

**Assessment of *Croton sparsiflorus* leaves extract on Corrosion
of Mild Steel in 1M HCl**

Nandhini, S

(12PCH008)

Thesis submitted to

**Avinashilingam Institute for Home Science and Higher
Education for Women, University**

Coimbatore- 641043

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

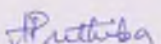
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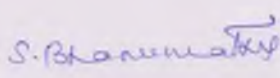
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**Signature of the
Supervisor**

 / 29. 8. 14
**Signature of the
Head of the Department**

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LIST OF ABBREVIATIONS

Θ	Surface coverage
E_{corr}	Corrosion potential
I_{corr}	Corrosion current
b_a	Anodic tafel slope
b_c	Cathodic tafel slope
R_p	Polarization resistance
R_{ct}	Charge transfer resistance
C_{dl}	Double layer capacitance
CR	Corrosion rate
IE	Inhibition Efficiency
MS	Mild steel
Mv	milli Volt
Conc.	Concentration
LPR	Linear Polarization Resistance
HCl	Hydrochloric acid
Mpy	mils per year
CSL	<i>Croton sparsiflorus</i> Leaves

JNTRODUCTION

1. INTRODUCTION

Corrosion is a common place occurrence, like the rusting and flaking of an old iron yard piece. Energy, often large amounts, is poured into winning the desired metals from their natural ores; manufacturing some metal products can be very costly. Corrosion causes deterioration of manufactured products, damaging their structure and ultimately rendering the product useless. Allowing corrosion is not cost efficient and can inhibit productivity; understanding and preventing corrosion is important for maintaining infrastructures and machinery or any products that face corrosion.

“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”.
(www.npl.co.uk/upload/pdf/basics-of-corrosion-control.pdt)



Fig.1 Rust



Fig.2 Rust on structural components

1.1 FACTORS INFLUENCING CORROSION REACTIONS

Factors Associated Mainly with the Metal

- ✚ Effective electrode potential of a metal in a solution

- ✚ Overvoltage of hydrogen on the metal
- ✚ Chemical and physical homogeneity of the metal surface
- ✚ Inherent ability to form an insoluble protective film.

Factors Which Vary Mainly with the Environment

- ✚ Hydrogen-ion concentration (pH) in the solution
- ✚ Influence of oxygen in solution adjacent to the metal
- ✚ Specific nature and concentration of other ions in solution
- ✚ Rate of flow of the solution in contact with the metal
- ✚ Ability of environment to form a protective deposit on the metal
- ✚ Temperature
- ✚ Cyclic stress (corrosion fatigue)
- ✚ Contact between dissimilar metals or other materials as affecting localized corrosion.




1.2 CONSEQUENCES OF CORROSION

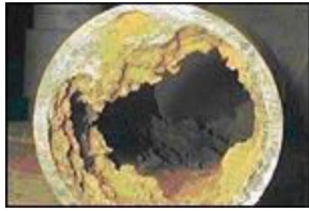
Some important consequences of corrosion are summarized below:

- ✚ Plant shutdowns. Shutdown of nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.
- ✚ Loss of products, leaking containers, storage tanks, and water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards. It is well known that at least 25% of water is lost by leakage.
- ✚ Loss of efficiency. Insulation of heat exchanger tubings and pipelines by corrosion products reduces heat transfer and piping capacity.
- ✚ Contamination. Corrosion products may contaminate chemicals, pharmaceuticals, dyes, packaged goods, etc. with dire consequences to the consumers.

- ✦ Nuclear hazards. The Chernobyl disaster is a continuing example of transport of radioactive corrosion products in water, fatal to human, animal and biological life.

1.3 DIFFERENT FORMS OF CORROSION:

Illustration	Form of Corrosion
	<p>Uniform Corrosion</p> <p>This is also called general corrosion. The surface effect produced by most direct chemical attacks (e.g., as by an acid) is a uniform etching of the metal.</p>
	<p>Galvanic Corrosion</p> <p>Galvanic corrosion is an electrochemical action of two dissimilar metals in the presence of an electrolyte and an electron conductive path. It occurs when dissimilar metals are in contact.</p>
	<p>Concentration Cell Corrosion</p> <p>Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution.</p>



Pitting Corrosion

Pitting corrosion is localized corrosion that occurs at microscopic defects on a metal surface. The pits are often found underneath surface deposits caused by corrosion product accumulation.



Crevice Corrosion

Crevice or contact corrosion is the corrosion produced at the region of contact of metals with metals or metals with nonmetals. It may occur at washers, under barnacles, at sand grains, under applied protective films, and at pockets formed by threaded joints.



Filiform Corrosion

This type of corrosion occurs on painted or plated surfaces when moisture permeates the coating. Long branching filaments of corrosion product extend out from the original corrosion pit and cause degradation of the protective coating.



Intergranular Corrosion

Intergranular corrosion is an attack on or adjacent to the grain boundaries of a metal or alloy.



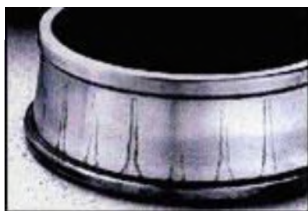
Stress Corrosion Cracking

Stress corrosion cracking (SCC) is caused by the simultaneous effects of tensile stress and a specific corrosive environment. Stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both.



