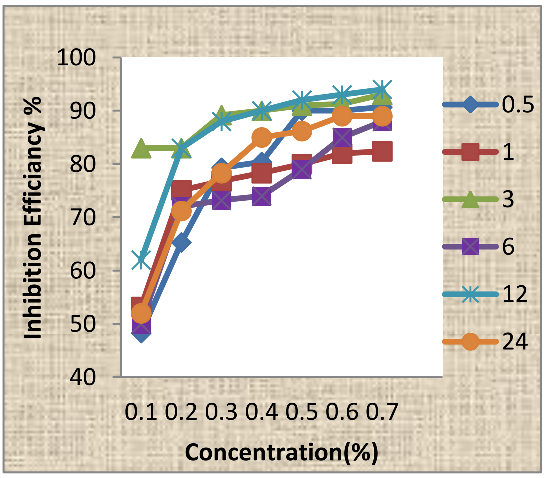


Figure 6

Plot of Concentration Vs inhibition Efficiency (CSS extract 0.5M H_2SO_4)

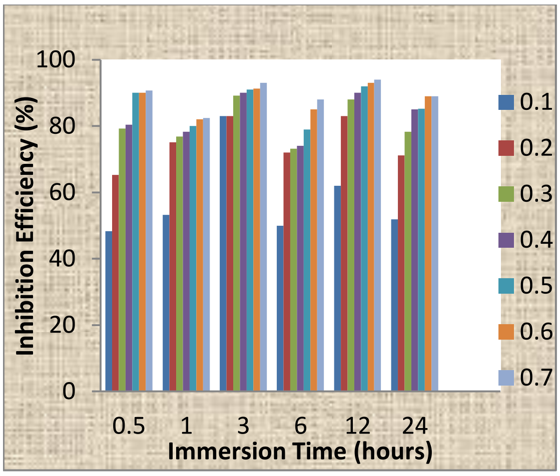


Figure 7

Plot of immersion time Vs Inhibition Efficiency (CSS extract in 0.5M H_2SO_4)

4.2.2.3 ROLE OF TEMPERATURE:

The corrosion rate in acid solutions increases exponentially with a temperature increase because the hydrogen evolution over potential decreases (**Popova *et al*, 2003**).

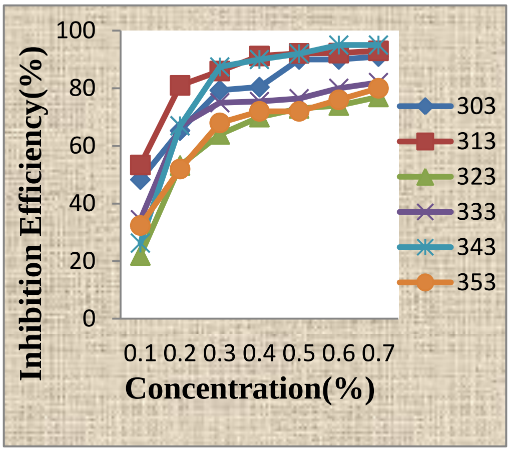
The mild steel samples were exposed to 1M HCl at specific temperatures (303K, 313K,323K, 333K, 343K, and 353K) for 30 minutes. The performance of the extract increased at all concentrations in all studied temperatures. The result indicated that a maximum of 95% was observed with 0.7% concentration at 343K. After 303K, the IE was found to decrease and then stabilise at 343K, and after that there is decrease in IE at 353K giving rise to an efficiency of 80 %.

These finding confirmed that the inhibitor formed a stable layer at higher temperatures and it could be used as pickling inhibitor up to 353K.These findings reflect that the *Croton sparciflorus* extract could withstand at high temperatures. These types of inhibitors are well suited for industrial purposes.

Table 5

Role of temperature on Corrosion of MS in the presence of Various Concentration of CSS extract in 0.5M H_2SO_4

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.	0.1	1194	48	2781	54	10850	22	7242	35	7600	26	20676	33
2.	0.2	802	65	1152	81	6465	53	3668	67	3395	67	14765	52
3.	0.3	478	79	836	86	5033	64	2806	75	1297	88	9894	68
4.	0.4	452	81	520	91	4197	70	2721	76	1024	90	8658	72
5.	0.5	230	90	469	92	3736	73	2602	77	862	92	8632	72
6.	0.6	230	90	461	92	3668	74	2201	80	563	95	7387	76
7.	0.7	213	91	435	93	3190	77	2030	82	563	95	6124	80



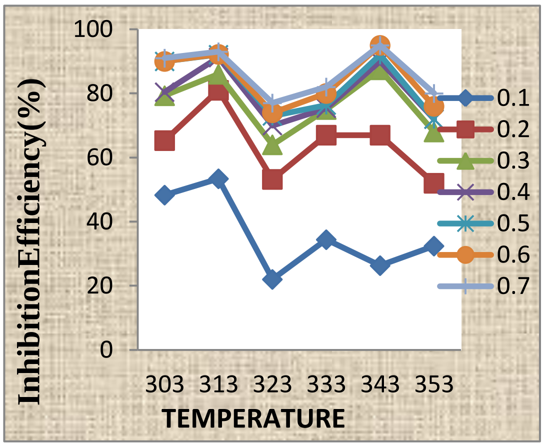


Figure 8

Variation as a function of concentration

(CSS Extract on 0.5M H_2SO_4)

Figure 9

Variation as a function of temperature

(CSS Extract on 0.5M H_2SO_4)

4.3 ADSORPTION ISOTHERMS

Adsorption isotherm has been generally studied since organic molecules inhibit corrosion by adsorption at the metal solution interface. Adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with electrode surface. A useful method that assists in the understanding of the mechanism of organo chemical reactions in the adsorption process is the adsorption isotherms (**Bockris.,1993**). The adsorption of organic substance (surfactant) at the metal solution interface may be written according to the following displacement reaction:

$$\text{Organic}_{(\text{ solution})} + nH_2O_{(\text{ads})}\ \text{Organic}_{(\text{ads})} + nH_2O_{(\text{solution})}$$

When n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. Clearly the value of n depends on how the molecule arrange on the surface due to surface roughness and the interaction among the molecules. Basic information on the interaction between the inhibitor molecules and the surface of mild steel can be provided by adsorption isotherm. A correlation between surface coverage **(**θ**)** and concentration of inhibitor **(**1-θ**)** in electrolyte can be represented by the Langmuir adsorption isotherm.

$C_{\text{INHIBITOR}}$ = I/K + $C_{\text{INHIBITOR}}$ [where K is the adsorption constant]

θ

Surface coverage values (θ) for the inhibitor were obtained from the weight loss measurements for various concentrations at 303K .

4.3.1 LANGMUIR ADSORPTION ISOTHERM

A plot of log (θ /1- θ) Vs log C gave a straight line which obviously shows that the adsorption of the CS extract can be fitted to Langmuir adsorption isotherm **(Figure 10, 11)**.These results demonstrated that the inhibition of MS by CSS in both acidic solutions may be attributed to adsorption of the compounds on the MS surface. It also confirmed the monolayer adsorption.

4.3.2 TEMKIN ISOTHERM

Efforts are also carried out to plot θ Vs log C and the results indicate that the MS/acidic solution interface furnishes a straight line suggesting that the adsorption of CS extract at the MS/acidic solution interface obeyed Temkin isotherm **(Figure 12,13).**

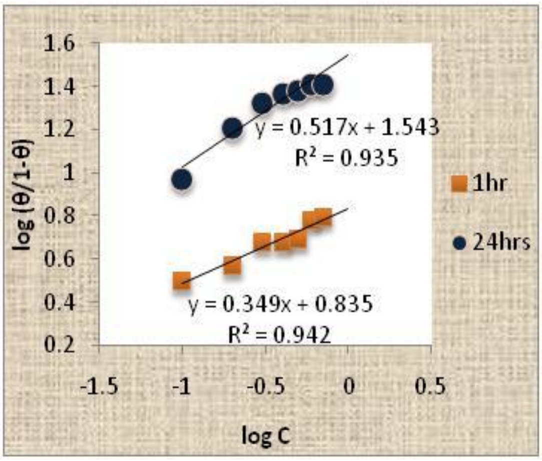


Figure 10

Langmuir Adsorption isotherm for MS/HCl/CSS extract

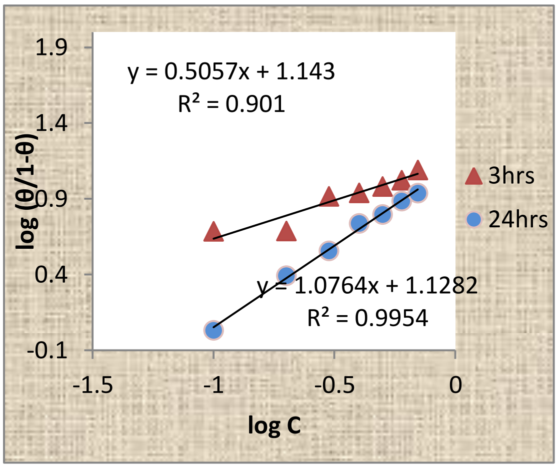
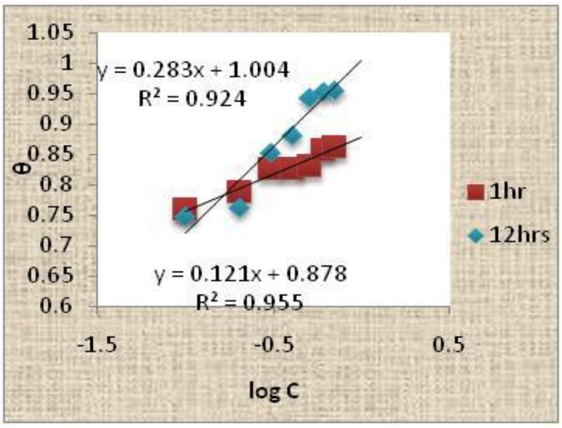