Corrosion Fatigue

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion.



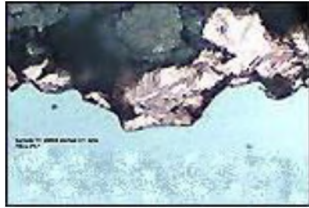
Fretting Corrosion

The rapid corrosion that occurs at the interface between contacting, highly loaded metal surfaces when subjected to slight vibratory motions is known as fretting corrosion.



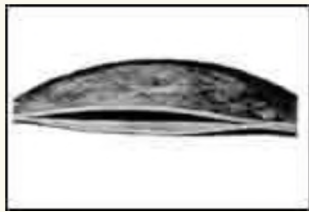
Erosion Corrosion

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities.



Dealloying

Dealloying is a rare form of corrosion found in copper alloys, gray cast iron, and some other alloys. Dealloying occurs when the alloy loses the active component of the metal and retains the more corrosion resistant component in a porous "sponge" on the metal surface.



Hydrogen Damage

Hydrogen embrittlement is a problem with high-strength steels, titanium, and some other metals. Control is by eliminating hydrogen from the environment or by the use of resistant alloys.



Corrosion in Concrete

Concrete is a widely-used structural material that is frequently reinforced with carbon steel reinforcing rods, post-tensioning cable or prestressing wires. The steel is necessary to maintain the strength of the structure, but it is subject to corrosion.



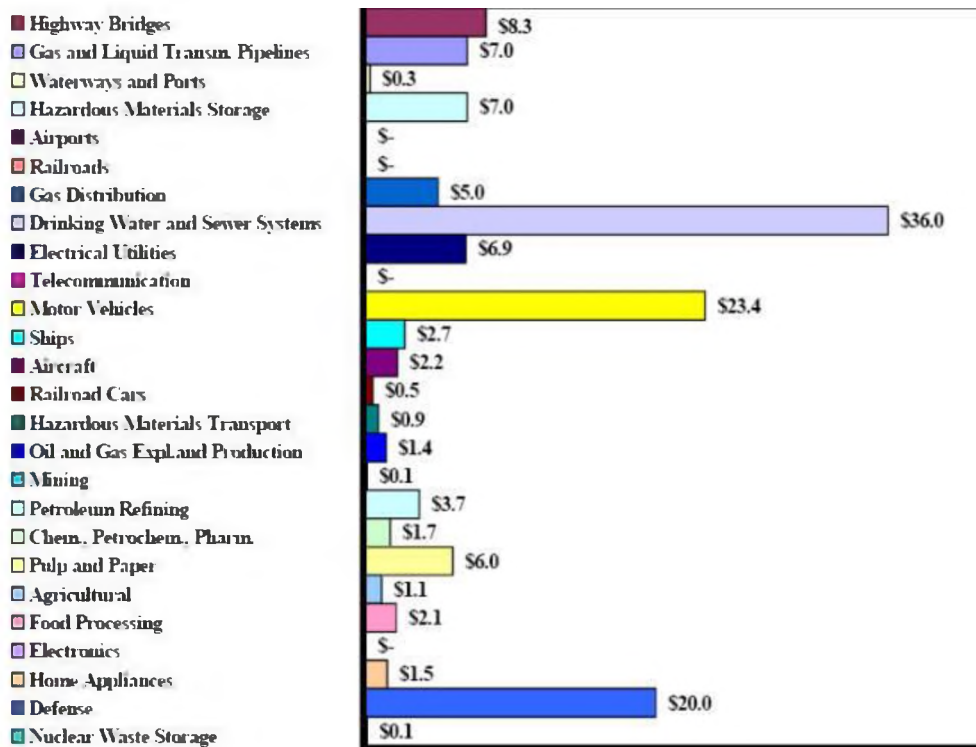
Microbial Corrosion

Microbial corrosion (also called microbiologically -influenced corrosion or MIC) is corrosion that is caused by the presence and activities of microbes. This corrosion can take many forms and can be controlled by biocides or by conventional corrosion control methods.

1.4 CORROSION COST TO SOCIETY

Corrosion is recognized as one of the most serious problems in our modern societies and the resulting losses each year are in hundreds of billions of dollars. Cost of corrosion studies have been undertaken by several countries including, the United States, the United Kingdom, Japan, Australia, Kuwait, Germany, Finland, Sweden, India, and China.

A recent report describes the annual direct and indirect costs of metallic corrosion in the United States and preventive strategies for optimum corrosion management. The total direct cost of corrosion is estimated at \$276 billion per year, which is 3.1 percent of the 1998 U.S. gross domestic product (GDP). This cost was determined by analyzing 26 industrial sectors, in which corrosion is known to exist, and extrapolating the results for a nationwide estimate. The sectors were divided among five major categories.([corrosion doctors org/principles/cost.htm](http://corrosion.doctors.org/principles/cost.htm))



\$ = Billion 1998 dollars

1.4.1 DIRECT COSTS

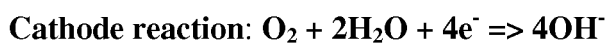
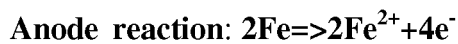
- ✘ Infrastructure \$22.6 billion
- ✘ Utilities \$47.9 billion
- ✘ Transportation \$29.7 billion
- ✘ Production and Manufacturing \$17.6 billion
- ✘ Government \$20.1 billion
- ✘ Total: \$137.9 BILLION

1.4.2 INDIRECT COSTS

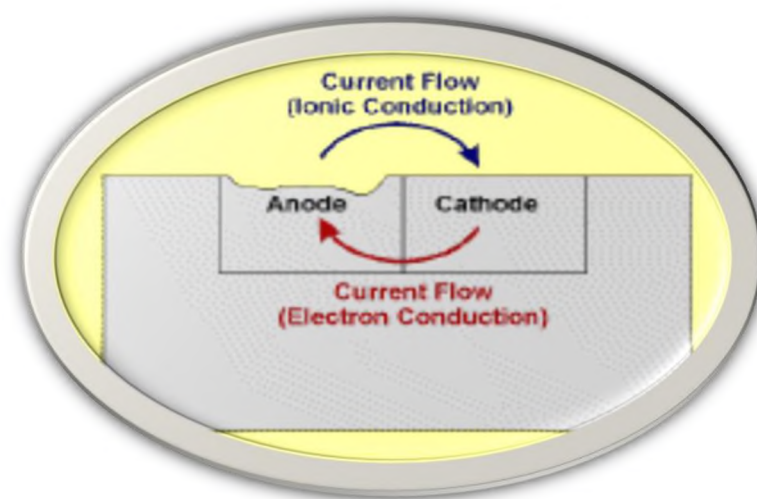
- ✘ Cost of labor attributed to corrosion management activities
- ✘ Cost of the equipment required because of corrosion-related activities
- ✘ Loss of revenue due to disruption in supply of product
- ✘ Cost of loss of reliability
- ✘ Grand Total: \$275.5 BILLION

1.5 ELECTROCHEMICAL CORROSION THEORY

Electrochemical corrosion involves two half-cell reactions; an oxidation reaction at the **anode** and a reduction reaction at the **cathode**. For iron corroding in water with a near neutral pH, these half-cell reactions can be represented as:



There are obviously different anodic and cathodic reactions for different alloys exposed to various environments. These half-cell reactions are thought to occur (at least initially) at microscopic anodes and cathodes covering a corroding surface. Macroscopic anodes and cathodes can develop as corrosion damage progresses with time.



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

From the above theory it should be apparent that there are four fundamental components in an electrochemical corrosion cell:

- ✚ An anode
- ✚ A cathode.
- ✚ A conducting environment for ionic movement (electrolyte).
- ✚ An electrical connection between the anode and cathode for the flow of electron current.

If any of the above components is missing or disabled, the electrochemical corrosion process will be stopped. Clearly, these elements are thus fundamentally important for corrosion control.

1.6 CORROSION CONTROL METHODS

There are four basic methods for Corrosion Control & Corrosion Protection.

- 1. Materials resistant to Corrosion**
- 2. Protective coatings**
- 3. Cathodic protection**
- 4. Corrosion Inhibitors**

In most cases, effective corrosion control is obtained by combining two or more of these methods. Corrosion control should be considered at the design stage of a given facility or system. The methods selected must be appropriate for the materials used, for the configurations, and for the types and forms of corrosion which must be controlled.

1.6.1 MATERIALS RESISTANT TO CORROSION.

There are no materials that are immune to corrosion in all environments. Materials must be matched to the environment that they will encounter in service. Corrosion Resistance Data are used to assess the suitability of a material in an environment.

1.6.2 PROTECTIVE COATINGS:

Protective coatings are the most widely used corrosion control technique. Essentially, protective coatings are a means for separating the surfaces that are susceptible to corrosion from the factors in the environment which cause corrosion to occur. Remember, however, that protective coatings can never provide 100 percent protection of 100 percent of the surface. If localized corrosion at a coating defect is likely to cause rapid catastrophic failure, additional corrosion control measures must be taken. Coatings are particularly useful when used in combination with other methods of corrosion control such as cathodic protection or galvanic corrosion.

1.6.3 CATHODIC PROTECTION

Cathodic protection interferes with the natural action of the electrochemical cells that are responsible for corrosion. Cathodic protection can be effectively applied to control corrosion of surfaces that are immersed in water or exposed to soil.

Cathodic protection in its classical form cannot be used to protect surfaces exposed to the atmosphere. The use of anodic metallic coatings such as zinc on steel (galvanizing) is, however, a form of cathodic protection, which is effective in the atmosphere.

1.6.4 CORROSION INHIBITORS

A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rates of a material, typically a metal or an

alloy. Just as some chemical species (e.g., salt) promote corrosion, other chemical species inhibit corrosion. Chromates, silicates, and organic amines are common inhibitors. The mechanism of inhibition can be quite complex. In the case of the organic amines, the inhibitor is adsorbed on anodic and cathodic sites and stifles the corrosion current. Other inhibitors specifically affect either the anodic or cathodic process. Still others promote the formation of protective films on the metal surface.