Figure 11

Langmuir adsorption isotherm – for-MS/H_2SO_4/CSS extract



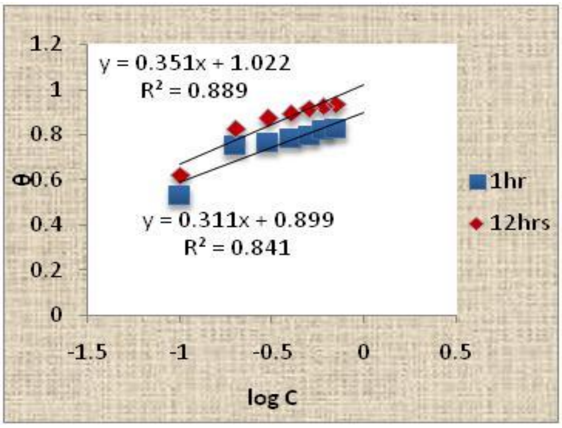


FIGURE 12

Temkin Adsorption isotherm for -MS/HCl/CSS extract

FIGURE 13

Temkin adsorption isotherm for-MS/H_2SO_4/CSS extract

4.3.3STATISTICAL ANALYSIS OF ADSORPTION ISOTHERM

Comparing the linearity of Langmuir and Temkin adsorption isotherm, the correlation co-efficient values were calculated. The correlation co-efficient obtained for the fitness of the data to adsorption models were furnished in the **Table 6**. From these findings, it can be inferred that CSS was adsorbed on MS surface obeying Langmuir and Temkin isotherms. This confirms that adsorption behavior of the inhibitor is strongly influenced by temperature. The correlation values are significant at 1% level. Hence Langmuir and Temkin adsorption isotherm are both appreciable at all temperatures in the presence of investigated inhibitor in both acid media.

Table 6

Values of correlation coefficient obtained for Langmuir and Temkin Adsorption isotherm

TEMPERATURE (K)	**CORRELATION VALUES (R^2)**			
	CSS IM HCl EXTRACT		**CSS 0.5M H_2SO_4 EXTRACT**	
	LANGMUIR	**TEMKIN**	**LANGMUIR**	**TEMKIN**
303	0.9361	0.9438	0.9834	0.9830
313	0.9705	0.9774	0.9414	0.9170
323	0.9748	0.9315	0.9492	0.9442
333	0.8114	0.8936	0.8703	0.9612
343	0.9362	0.9613	0.9665	0.9433
353	0.9671	0.9377	0.9977	0.9815

4.3.4 ACTIVATION ENERGY

Activation energy of corrosion reaction was calculated from Arrhenius equation,

$$\mathbf{Log\ C.R. = \frac{-E_a}{2.303\ RT} + Constant}$$

Where E_a is the apparent effective energy, R the gas constant and A the Arrehenius pre exponential factor. A plot of logarithm of the corrosion rate (C.R) Vs 1/T gave a straight line as shown in **Figure 14 and 15** with slope of $-E_a$ / 2.303 R. The average value of activation energies for the corrosion process in 1M HCl was found to lie around 44 KJ/mol. Analysing the table the E_a decreases in the presence of CSS extract.

This means that the extract is more effective at intermediate temperature and this indicates the physical adsorption of CS extract on MS surface.

However the variation of IE with temperature could conclude the possibility of chemisorption also. This extract functions by physical adsorption at low temperature and chemisorption at higher temperature. Literature studies reveals unchanged or lowered activation energies in inhibited solution may be interpreted as being indicative of chemisorption, while the opposite is the case with physical adsorption. Analysing the **Table 7 and 8** the activation energy increases with with increase in inhibitor concentration. This behaviour is the indication for the formation of the adsorption film of physical electrostatic nature.

It is noticeable that the lowest values of Ea were obtained with highest inhibition efficiency. This interesting outcome has earlier been observed and discussed in literature with different approaches. **Machu, (1938)** in his studies, on the influence of temperature on inhibitor action concluded that with powerful inhibitors, the Ea was lower for the inhibited solution than that of uninhibited solutions. This type of behaviour means that an inhibitor becomes more effective as the temperature increases. According to by **Putilova, (1960)** as there is an increase in surface area of the metal covered by the inhibitor molecules as the temperature rises. **Riggs, (1967)** reported that in the presence of adsorbed inhibitor, the dissolution of the metal proceeds with two distinct processes (corresponding to the covered area and the bare metal surface). At high degree of coverage the dissolution process is not only determined by the reaction of the metal from the bare surface but also involves the adsorbed inhibitor and consequently the Ea can assume values greater or smaller than those calculated in the absence of the inhibitor.

In the current investigation the values were found to be lower than the uninhibited solution in the presence of CSS in the acidic solution. Experiments conducted by **Bag *et al*., (1996)** also reflected lower Ea values for the inhibited systems. Studies carried out by **Taha *et al*., (1995)** revealed that the presence of inhibitors decreased the Ea of the reaction to an extent depending on the nature of inhibitor. Values of activation energy infer the strong adsorption of inhibitor molecules on MS surface in the present study.

4.3.5 Activation parameters of MS in the presence of CSS extract in acid medium

An alternative formulation of Arrhenius equation is

$$\mathbf{CR} = \frac{RT}{Nh} \exp \frac{\Delta Sa}{R} \exp \frac{\Delta Ha}{R}$$

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 **(Figures 16 and 17)** with a slope of - ΔHa /2.303R and an intercept of $\log(R/Nh + \Delta S_a/2.303R)$ from which the values of ΔHa and ΔSa were calculated and listed in **Table 7 and 8.**

The values of ΔH_a & E_a are nearly the same and are higher in the presence of the inhibitor. This indicates that the energy barrier of the corrosion reaction increased in the presence of the inhibitor without changing the mechanism of dissolution. The positive values of ΔH_a for both corrosion processes with and without the inhibitor and reveal the endothermic nature of the steel dissolution process and indicate that the dissolution of steel is difficult.

The large negative value of ΔS_a for mild steel in acid medium implies that the activated complex is the rate determining step, rather than the dissolution step. In the presence of the inhibitor, the value of ΔS_a increased and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes. The positive values of ΔS_a reflect the fact that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of the inhibitor onto the steel surface.

Table 7
Values of Ea , ΔHa And ΔSa of MS in Various Concentration of CSS in HCl medium

S.No	Conc V/V (%)	Activation energy -E_a kJ/mol	ΔH_a kJ/mol	ΔS_a kJ/mol
1	Blank	52.51	51.46	-69.52
2	0.1	48.61	47.78	-50.22
3	0.2	34.01	34.11	-45.54
4	0.3	38.84	38.56	-42.76
5	0.4	35.01	34.98	-39.34
6	0.5	31.18	31.09	-33.89
7	0.6	34.73	34.67	-36.90
8	0.7	46.50	45.49	-50.23

Table 8
Values of E_a , ΔH_aAnd Δ$S_a$of MS in various concentration of CSS in H_2SO_4 medium

S.No	Conc V/V (%)	Activation energy -E_a kJ/mol	ΔH_a kJ/mol	ΔS_a kJ/mol
1	Blank	49.23	49.98	-50.33
2	0.1	59.62	59.45	-60.33
3	0.2	38.40	38.33	-45.74
4	0.3	62.91	61.23	-65.23
5	0.4	39.93	38.78	-39.98
6	0.5	70.02	71.23	-74.35
7	0.6	53.06	53.67	-58.32
8	0.7	54.15	55.89	-60.21