The use of inhibitors is favored in closed systems where the necessary concentration of inhibitor is more readily maintained. A useful method to protect metals and alloys deployed in service in aggressive environments against corrosion is addition of organic or inorganic species to the solution as corrosion inhibitors in contact with the surface in order to inhibit the corrosion reaction and hence reduce the corrosion rate (I. U. Anozie et al., 2011). Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. Inhibitors are added to many systems, namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, and so forth (Ambrish Singh 2012).

Acid pickling is an accepted treatment of a metallic surface to remove impurities, stains, steel rust, with an acid solution such as hydrochloric acid, (HCl) and sulphuric acid, (H₂SO₄), usually before subsequent processing such as extrusion, rolling, painting, galvanizing or plating with zinc, aluminum, etc. However, inhibitor application is required since the corrosive media impairs the metal used (Herbert H. Uhlig 1979), (Ramses Garcia Inzunza).

1.7 IMPORTANCE OF GREEN INHIBITOR

The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that are biocompatibility in nature, environmentally acceptable, readily available and renewable source. Due to bio-degradability, Eco

friendliness, low cost and easy availability, the extracts of some common plants based chemicals and their by-products have been tried as inhibitors for metals under different environments (Abdel-Gaber *et al.* 2006, Ebenso and Ekpe 1996, Ebenso *et al.* 2004, Ekpe *et al.* 1994, Kliskic *et al.* 2000).

Green corrosion inhibitors can be grouped into two categories, namely organic green inhibitor and inorganic green inhibitors. Molecular structure of inhibitor is the main factor determining its characteristics. Presence of hetero atom (S, N, and O) with free electron pairs, aromatic rings with delocalized π -electrons, high molecular weight alkyl chains, substituent group in general improves inhibition efficiency. It is noticed that organic compounds show higher inhibition efficiency as compared to inorganic.

1.8 SELECTION PROCESS OF GREEN CORROSION INHIBITORS

In addition to corrosion inhibition, an important aspect to be considered in the selection process is the effects on the use and discharge of chemicals to health, safety and the environment. Literature study shows that green corrosion inhibitor with minimum or no health and environmental hazards which is applicable to wide range of metals and various environmental conditions is to be discovered or invented.

1.9 *Croton sparsiflorus*- PLANT PROFILE

The genus *Croton* (Euphorbiaceae) comprises well over 1300 species growing as trees, shrubs, and herbs in tropical and subtropical regions of both hemispheres. Its various species are reported to possess diverse medicinal properties. One of its species is *Croton sparsiflorus* Morong, which is a woody shrub growing in sandy clay soil in Asia and South America. In Pakistan it grows in the Punjab and Sind provinces. It is used as a potent hypotensive agent and for the treatment of a variety of ailments like fever, inflammation, hypertension, and it causes sharp fall in blood pressure.

PLANT PROFILE



Scientific classification

Kingdom: Plantae

(unranked) : Angiosperms

(unranked): Eudicots

(unranked): Rosids

Order : Malpighiales

Family : Euphorbiaceae

Subfamily: Crotonoideae

Tribe : Crotoneae

Genus : Croton

Phytochemical constituents in *C.sparsiflorus*

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.

1.10 OBJECTIVES:

- To select an eco-friendly, cost effective, naturally occurring plant material as corrosion inhibitor for mild steel in HCl.
- Utilization of the naturally occurring plant source namely *Croton sparsiflorus* leaves (CSL) as inhibitor for the present study.
- To evaluate the corrosion studies of mild steel in 1 M HCl at room temperature and higher temperature using the classical weight loss method.
- To determine the corrosion inhibitive property of CSL exerted on mild steel in 1 M HCl by varying the concentration, time of immersion and temperature.
- 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 weight 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.

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

Thus a new branch of environmental chemistry has emerged which provides environmental friendly corrosion inhibitors specifically termed as 'Green inhibitors'. Green inhibitors are non-toxic, biodegradable and eco-friendly, and have proven effective in controlling the corrosion of steel, stainless steel, mild steel, iron, aluminum, copper, and 2024-T3 Aluminum alloy, steel in concrete structures, carbon steel, AA5083 Al-Mg alloy, nickel and zinc. The inhibitive effect of some plants solution extract is due to the adsorption of phytochemical molecules present in the plant on the surface of the metal which protects the metal surface and thus do not permit the corrosion process to take place.

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

- **Maheswari et al., (2001)** reported the inhibitive effect of acid extracts of flowers and leaves of *Thespesia Populnea* on the corrosion of mild steel in 1M HCl. The mass loss method and potentiostatic studies revealed the effectiveness of the extract. An efficiency of 94.87% was found for 0.35% extract at 333K.
- **Prithiba et al., (2002)** evaluated the effective inhibition of *Ervatamia coronaria* leaves extract on the corrosion of mild steel in 1M HCl and 0.5M H₂SO₄ at ambient temperature. Mass loss and potential measurement techniques have been used. The inhibitor efficiency increased with the concentration of the extract and the system obeyed Langmuir adsorption isotherm.
- **Oguzie, (2005)** studied the inhibition of acid corrosion of mild steel by *Telfaria occidentalis* extract in 2 M HCl and 1?M H₂SO₄ solutions. Inhibition efficiency increased with extract concentration but decreased with rise in temperature. Synergistic effects increased the efficiency of the extract in the presence of halide additives in the order KCl<KBr<KI. Result found that the environmentally friendly inhibitor could find possible applications in metal surface anodising and surface coatings.
- **Emeka E et al, (2005)** studied the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel in 2 M HCl and 1 M H₂SO₄ by using the gasometric technique at temperatures of 30 and 60 °C. The results indicate that the extracts inhibit the corrosion process in both acid media and inhibition efficiency increased with concentration.
- The inhibitive effect of cocoa (*Theobroma Cacao*) and kolanut (*Cola acuminata*) extracts on the corrosion of mild steel in seawater at room temperature has been evaluated by **Umoru et al.,(2006)** .The study was carried out using the gravimetric technique. The results showed kola and cocoa leaves extracts as potential inhibitors of mild steel corrosion in seawater and marine