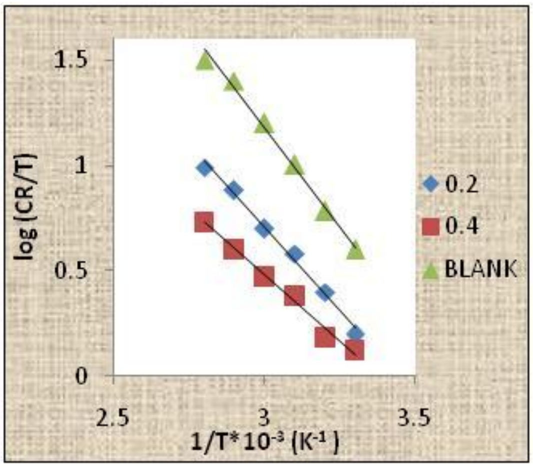


Figure 14

Arrhenius plot (MS/HCl /CSS)

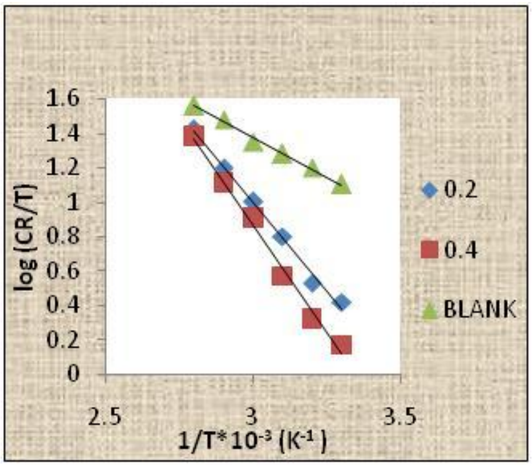


Figure 15

Arrhenius plot (MS/H_2SO_4/CSS)

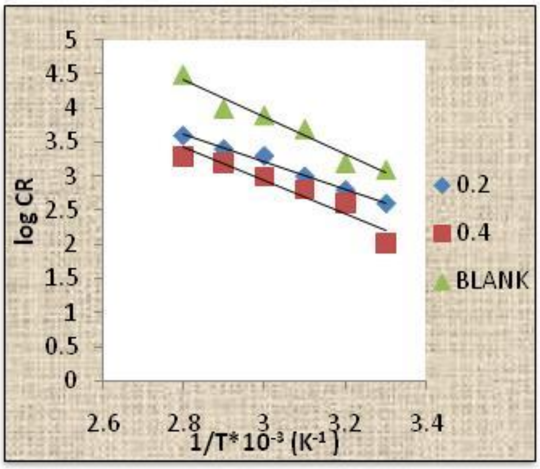


Figure 16

Transition state plot-MS/CSS/HCl

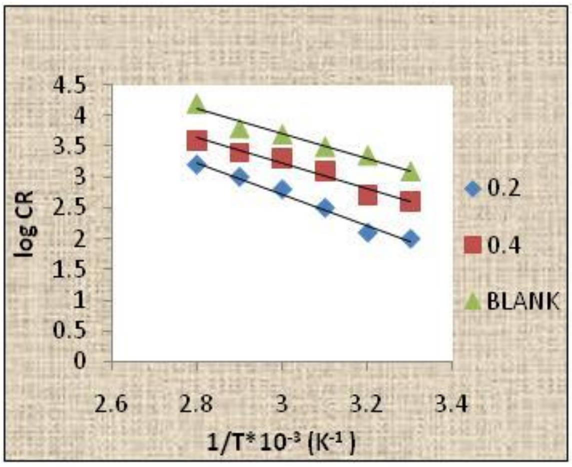


Figure 17

Transition state plot-MS/CSS/H_2SO_4

4.3.6 FREE ENERGY OF ADSORPTION

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 heats of adsorption suggested that in the system there exists a favourable condition for adsorption of inhibitors on the metal surface.

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, is reported in **Tables 9 & 10** and represented in **Figures 18, 19**. Analysis of the tables inferred that the ΔG_{ads} values ranged from -11 KJ/mol to – 20 KJ/mol from 303K to 353 K. For present system studied in 1M HCl and

0.5H_2SO_4media the value of ΔG increases with increase in concentration and increases with increase in temperature. **Moretti *et al*, (2002), Abdulaziz *et al*, (1989, 1990), Gomel *et al*, (1995), Rudresh *et al*, (1982)** reported that the negative values of □Gads adsorption are characteristic of strong interaction between the inhibitor and the electrode, forming a adsorbed layer on the metallic surface and spontaneity of adsorption.

The negative value of ΔGads ensures that the spontaneity of the adsorption process and stability of the adsorption layer on the steel surface. Generally values of ΔGads upto -20 KJ/mol is consistant with electrostatic interaction between the charged metal (physisoption) while those more negative than -40 KJ/mol are associated with chemisorption as a result of sharing or transfer of unshared electron pairs or π electrons of organig molecules to the metal surface to form a coordinate type of bond .

The plot ΔG_{ads} Vs 1/T gives a straight line with slope that equals to ΔH_{ads} . The calculated values are depicted in **Tables 9 and 10** indicated that the ΔG_{ads} values were negative and indicated the stability of the adsorbed layer on the steel surface and spontaneity of adsorption process. Also the values increase (become less negative) with the increase in temperature which indicates the occurrence of exothermic process.

4.3.7 HEAT OF ADSORPTION (ΔH) AND CHANGE IN ENTROPY (ΔS)

Thermodynamic parameters ΔH and ΔS could be arrived at, from the temperature studies and using a plot of -ΔG Vs T. The values of thermodynamic parameters are listed in **Tables 9 and 10 .**The positive sign of enthalpies reflect the endothermic nature of dissolution process. The negative values of ΔS mean that the process of adsorption is accompanied by an decrease in entropy.It might be explained as follows: Before the adsorption of CSS onto steel surface the chaotic degree of steel surface was high but when inhibitor molecules was oderly adsorbed on to the steel surface, as a result a decrease in entropy. The negative values of ΔS indicates that activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder take place during the course of transition from reactant to the activated complex**. (Saliyan and Adhikari, 2007)**The positive sign of enthalpies reflect the endothermic nature of dissolution process.**(Singh *et al*., 2009.)**

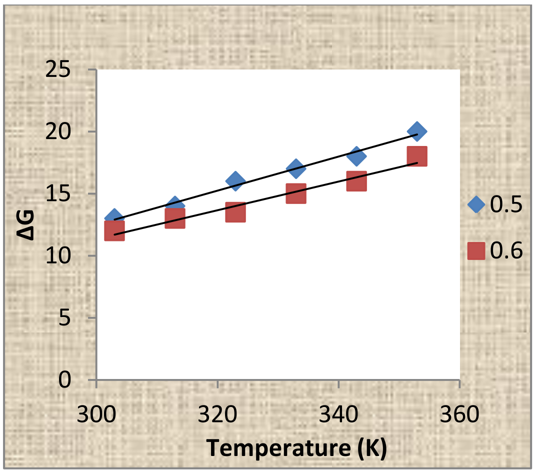


Figure 18

- ΔG Vs temperature for CSS Extract in HCl

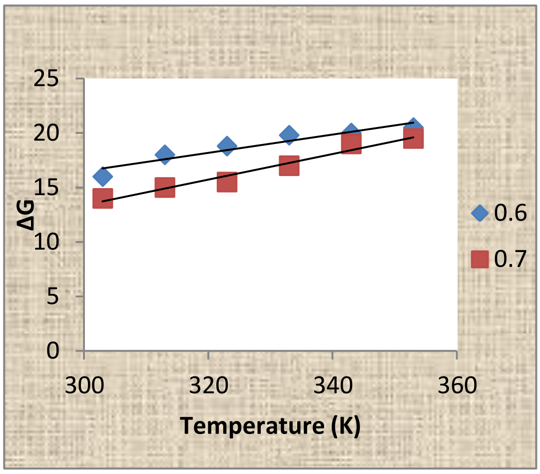


Figure 19

- ΔG Vs temp for CSS Extract in H_2SO_4

Table 9

Values of -ΔG, ΔH And ΔS of MS In various concentration of CSS in HCl medium

S.No	Conc of inhibitor V/V (%)	Free energy of adsorption -ΔG (kJ/mol)						Change in entropy ΔS kJ/mol	Change in enthalpy ΔH kJ/mol
		303K	313K	323K	333K	343K	353K		
1	BLANK	-	-	-	-	-	-	-	-
2	0.1	18.70	16.23	18.42	18.47	16.91	19.86	-0.214	16.67
3	0.2	17.10	15.18	18.11	19.17	18.03	21.21	-0.154	15.55
4	0.3	17.09	14.31	18.11	18.42	16.97	20.32	-0.034	15.28
5	0.4	18.47	14.56	18.05	18.02	17.48	19.90	0.165	14.51
6	0.5	18.09	13.98	18.51	19.27	17.18	19.73	0.111	14.89
7	0.6	17.73	13.94	18.16	18.87	17.33	19.29	-0.285	16.41
8	0.7	17.90	14.34	18.43	18.90	17.95	19.59	0.119	14.84

Table 10

Values of -ΔG, ΔH And ΔS of MS in various concentration of CSS in H_2SO_4 medium

S.No	Conc of inhibitor V/V (%)	Free energy of adsorption -ΔG (kJ/mol)						Change in entropy ΔS kJ/mol	Change in enthalpy ΔH kJ/mol
		303K	313K	323K	333K	343K	353K		
1	BLANK	-	-	-	-	-	-	-	-
2	0.1	15.72	16.26	13.48	15.68	15.05	16.37	-1.54	10.67
3	0.2	15.74	28.34	15.43	17.48	11.42	16.69	-1.33	11.91
4	0.3	16.51	18.28	16.22	17.40	20.39	17.46	-1.42	12.64
5	0.4	15.96	18.92	15.89	11.09	20.32	17.18	-1.25	12.75
6	0.5	17.38	18.64	14.87	11.09	20.23	16.53	-0.78	13.31
7	0.6	16.92	18.21	14.87	16.35	21.01	16.62	-0.74	13.90
8	0.7	16.75	17.97	14.97	11.09	20.57	16.87	-0.84	13.72

4.4 ELECTROCHEMICAL MEASUREMENTS:

Linear polarization measurements, Tafel intercept method and Electrochemical impedance measurements are carried out for mild steel acid corrosion in the presence of CSS extract. Electrochemical studies are helpful to predict the nature of inhibitor anodic, cathodic or mixed type and to 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) are recorded in **Table 11**.

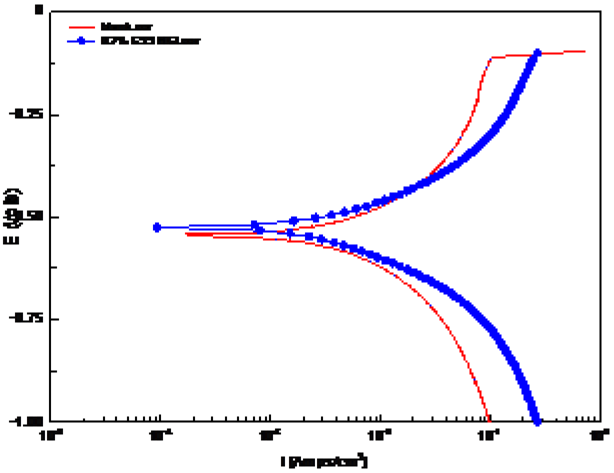


Figure 20 Potentiodynamic polarization plots for MS in 1M HCl in the presence and absence of CSS extract

From the table, it can be inferred that the values of corrosion current density I_{corr} decreases 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) change with increasing concentration of the extract. Potentiodynamic curves of mild steel in 1M HCl in the presence of CSS extract are recorded in **Figure (20)**.

Increase in R_p value with increase in concentration of the inhibitor under study indicates the effective inhibitive action of the CSS extract. The maximum inhibition efficiency using R_p values was found to be 80 %.

Table 11 Electrochemical polarization parameters for the corrosion of MS in the presence of CSS extract in 1M HCl

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 (%)
1	Blank	-544	5173	217	187	-	7	-
2	0.7	-515	357	72	63	93	35	80

From the above experimental results the following conclusion can be drawn.

- Values of E_{corr} indicate that the CSS extract behaves as mixed type inhibitor
- Values of b_a and b_c indicate, the extract is acting as mixed type by controlling the cathodic hydrogen evolution as well as anodic metallic dissolution.

  Decrease in I_{corr} values and increase in R_p values with increase in concentration of CSS extract revealed that the inhibition process is taking place by adsorption of the extract on mild steel.

- Inhibition efficiency calculated using I_{corr} and R_p indicate that inhibition efficiency increase with increase in concentration of the extract and maximum inhibition efficiency was found to be 80 % using R_p values and 93 %using I_{corr} values.

4.4.1 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Electrochemical impedance spectroscopy is sophisticated technique and it is an important tool to study the mechanism of inhibition process. Nyquist representation of the impedance with and without the addition of CSS is given in **Figure 21**. The Nyquist plots are depressed semi circles with centres below the real axis. This indicates that the corrosion process is charge transfer controlled. The corrosion parameters obtained are presented in **Table 12**.

The inhibitor efficiency was calculated using the relationship

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

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

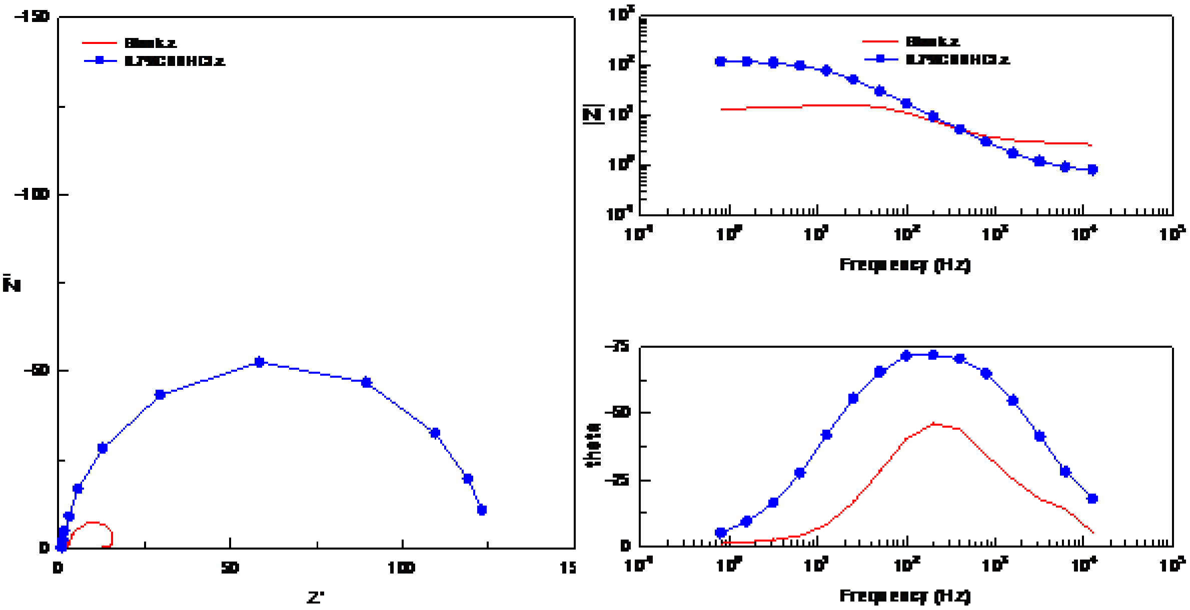


Figure 21 Impedance plots in Nyquist and Bode format for MS in 1M HCl in the presence and absence of CSS extract

TABLE 12

R_{ct}, C_{dl}, &IE of MS in presence of CSS extract in 1M HCl

Sl.no	Concentration (%)	R_{ct} (Ω cm^2)	IE (%)	C_{dl} (F/cm^2)	θ
1	**Blank**	**11**	**-**	**18**	**-**
2	**0.7**	**129**	**91**	**09**	**0.5**

Maximum inhibition efficiency using R_{ct} values was found to be 91% at 0.7%. Concentration values of C_{dl} decreases with increase in concentration of the extract indicate that the inhibition is taking place through adsorption process.

4.4.2 ELECTROCHEMICAL MEASUREMENTS CSS in 0.5M H_2SO_4:

The polarization behaviour of mild steel in 0.5M H_2SO_4containing different concentrations of is shown in Fig. Electrochemical parameters - corrosion current (E_{corr}), current density (I_{corr}), Tafel slope constants (b_a and b_c) , Linear polarization resistance (R_p) extracted from these curves are given in **Table 13**.

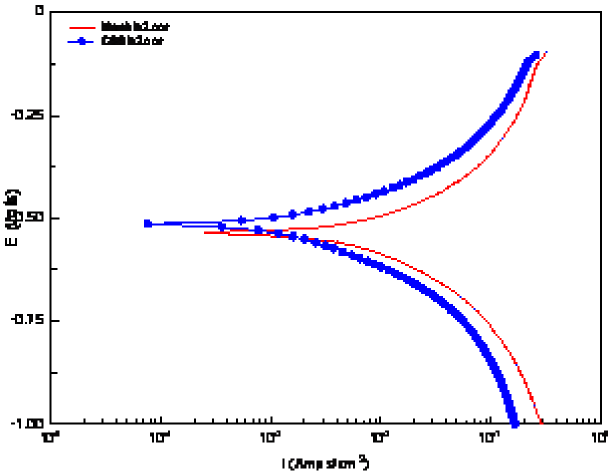


Figure 22 Potentiodynamic polarization plots for MS in 0.5M H_2SO_4 in the presence and absence of CSS extract

Table 13 Electrochemical Polarization Parameters for the corrosion of MS in the presence of CSS extract in 0.5 M H_2SO_4

S.No	Conc v/v(%)	$-E_{corr}$ mV/SCE	I_{corr} μA/cm²	b_a mV/dec	b_c mV/dec	IE (%)	R_p (Ω/cm²)	IE (%)
1	Blank	-531	5340	90	135	-	5	-
2	0.7	-513	1108	121	123	79	16	68

From the table, it can be inferred that the CSS extract bring down I_{corr} value at all concentrations suggesting that CSS extract are effective corrosion inhibitors. Moreover, it can be seen that CSS extract doesn't cause a significant shift in E_{corr} values indicating that it acts as a mixed type inhibitor in 0.5MH_2SO_4. The values of Tafel slopes (b_a and b_c) change with increasing concentration of the extract.