environment. The highest inhibition efficiency was obtained when the concentration of the inhibitors were increased up to optimum. The results reveal a sign of synergism when 4% of each of the extracts were used to inhibit corrosion in the seawater.

- **Bouyanzer et al., (2006)** analyzed the inhibition of the corrosion of mild steel in molar hydrochloric acid solution by natural oil extracted from *Pennyroyal Mint* (*Mentha pulegium*) using weight loss measurement, electrochemical polarization and EIS methods. The inhibition efficiency was found to increase with oil content to attain 80% at 2.76g/L. Pennyroyal Mint oil acted as a cathodic inhibitor.
- **Subha et al.,(2006)** evaluated the influence of *Calendula officinalis* towards the corrosion of mild steel in 1M HCl by weight loss method and polarization technique. The results showed that the inhibition efficiency 94.67% was found at 5% concentration of the inhibitor after 2 hours.
- 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 in 5% and 15% HCl with addition of plant extract was studied in the temperature range 50-80⁰ C. Inhibition efficiency was found to increase with increase in extract concentration till 2400 ppm. The adsorption of the inhibitor on the metal surface obeyed the Langmuir adsorption isotherm.
- **Shyamala et al.,(2008)** studied the corrosion inhibition effect of aqueous extract of *Eclipta alba* in 1 N hydrochloric acid by weight loss, potentiodynamic polarization and impedance methods and the extract of *Eclipta alba* was found to be effective corrosion pickling inhibitor. The effect of immersion time and temperature revealed that the extracts of *Eclipta alba* with an optimum concentration of 8.0% v/v showed maximum inhibition efficiency of 99.6% at 3 h immersion time and 30 degree C. Arrhenius plots for mild steel immersed in 1 N HCl solution in the absence and presence of optimum concentration (8.0% in v/v) of *Eclipta alba* extract showed the effect of temperature. Polarization

studies indicate that this plant extract acts as a mixed type inhibitor. The adsorption of *Eclipta alba* was found to follow Langmuir adsorption isotherm.

- **Rajalakshmi et al. (2008)** studied the role of steel 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%.
- **Emeka E.Oguzie (2008)** studied the inhibitive behaviour on mild steel in 2 M HCl and 1 M H₂SO₄ by leaf extracts of *Occimum viridis*, *Telferia occidentalis*, *Azadirachta indica* and *Hibiscus sabdariffa* and extract seeds of *Garcinia kola* by gasometric technique at 30⁰ and 60⁰C. Inhibition efficiency was found to increase with increase in extracts concentration. Synergistic effects increase with increased the inhibition efficiency in the presence of halide additives.
- **Pandian Bothi Raja et al., (2008)** observed the performance of *Black pepper* extract on mild steel in 1M H₂SO₄ by conventional weight loss studies (303-323 K), electrochemical studies Viz., Tafel polarization, AC impedance and scanning electron microscope (SEM) studies. Results of weight loss study revealed that Black pepper extract acts as a good inhibitor even at high temperature and it obeys Temkin adsorption isotherm.
- **Emeka et al, (2008)** investigated the inhibiting action of the calyx extract of *Hibiscus sabdariffa* on mild steel corrosion in 2 M HCl and 1 M H₂SO₄ solutions was assessed using a gasometric technique. The results demonstrate that *Hibiscus sabdariffa* extract suppressed the corrosion reaction in both acid media and inhibition efficiency increased with extract concentration with slightly higher values obtained in 1 M H₂SO₄. Synergistic effects increased the efficiency of the extract in the presence of halide additives. Adsorption characteristics of the extract were approximated by the Langmuir isotherm.
- In this investigation **Karthikaiselvi et al.,(2009)** studied the inhibitive effect of acid extract of *Myristica frangans* on mild steel in 1M HCl by weight loss, DC Polarization method and AC impedance spectroscopy. Results indicated that the inhibition efficiency of extract increased with increase in inhibitor concentration

and with temperature. The adsorption of extract followed Langmuir adsorption isotherm. Thermodynamic functions have been evaluated from temperature studies. Electrochemical measurements revealed that the extract acted as a mixed type inhibitor.