Increase in R_p value with increase in concentration of the inhibitor under study indicates the effective inhibitive action of the CSS extract. The maximum inhibition efficiency using R_p values was found to be 68 % .The values of R_p increases with increase in concentration of the extract. Inhibition efficiency calculated using I_{corr} and R_p indicate that inhibition efficiency increase with increase in concentration of the extract and maximum inhibition efficiency was found to be 68 % using R_p values and 79 % using I_{corr} values.

4.4.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Electrochemical impedance spectroscopy is sophisticated technique and it is an important tool to study the mechanism of inhibition process. Nyquist representation of the impedance with and without the addition of CSS is given in **Figure 23**. The corrosion parameters obtained are presented in **Table 14** . It is apparent from these plots that the impedance in all cases corresponds to a capacitive loop. The semicircle diameters depend on the concentration and they increase with increasing of concentration. This indicates that the impedance of inhibited substrate increases with increasing inhibitor concentration and consequently the inhibition efficiency increases.

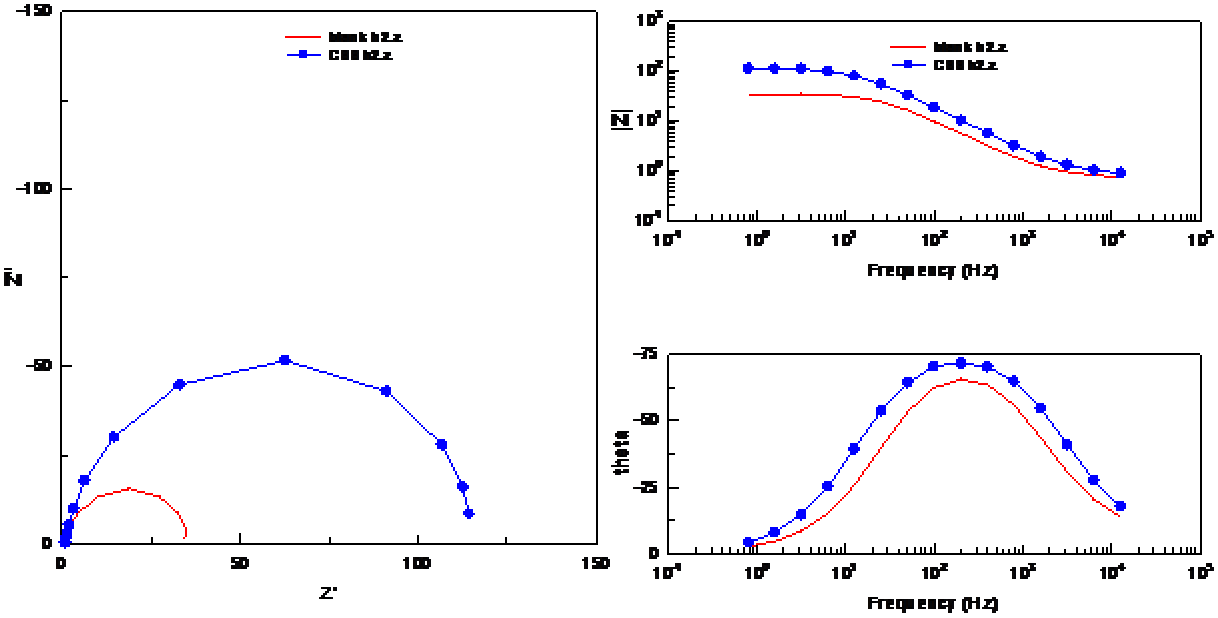


Figure 23 Impedance plots in Nyquist and Bode format for MS in 0.5M H_2SO_4 in the presence and absence of CSS extract

Table 14

R_{ct}, C_{dl}, & IE of MS in presence of CSS extract in 0.5M H_2SO_4

S.No	Concentration (%)	R_{ct} (Ωcm^2)	IE (%)	C_{dl} (f/cm^2)	θ
1	**Blank**	**32**	**-**	**17**	**-**
2	**0.7**	**108**	**70**	**10**	**0.4117**

However, the addition of inhibitor improves R_{ct} values and brings down C_{dl} values. These observations clearly bring out the fact that the corrosion of mild steel in 1M HCl is controlled by a charge transfer process and the corrosion inhibition occurs through the adsorption CSS on mild steel surface. Decrease in the C_{dl} values, with can result from a decrease in local dielectric constant and/or an increase in corrosion current density, the thickness of the electrical double layer, suggested that the molecules function by adsorption at the metal-solution interface .Maximum inhibition efficiency using R_{ct} values was found to be 70 % at 0.7%. Concentration values of C_{dl} decreases with increase in concentration of the extract indicate that the inhibition is taking place through adsorption process. This confirms that the plant constituents are adsorbed on the metal surface resulting in decrease in double layer capacitance. The increasing charge transfer resistance R_{ct} values imply reduced corrosion rate in the presence of the plant extract. This confirms that the plant extract show good corrosion inhibition efficiency in 0.5M H_2SO_4.

4.5 PERFORMANCE EVALUATION OF CSS EXTRACT USING CONVENTIONAL MASS LOSS METHOD AND ELECTROCHEMICAL MEASUREMENTS

Performance evaluation of CSS extract using mass loss and electrochemical methods are pictorially represented in **Figure 24**. The CSS extract was found to have a significant protective effect in 1M HCl but it is lower in 0.5M H_2SO_4. The inhibitive ability of CSS in 1M HCl is greater than that in 0.5M H_2SO_4 which implies that the adsorption of inhibitor could be influenced by the nature of anions in acidic solutions. It is well known that Cl- ions have stronger tendency to adsorb than do SO_4^{2-} ions and the electrostatic influence on the inhibitor adsorption may be the reason for an increased protective effect in halide containing solution **(Bentiss *et al*, 2002)** Moreover the lesser interference of SO_4^{2-} ions with the adsorbed protonated cations may lead to lower adsorption **(Umoren et al, 2008)**. So the adsorption of investigated inhibitors on steel surface in 1M HCl solution is stronger than that in 0.5M H_2SO_4 solution, which leads to higher inhibition performance in HCl than that in H_2SO_4.

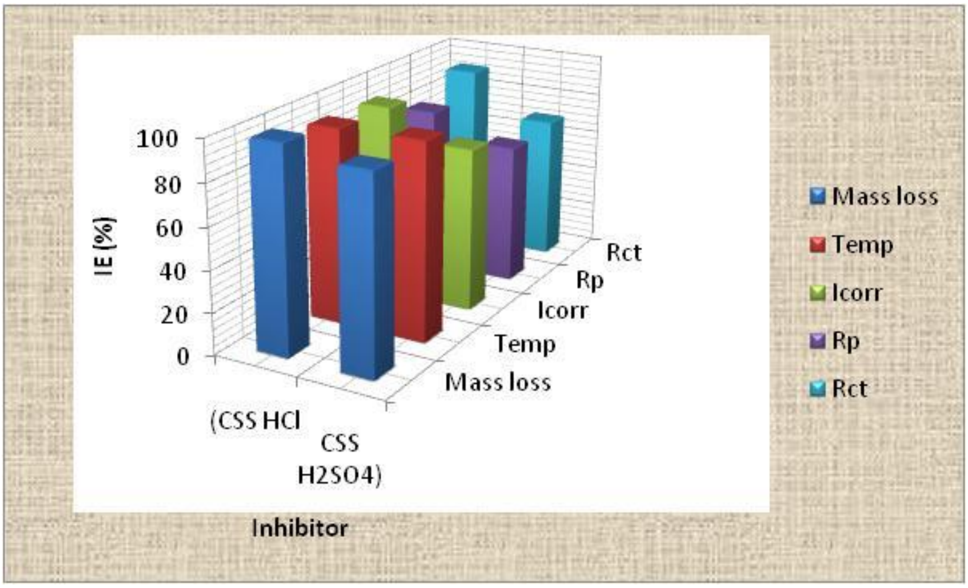


Figure 24 Performance evaluation of CSS extract using mass loss and electrochemical methods

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 weight 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.

4.6 SURFACE ANALYSIS

4.6.1 FT- IR SPECTRAL ANALYSIS

Table 15 IR spectrum of (a) acid extract of concentrates (b) adsorbed material of MS in the presence of HCl extract of CSS as an inhibitor

Powdered Plant material			**Corrosion product of**		
Frequency cm^{-1}	**Assignment**	**Functional Groups**	**Frequency** cm^{-1}	**Assignment**	**Functional Groups**
3356	OH stretch	Alcohol	3441.01	O–H stretch, H–bonded	1°, 2° amines, amides
2924.09	C–H stretch	Alkanes	2947.23	C–H stretch	Alkanes
-	-	-	-	-	-
2376.30	-C≡N stretch	Aliphatic amines	2314.58	–C ≡N stretch	Aliphatic amines
1627.92	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers	1689.64	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers
1427.32	C–H bend	Aliphatic amines	1527.62	C-C in ring	aromatics
1327.03	C–O-C stretch	Ethers	1404.18	C–H bend	Aliphatic amines
1249.87	C-O stretch	carboxylic acids	-	-	-
1064.71	C-O stretch	carboxylic acids	1033.85	C-O stretch	carboxylic acids
779.24	O–H bend	Alcohols	779.24	O–H bend	alcohols
			671.23	- γ -Fe_2O_3	-

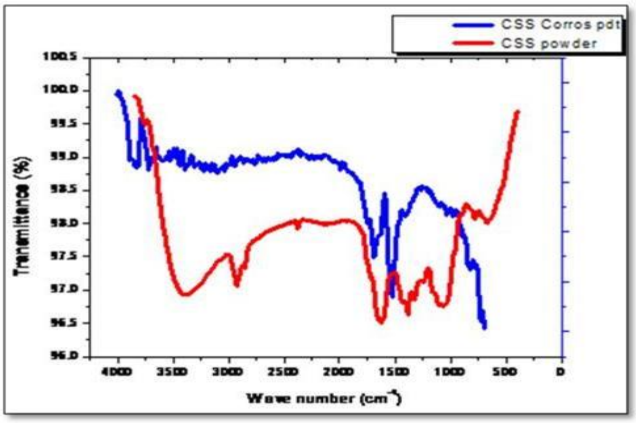
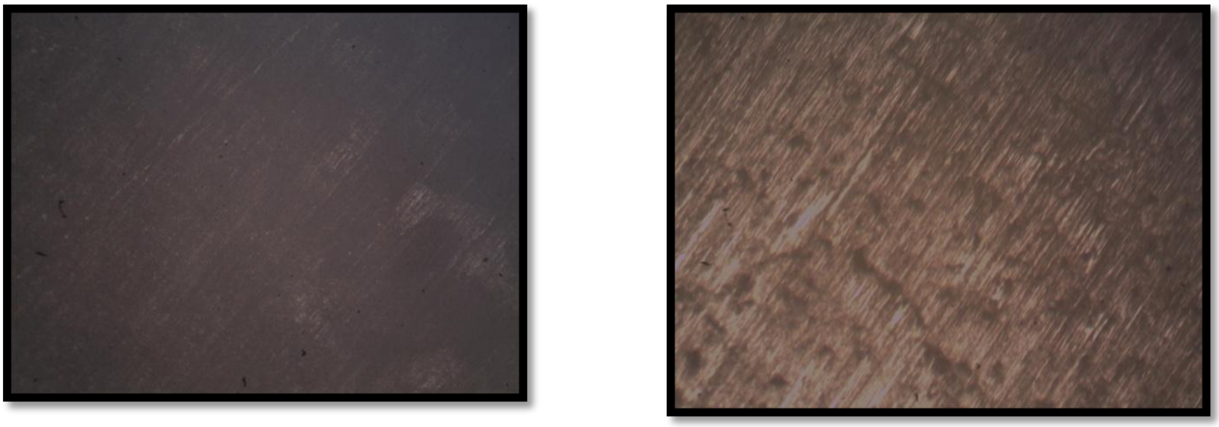


Figure 25 IR spectrum of CSS extract and corrosion products in 1M HCl

In the presence of the inhibitor, IR spectrum of the corrosion product **(Figure 25)** revealed that the –OH stretch (3356cm^{-1}) was shifted from 3441.56 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 2947.23 cm^{-1}. From the Figure(a & b) 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 CSS absorption shifts of –C ≡ N stretch (2376.30cm^{-1} to2314.58 cm^{-1}), C-H bend (1427.32cm^{-1} to 1527.62cm^{-1}) and C-Ostretch (1064.71cm^{-1} to 1033.85 cm^{-1}). The shift in the absorption frequencies of the inhibitor on the metal surface strongly supports the interaction between the phytochemical compounds of the inhibitor and metal surface. The band at 450 cm^{-1}to 700 cm^{-1}probably originates mainly from γ -Fe_2O_3 (670.07cm^{-1}). Some missing bonds are there in corrosion products indicating that there is interaction (Fe- complex formation) between the leaves extract of and the surface of mild steel.

4.6.2 OPTICAL ELECTRON MICROSCOPY

An optical electron microscope was used to evaluate the change in surface caused by contact with the acid solutions and to monitor the effect of adding the inhibitor. The optical electron micrographs of the mild steel in the initial state after pickling with HCl and in the presence of inhibitor is shown in **Figure 26 b** and **Figure 26 c**. Initial MS micrograph was smooth with grains**.** Due to the exposure of mild steel to the acid, (**Figure 26 b)** pits were formed on the surface. In the micrographs and the pits disappeared in the presence of inhibitor. This is due the presence of adsorbed layer of inhibitor molecules. Therefore it can be concluded that corrosion does not occur in the presence of inhibitor and hence corrosion was inhibited strongly when the inhibitor is present in acid media (**Keera, 2003**).



(a) PHOTO MICRO GRAPH OF MS

(b) PHOTO MICRO GRAPH OF MS IN THE PRESENCE OF HCl

(c) PHOTO MICRO GRAPH OF MS IN CSS/ 1M HCl

Figure 26

4.7 MECHANISM OF INHIBITION

To understand the mechanism of inhibition, the adsorption behaviour of the organic adsorbates on the on the metal surface must be known. The surface coverage (θ) values were evaluated from weight loss values. The θ values for different concentrations of inhibition were tested graphically by fitting into Langmuir and Temkin adsorption isotherm.

As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitor at the metal-solution interface is the first step in the mechanism of action of inhibitor in aggressive media. Four types of adsorption may take place involving organic molecules at the metal- solution interface.

∗ Electrostatic interaction between charged molecule and charged metal.

∗ Interaction of unshared electron pairs in the molecule with the metal.

- Interaction of the p electrons with the metal.

- Combination of the above **(Paul Schweinsberg *et al.*,(1998)**

Phytochemical analysis from literature revealed that the main constituents are Sparsioamide , a new sphingolipid, sparsioside , a new diglyceride galactoside, **(Rashad Mehmood et al).**Crotosparsamide , a new cyclic nonapeptide, p-hydroxy methyl cinnamate , kaempferol , carbohydrate (reducing sugars), alkaloids, steroids, flavonoids, saponin & tannins

In the present study, the phytochemical constituents typically contain nitrogen, sulphur or oxygen in the system and corrosion inhibition occurs via adsorption on the constituents on the metal surface. Skeletal representation of adsorption of the inhibitor on MS is pictorially represented in **Figure 27**.The inhibitor act as the interface created by corrosion product between the corroded and the metal surface. Thus the formation of adsorbed layer between the metal surface and the phytochemical constituents of the plant extract for the inhibitive effect.