- **Raja et al., (2009)** investigated the corrosion inhibition potential of *Calotropis procera* in sulphuric acid medium on mild steel with a view to developing green corrosion inhibitors. It was studied for its corrosion inhibitive effect by weight loss, electrochemical, SEM and UV methods. Using weight loss measurement data, mechanism of inhibitive action is probed by fitting in adsorption isotherm.
- **Nnabuk Okon Eddy et al., (2009)** tested the inhibitive and adsorption properties of ethanol extract of *Terminalia catappa* for the corrosion of mild steel in H₂SO₄ 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, anthraquinone, cardiac glycosides, flavonoid, terpene, and alkaloids in the extract.
- **Ostovari et al., (2009)** investigated the corrosion inhibition effect of henna extract (*Lawsonia inermis*) and its main constituents (lawsone, gallic acid, α-d-Glucose and tannic acid) on mild steel in 1M HCl solution through electrochemical techniques and surface analysis (SEM/EDS). Polarization measurements indicated that the compounds act as mixed inhibitors. The inhibition efficiency increases with inhibitor concentration and a maximum inhibition efficiency of 92.06% was obtained with 1.2g/L of henna extract.
- The inhibition effect of naturally occurring biological molecule *caffeic acid* on the corrosion inhibition of mild steel in 0.1 M H₂SO₄ was investigated by **de Souza et al., (2009)**. Weight loss, potentiodynamic polarization, electrochemical impedance and Raman spectroscopy techniques were conducted and confirmed that the adsorption of *caffeic acid* onto the mild steel surface enhances the inhibition of the corrosion process. *Caffeic acid* inhibited corrosion by

decreasing the available cathodic reaction area and modified the activation energy of the anodic reaction.

- **Urvija Garg et al.,(2009)** studied the inhibition of corrosion of mild steel in HCl solution by naturally occurring *Acacia senegal* in relation to the concentration of inhibitor and concentration of corrosive medium. It has been observed that the *Acacia senegal* alcoholic extract acts as a good corrosion inhibitor in hydrochloric acid solution and the adsorption of the extract provides a good protection against mild steel corrosion.
- **Eddy et al.,(2009)** determined the inhibitive and adsorption properties of ethanol extract of *Lasianthera africana* for inhibition of corrosion of mild steel in H₂SO₄ using gravimetric, thermometric, gasometric, and infrared (IR) methods. The extract was found to be a good inhibitor of corrosion of mild steel in H₂SO₄. Inhibitive properties of the extract were attributed to enhancement in adsorption of the inhibitor on mild-steel surface. Adsorption of the inhibitor was found to be exothermic, spontaneous, and consistent with assumptions of Langmuir and Temkin adsorption isotherms. Synergistic study revealed that, of the investigated halides, only KCl may enhance adsorption of the inhibitor, whereas KBr and KI antagonized its adsorption. Based on the decrease in efficiency of the inhibitor with temperature, with values of activation energy and free energy of adsorption below the threshold values of -40 and 80 kJ mol⁻¹, respectively, a physical adsorption mechanism has been proposed .
- **Satapathy et al .,(2009)** investigated the corrosion inhibition effect of *Justicia gendarussa* extract (JGPE) on mild steel in 1 M HCl medium using weight loss and electrochemical techniques and reported that a maximum of 93% Inhibition efficiency can be achieved with 150 ppm JGPE at 25°C. The polarization studies showed that JGPE acted as mixed-type inhibitor. JGPE was found to obey Langmuir adsorption isotherm. AFM and ESCA confirmed the adsorption of JGPE on mild steel surface.

- *Eddy et al.*, (2009) analyzed the inhibitive and adsorption properties of ethanol extract of *Phyllanthus amarus* for the corrosion of mild steel in H₂SO₄ using gravimetric, thermometric and gasometric methods. Ethanol extract of *Phyllanthus amarus* leaves was a good adsorption inhibitor for the corrosion of mild steel in H₂SO₄. Thermodynamic consideration proved that the adsorption of the extract is exothermic and spontaneous. The adsorption characteristic of the inhibitor was consistent with the assumptions of Langmuir adsorption isotherm. From the results and findings of the study, a physical mode of adsorption was proposed for the adsorption of the extract. The inhibition potentials of ethanol extract of *Phyllanthus amarus* leaves were enhanced by its phytochemical constituents.
- *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 H₂SO₄ solutions using weight loss and gasometric techniques. The results obtained indicated that the extracts functioned as good inhibitors in H₂SO₄ solutions. Inhibition efficiency was found to increase with extracts concentration and temperature, and followed the trend: SD > RT > LV.
- *Quraishiet al* (2009) studied the corrosion inhibition of mild steel in hydrochloric solution by Black pepper extract (*Piper nigrum* fem. Piperaceae). The techniques employed for study were weight 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 obtained at 120 ppm at 35 °C. 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, ΔG_{ads} , 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.

- *Anand et al.,(2010)* analyzed the inhibition efficiency (IE) of an aqueous extract of *Allamanda blanchetii* (Purple) in controlling corrosion of mild steel which has been evaluated by weight loss method in the absence and presence of corrosion inhibitor at different time intervals at room temperature. The result showed that the corrosion inhibition efficiency of *Allamanda blanchetii* was found to vary with different time interval and different acid concentrations. Also, it was found that the corrosion inhibition behaviour of *Allamanda blanchetii* is greater in sulphuric acid than citric acid medium. The surface analysis study confirmed the corrosion of the mild steel and its inhibition by the inhibitor *Allamanda blanchetii*.

- *Ambrish Singh et al.,(2010)* found out the inhibition of the corrosion of mild steel in hydrochloric acid solution by the seed extract of **Kuchla** (*Strychnos Nuxvomica*) using weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization and linear polarization techniques. Inhibition efficiency was found to increase with increasing concentration of the extract. The effect of temperature, immersion time and acid concentration on the corrosion behaviour of mild steel in 1 M HCl with addition of extract was also studied. The adsorption of the extract on the mild steel surface obeyed the Langmuir adsorption isotherm. Values of inhibition efficiency calculated from weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) are in good agreement. Polarization curves showed that **Kuchla** (*Strychnos Nuxvomica*) seed extract behaves as a mixed-type inhibitor in hydrochloric acid. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated. The adsorbed film on mild steel surface containing **Kuchla** (*StrychnosNuxvomica*) seed extract inhibitor was also measured by Fourier transform infrared spectroscopy (FTIR). The results obtained showed that the seed extract of **Kuchla** (*Strychnos Nuxvomica*)

could serve as an effective inhibitor of the corrosion of mild steel in hydrochloric acid media.

- Evaluation of the effective performance of acid extract of *Ervatamia coronaria* leaves extract on the inhibition of mild steel in 1M HCl and 0.5M H₂SO₄ at ambient temperature by *Rajalakshmi et al.,(2010)* using weight loss and electrochemical measurements. Electrochemical studies showed that the plant extracts act as mixed type inhibitors and maximum efficiency extract was found to be 98%.
- *Patchaiah Kalaiselvi et al., (2010)* proved the inhibition efficiency of methanolic extract of *Artemisia pallens* on corrosion of mild steel in 4N HCl and conc. HCl. Weight loss and polarization techniques were studied in 4N HCl, whilst weight loss, SEM and FT-IR studies were carried out in concentrated HCl. Inhibition efficiency was found to increase with increase in extract concentration. The results obey the Langmuir adsorption isotherm. The Inhibition efficiency was found to be 93% at 1.5g l⁻¹ in 4N HCl and 96.5% at 40g l⁻¹ in conc. HCl.
- **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.
- The leaves extract of *Murraya koenigii* has been evaluated as an inhibitor for the corrosion of mild steel in hydrochloric acid and sulphuric acid by **Quraishi et al., (2010)** using weight loss, electrochemical impedance spectroscopy (EIS), linear polarization and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The

inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of the extract on the mild steel surface was found to obey Langmuir adsorption isotherm.

- **Vinod Kumar et al, (2010)** tested the seed husk extract of *Jatropha curcas* for mild steel corrosion inhibition in acid medium. Traditional weight loss data obtained at four different temperatures were used to evaluate inhibition efficiency (IE) and thermodynamic parameters, change in free energy of the reaction (ΔG), corrosion rate and energy of activation for corrosion reaction of mild steel (E). All the results obtained reflect that the seed husk extract of *J. curcas* as an effective eco-friendly and alternate corrosion inhibitor for mild steel in acid medium.
- **Ambrish Singh et al, (2010)** studied the inhibition of the corrosion of mild steel in HCL acid solution by the extract of **Kalmegh (*Andrographis paniculata*)** leaves extract by using weight loss, electrochemical impedance spectroscopy, linear polarization, and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the extract. The adsorption of the molecules of the extract on the mild steel surface obeyed the Langmuir adsorption isotherm.
- **Peter et al,(2010)** evaluated 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 indicate that the extracts functioned as good inhibitors in H_2SO_4 solutions. Inhibition efficiency was found to increase with extracts concentration and temperature. The experimental data obeyed the Freundlich adsorption isotherm.
- **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 H₂SO₄. 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 H₂SO₄.

- **Solomon et al., (2011)** investigated the Corrosion inhibition of mild steel in 1 M H₂SO₄ by leaves and stem extracts of *Sida acuta* using chemical (weight loss and hydrogen evolution) and spectroscopic (AAS, FTIR and UV-V) techniques at 30–60 degree celsius. It was found that the leaves and stem extracts of *S. acuta* inhibited the acid induced corrosion of mild steel. The inhibition efficiency was found to increase with increase in concentration of the extracts but decrease with rise in temperature. Inhibitive effect was afforded by adsorption of the extracts' components which was approximated by Freundlich adsorption isotherm.
- **Khalid Hasan et al., (2011)** investigated the inhibition of corrosion of mild steel using *Paniala (Flacourtia jangomas)* extract in 1M HCl and 0.5M H₂SO₄ solutions was investigated by weight loss method at 30°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 H₂SO₄, 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 H₂SO₄. 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 of mild steel specimens immersed in 0.5 M hydrochloric acid by *kola plant* and *tobacco* was investigated by **Loto et al.**, (2011) at ambient temperature by gravimetric and metallographic methods. The results obtained from the weight loss method, calculated corrosion rates, inhibitor efficiencies and the metallographic observation from metallurgical microscopy was reported. Addition of different concentrations of the plants extracts gave considerable reduction in the weight loss and in the corrosion rate of the test samples. Effective protection of the mild steel was achieved more from the tobacco extract and also from the extract of kola leaf.
- **Elyn et al.**,(2011) investigated the influence of *Xylopia ferruginea* leaves extract and partitions in different solvents on the corrosion behavior of mild steel (MS) in 1 M HCl using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Scanning Electron Microscope (SEM) techniques. The studies revealed that *Xylopia ferruginea* was an excellent green inhibitor and the inhibition efficiencies obtained from weight loss and electrochemical experiments were in good agreement. Potentiodynamic polarization studies clearly revealed that all inhibitors behaved as mixed-type inhibitors with predominant anodic effectiveness. The adsorption of inhibitors on MS surface was found to obey the Langmuir adsorption isotherm. SEM studies confirmed that the corrosion protection of MS was by the adsorption of inhibitors. The effectiveness as corrosion inhibitors was in the order of chloroform partition (CP) > n-hexane partition (HP) > methanol extracts (ME).
- **Hui Cang et al.**, (2012) investigated the corrosion inhibition of mild steel in sulphuric acid solution by the extract of *Stevia rebaudiana* leaves using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The effect of temperature on the corrosion behavior of mild steel in 0.5M H₂SO₄ with addition of extract was also studied. Thermodynamic parameters (E_a, ΔH and ΔS) for the inhibition process were