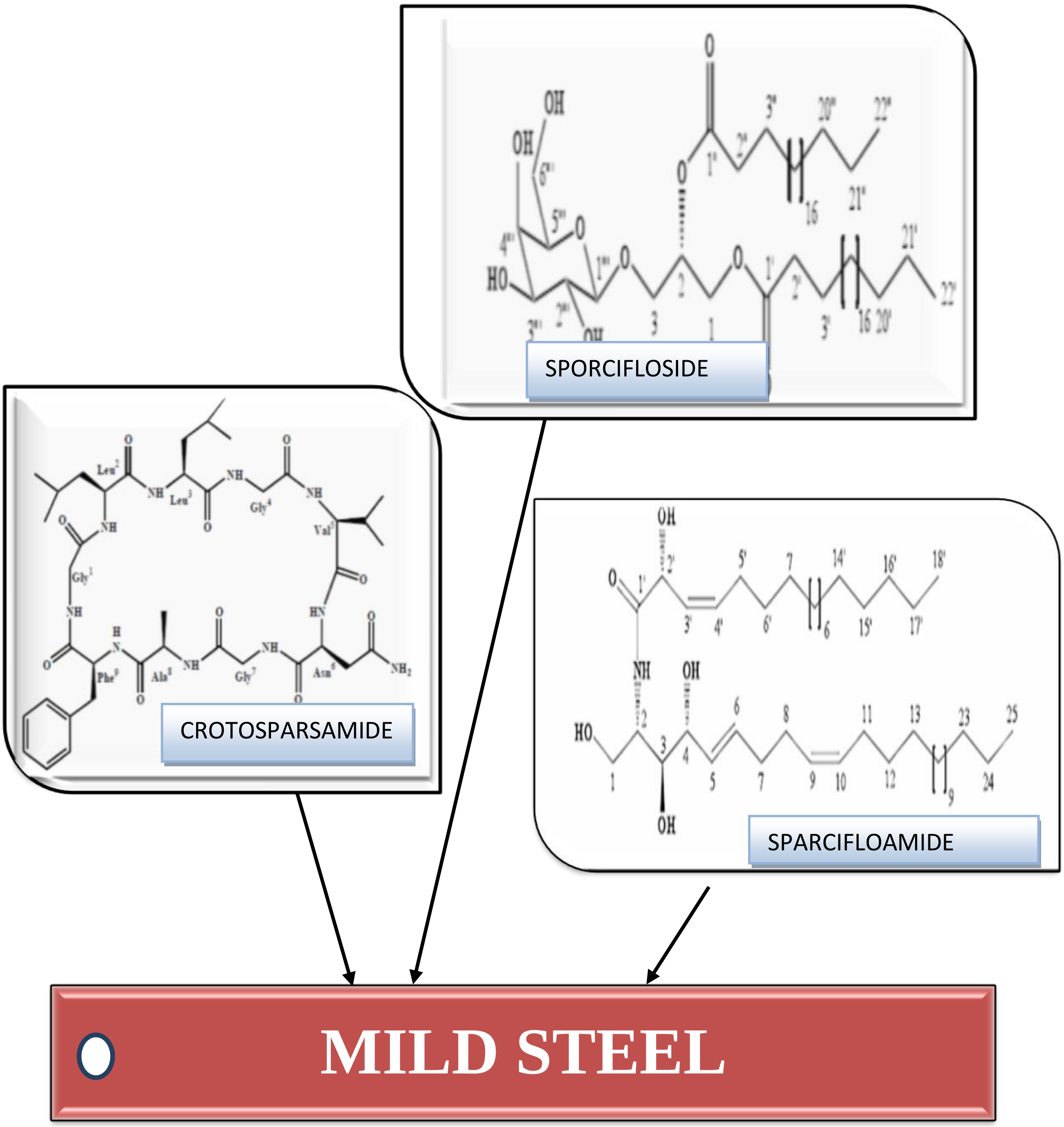


Figure 27 Skeletal representation of adsorption of inhibitor molecules of CSS on the surface of MS

SUMMARY & CONCLUSION

5. SUMMARY AND CONCLUSION

Metals and alloys are exposed to the acids in industries. A huge amount of HCl is used in the chemical industries for the removal of undesired scales and rust. The addition of corrosion inhibitors effectively secures the metal against an acid attack. Many studies in this regard using organic inhibitors have been reported. Most of the inhibitors are organic compounds with N, S and O having hetero atoms having higher electron density, making them the reaction centers. These compounds are adsorbed on the metallic surface and block the active corrosion sites. Most of them are highly toxic to both human beings and the environment. Hence, use of natural products as eco-friendly and harmless corrosion inhibitors.

Efforts have been taken to find out the inhibition efficiency of CSS on corrosion of mild steel in 1M HCl and 0.5M H_2SO_4 by mass loss and electrochemical techniques. The experiments were conducted to optimize the concentration of the inhibitors and time of exposure at room temperature and at high temperatures. To understand the nature of the adsorption process, thermodynamic and kinetic parameters were evaluated using temperature studies results. Experimental results were fitted into various adsorption isotherms. Electrochemical techniques-Linear polarization techniques, Tafel intercept method and electrochemical impedance spectroscopy was performed. The results obtained by Tafel, Linear polarization resistance and impedance spectroscopy have been correlated with the classical weight loss measurements. A possible mechanism of inhibition process was also suggested.

The results obtained during this investigation have been summarized as follows:

- A maximum of 99 % inhibition efficiency was obtained for 0.7% concentration of CSS.
- The CSS extract was temperature resistant. The inhibition efficiency of the extract increases with the concentration and temperature up to 313 K. After that a slight decrease is observed at 353 K.
- Thermodynamic parameters showed that the inhibition is due to spontaneous adsorption of inhibitor on the metal surface.

- Values of Tafel constant b_a and b_c confirm that the CSS extract act like mixed type inhibitor.

- The inhibitor was found to follow Langmuir and Temkin adsorption isotherm.
- Increase in R_p and R_{ct} values and decrease in I_{corr} and C_{dl} values confirm that CSS extract is adsorbed on the mild steel surface and inhibition process is by monolayer adsorption.
- CSS in HCl medium effectively inhibit the corrosion and prove to be a low cost inhibitor, biodegradable and environmentally friendly inhibitor.
- FTIR spectroscopic studies revealed that the phytochemical constituent of the plant extract was adsorbed on the surface resulting in the characteristic adsorption bands of the functional group in the plant extract.
- Cost effective, long-lasting and nontoxic to the environment

The present study revealed that the stem extract of *Croton sparsiflorus* play a major role in reducing the metal dissolution and protect the MS surface from corrosion.

BIBLIOGRAPHY

BIBLIOGRAPHY

- Abdel-Gaber A.M, Abd-El-Nabey.,B.A., Sidahmed.I.M,El-Zayady. A.M. and Saadawy M (2005),*Inhibitive action of some plant extracts on the corrosion of steel in acidic media*, CorrosionScience ,48 (9): 2765-2779.
- Abboud.A, ChagraouiA., TananeO., El BouariA. and HannacheH..,(2013),*Punica granatum* leave extract as green corrosion inhibitor for mild steelin Hydrochloric acid, MATEC Web of Conferences **5**.
- Aisha M. Al-Turkustani, Nabeeh M. Al-Marhabi.,(2012),Inhibition of Mild Steel Corrosion Using *Plectranthus Tenuiflorus (Shara)* Plant as Safe and Green Inhibitor inAcidic Solutions,Global Journal of Science Frontier Research Chemistry,Volume 12.
- Aisha M. Al- Turkustani, Sanaa T. Arab, Areej A. Al- Reheli.,(2010),Corrosion and Corrosion Inhibition of Mild Steel in H_2SO_4 Solutions by *Zizyphus Spina-Christi* as Green Inhibitor,International Journal of Chemistry,Vol. 2, No. 2.
- Ajanaku Kolawole Oluseyi, Ajanaku Christiana Oluwatoyin, Akinsiku Anuoluwa Abimbola, Falomo Ayorinde,Edobor-Osoh Abiola and John Oluwatosin Moriamo.,(2012),Eco-Friendly Impact of *Vernonia amygdalina*as Corrosion Inhibitor on Aluminium in Acidic Media,Chemistry Journal,Vol. 02, Issue 04, pp. 153-157.
- Ananth KumarS., SankarA., VijayanM., Ramesh KumarS..,(2013), *Oxystelma esculentum*Stem Extracts as Corrosion Inhibitor for Mild Steel in Acid Medium,International Journal of Modern Engineering Research,Vol. 3,pp-2456-2459.
- AnantakrishnanS. V., S. Aravamuthachari, V. S. GovindarajanA study of the constituents of the seeds of*croton sparsiflorus (Morung)*—Part II,) Proceedings of the Indian Academy of Sciences December 1941, Volume 14, Issue 6, pp 616-629.
- AnbarasiK., V. G. Vasudha.,(2014),Mild Steel Corrosion Inhibition by *Cucurbitamaxima*Plant Extract in Hydrochloric Acid Solution,Journal of Environironmental Nanotechnology.
- Ben Hmamou.D , Salghi .R, Zarrouk.A , Messali.M , Zarrok .H., Errami1M., HammoutiB. , Bazzi .Lh, Chakir.A.,Inhibition of steel corrosion in hydrochloric acid solution by *chamomile extract*,Der Pharma Chemica,4(4):1496-1505.

- ChauhanJ.S., Anita Dixitand D. K. Gupta.,Corrosion inhibition of Zn in HCL by *Nictanthes* plant extract,Asian Journal of Advanced Basic Science,1(1), 58-61**.**
- Di Geng .,Chemical Constituents from Euphorbia helioscopia 2011, Advanced Materials Research, 396-398, 133710.4028/www.scientific.net/AMR.396-398.1337.
- Durre Shahwar, Sami Ullah, Muhammad Asam Raza, Uzma Sana, Asma Yasmeen,Sadia Ghafoor and Naeem Ahmad.Acetylcholine esterase and antioxidant potential of some members of Asteraceae and Euphorbiaceae,Journal of Medicinal Plants Research Vol. 5(32), pp. 7011-7016, 30 December, 2011.
- Ebenso. E. E., Eddy. N. O.2 and Odiongenyi.A. O (2008), Corrosion inhibitive properties and adsorption behaviour of ethanol extract of *Piper guinensis* as a green corrosion inhibitor for mild steel in H_2SO_4 , African Journal of Pure and Applied Chemistry Vol. 2 (11), pp. 107-115.
- Eyad M. Nawafleh*, Tareq T. Bataineh, Muna K. Irshedat, Mahmoud A. Al-Qudah and Sultan T. Abu Orabi.,(2013),Inhibition of Aluminum Corrosion by *Salvia Judica* Extract,Research Journal of Chemical Sciences, Vol. 3(8), 68-72.
- Eddy. N. O., Odoemelam. S. A. and Odiongenyi. A. O., (2008) ,Ethanol extract of Musa Acuminate peel as an eco-friendly inhibitor for the corrosion of mild steel in sulphuric acid", Advances in natural and applied Sciences, 2(1): 35-42.
- Emeka E. Oguzie., (2005), "Studies on the inhibitive effect of Occimum viridis extract on the acid corrosion of mild steel", Materials Chemistry and Physics, Article in press, 99 (2-3): 441-446.
- Farooqi, I H, Quraishi, M A, Saini, P A, (1997), "Natural compounds as corrosioninhibitors for mild steel in industrial cooling systems" EUROCORR '97, 2 Trondheim; Norway: 247-252, 22-25.
- Ferreira AM, Carvalho MJ, Sequeira MM, Silva AM, Carvalho LH. Chemical constituents of Euphorbia hyberna L. (Euphorbiaceae)Nat Prod Res. 2013;27(3):282-5. Doi: 10.1080/14786419.2012.668688. Epub 2012 Mar 12.
- HemalathaJ., A. Sankar, S. Ananth Kumar, S. Ramesh Kumar.,(2013), *Nelumbo nucifera* flower extract as mild steel corrosion inhibitor in 1N H_2SO_4 medium, International Journal of Computer Engineering & Science,Volume 3, pp. 15-20 **.**2231–6590.

- Hemayet Hossain, Md. Sariful Islam Howlader, Shubhra Kanti Dey , Arpona Hira, Arif Ahmed, G.M.Z. Rahman,Ferdoushi Jahan, Antidiarrhoeal Activity and Total Tannin Content of Ethanolic Leaf Extract of *Croton Sparsiflorus*,J. Pharm. Bioanal. Sci., Volume 1, Issue 2, Oct-Dec 2012, 50-55 ISSN: 2278-828X
- Jassbi AR, Zamanizadehnajari S, Tahara S.Chemical constituents of Euphorbia marschalliana Boiss. Z Naturforsch C. 2004 Jan-Feb;59(1-2):15-8.
- JamesA.O. and O. Akaranta.,Corrosion inhibition of Aluminzium in 2M Sulphuric acid using Acetone extract of *Red Onion skin*, International Journal of Applied Chemical Sciences Research, Vol. 2, No. 1, PP: 1 -10.
- Krishnaveni.K, J.Ravichandran.,(2014),Effect of aqueous extract of leaves of *Morinda tinctoria* oncorrosion inhibition of aluminium surface in HCl medium,Trans. Nonferrous Met. Soc. China 24, 2704−2712.
- Lakshmi. S, Painkili. V, Ramachandran. J, Vimala. B, (*2006),* Inhibition of corrosion of mild steel in acid media by seed powder extract of *Brassica-Juncea-Cruciferae*, Bull. Electrochem., 22(1): 11-5.
- Minhaj.A., Saini.P.A., Quraishi.M.A., Farooqi.I.H, (1999), A study of natural compounds as corrosion inhibitors for industrial cooling systems, Corrosion prevention and control, 4:32-36,.
- Mohammed Ajmal,Jaya Rawat and M.A.Quraishi, (1998), Influence of *polyamide macrocyclic* compounds on the inhibition of corrosion of mild steel inacid solutions,Bulletin of electrochemistry ,14,6-7, 99-203.
- Mohd. Hazwan Hussin and Mohd. Jain Kassim., Electrochemical Studies of Mild Steel Corrosion Inhibition in Aqueous Solution by *Uncaria gambir* Extract,Journal of Physical Science,Vol. 21(1), 1–13.
- Mahir H. Majeed, Abdul-Wahab A. Sultan and Hussein H.Al-Sahlanee.,(2014) ,Corrosion inhibition of carbon steel in 1M HCl solution by *Ruta graveolens* extract,Journal of Chemical and Pharmaceutical Research,6(5): 996-1001.
- National Convention of Electrochem., 13-14.M. Sangeetha, S. Rajendran, J. Sathiyabama, A. Krishnaveni, P. Shanthy,N.Manimaran, B. Shyamaladevi.,(2011),Corrosion Inhibition by an Aqueous Extract of *Phyllanthus Amarus*,*Portugaliae Electrochimica Acta*,29(6), 429-444.
- Oguzie. E.E., (2005), “Inhibition of acid corrosion of mild steel by Telfaria

occidentalis” Pigment & Resin Technology, 34(6): 321 – 326.

- Onuegbu T. U., Umoh E.T., Onuigbo U. A , (February 2013),*Eupatorium Odoratus* As Eco-Friendly Green Corrosion Inhibitor Of Mild Steel In SulphuricAcid , International Journal Of Scientific & Technology Research Volume 2,Issue 2.
- Olusegun Sunday J., Adeiza Barnabas A, Ikeke Kingsley I. and Bodunrin M.O.,(2013),*Jatropha Curcas* Leaves Extract as Corrosion Inhibitor for Mild Steel in 1M Hydrochloric Acid,Journal of Emerging Trends in Engineering and Applied Sciences,4(1): 138-143.
- Parikh K. S., Joshi K. J., (2004). Use of *Henna & Babul*: Picking inhibitors for mild steel in 5% hydrochloric acid, Chemical engineering world, (39): 64-68 .
- Pruthviraj.R.D., Prakash.C.H, B.V.Somasheklariah.,(2013)**,**Mild Steel Corrosion Inhibition by Plant Extract in 0.1 M Hydrochloric Acid Solution,Scholars Journal of Engineering and Technology,1(3):169-171.
- PasupathyA., S.Nirmala, P.Sakthivel, G.Abiramiand M.Raja.,(2014),Inhibitive Action of *Solanum Nigrum* Extract on the Corrosion of Zinc in 0.5N HCl Medium, International Journal of Scientific and Research Publications,Volume 4.
- Quraishi. M.A, Dileep Kumar Yadav and Ishtiaque Ahamad(2009),Green Approach to Corrosion Inhibition by *Black Pepper* Extract in Hydrochloric AcidSolution. The Open Corrosion Journal, 2, 56-60.
- Ramananda Singh.M. A green Approach: *(2013),* A corrosion inhibition of mild steel by *Adhatoda vasica* plant extract in 0.5 M H_2SO_4*J.* Mater. Environ. Sci. 4(1) 119-126.
- Rashad MEHMOOD, Amna BIBI, Abdul New secondary metabolites from *Croton sparsiorus Morong* Turk J Chem (2013) 37: 110-111 Turkish Journal of Chemistry.
- Rosaline Vimala1J., A. Leema Rose, S. Raja.,*Cassia auriculata* extract as Corrosion inhibitor for Mild Steel in Acid medium,International Journal of ChemTech Research,Vol.3, No.4, pp 1791-1801.
- Sethuraman M.G., Ajesh T.P., and Vinodkumar K.P., (2001), The effect of *Solanum trilobatum* extract on the corrosion of mild steel in HCl medium,10th

- Sheyreese M. Vincent., Cyril B. Okhio., (2005),Inhibiting corrosion with *GreenTea*, Journal of Corrosion Science and Engineering, 7(36): 354-359.
- Subhashini. S., Rajalakshmi. R., Elakkiya. T., Srimathi. M., (2008), Evaluation ofextract of Ficus Benghalensis as corrosion inhibitor of mild steel in HCl mediumat different *pH.*, Ultra Chemistry, vol:4(2), pages: 159-164.
- Subhashini. S., Rajalakshmi. R. and Safina. A.S., (Dec 2008), Biodegradable aquatic waste-fish scales as corrosion inhibitor for mild steel in acid medium, Material Science Research India, Volume 5 No. 2 Page No. 375-382.
- SivarajuM, K. Kannan.,Inhibitive properties of plant extract (*Acalypha indica L.*) on mild steel corrosion in 1N Phosphoric acid, International Journal of ChemTech Research,Vol.2, No.2, pp 1243-1253.
- Saedah R. Al-Mhyawi.,Inhibition of mild steel corrosion using *Juniperus* plants as green inhibitior,African Journal of Pure and Applied Chemistry,Vol.8(1),pp.9-22.
- Tedjani Yahia Namoussaa , Segni Ladjela, Noureddine Gherrafa,b, Mohamed RidhaOuahrania.,(2010),Investigation of the Inhibitive Properties of the Aqueous Extract of *Tamarix gallica L* on the Corrosion of Mild Steel in H_2SO_4 Medium,Journal of Chemical Pharmaceutical Research,2(4):808-811.
- Yan Li, Peng Zhao,Qiang Liang and Baorong Hou., (2005), *Berberine* as a natural source inhibitor for mild steel in 1 M H_2SO_4, Applied Surface Science,252(5): 1245-1253