calculated. These thermodynamic parameters show strong interaction between inhibitor and mild steel surface. The results obtained show that the extract of *Stevia rebaudiana* leaves could serve as an effective inhibitor for the corrosion of mild steel in Sulphuric media.

- **Ramananda Singh (2013)** analysed the inhibition effect of extract of *Adhatoda vasica* in aqueous 0.5 M H₂SO₄ on corrosion of mild steel and its mechanism of the inhibition by weight loss method, potentiodynamic polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency of *Adhatoda vasica* on corrosion of mild steel in 0.5 M H₂SO₄ solution increases on increasing in its concentration and decreases with rise in temperature. The results of the Potentiodynamic Polarization measurement reveals that the extract acts as mixed type inhibitor. The adsorption of the extract on mild steel surface was found to follow Langmuir isotherm.
- Assessment of the inhibitive action of *Petersianthus macrocarpus* leaves extract on corrosion of mild steel in 1M HCl and 0.5M H₂SO₄ solutions was done using gravimetric, electrochemical impedance and potentiodynamic methods. The inhibition efficiency of the inhibitor increased with increasing extract concentration. Results indicated that the extracts functioned as a good inhibitor in both corrodent solutions. Temperature studies in the range 313-333K reveal increase in inhibition efficiency of the extract with rise in temperature. The authors proposed a mechanism of chemical adsorption. The adsorption characteristics of the inhibitor were found to obey Langmuir adsorption isotherm. (Akalezi et al,2013).
- **Benali et al (2013)** tested the corrosion and inhibition behaviour of mild steel in sulfuric acid + 5% EtOH in the presence of tannin extract of *Chamaerops humilis* plant (LF-Ch) and potassium iodide (KI) using electrochemical methods. It was found that the inhibition efficiency increased with LF-Ch extract concentration. A synergistic effect was observed between KI and extract with optimum of concentration of 100 mg /L LF-Ch extract + 0.025% potassium iodide. Adsorption of extract alone or in combination with potassium iodide on

the metal surface obeyed the Langmuir adsorption isotherm. According to the authors, the adsorption of LF-Ch extract on the mild steel in aggressive medium leads to the formation of a protective film which grows in thickness and effectiveness with increasing exposure time.

- The effectiveness of leaves extract of *Emilia sonchifolia* and *Vitex doniana* as corrosion inhibitors of mild steel in 2.5M HCl medium using gasometric method at 30°C and 60°C (Ilomaeke et al, 2013). Adsorption of *Emilia sonchifolia* leaves extract on the surface of the mild steel follows Langmuir, Temkin and Freundlich adsorption isotherm while adsorption of *Vitex donania* leaves extract on the surface of the mild steel obeyed Langmuir and Temkin adsorption isotherm.
- Nwosu et al ,2013, investigated the effectiveness of leaf extract of *Achyranthes aspera* L. on the corrosion inhibition of mild steel in 0.5 M H₂SO₄ medium at room temperature using gravimetric technique .The results revealed that the extract can afford a maximum efficiency of 92.3%. *A. aspera* L. extract was adsorbed on the mild steel surface in accordance with Langmuir, Frumkin, and Flory-Huggins adsorption isotherm models. The thermodynamic data inferred that the adsorption of the inhibitor onto the surface of mild steel was spontaneous in nature.
- *Eupatorium odoratum* (E.O) was utilised as a corrosion inhibitor for mild steel in 1.0M H₂SO₄ acid medium. The weight losses of the mild steel were taken for complete four days, for two temperatures namely 30°C and 60°C. The rates of corrosion of the mild steel was found to increase with increase in concentration of the acid and also decrease with increase in concentration of the *Eupatorium odoratum* extract. The extract afforded a maximum efficiency of 71% at the concentration of 0.5g/l. The activation energy values showed that the *Eupatorium odoratum* extract is physically adsorbed on the mild steel coupons. (Onuegbu et al ,2013).
- Extract of various plants (*Wrightia tinctoria*, *Clerodendrum phlomidis*, *Ipomoea triloba*) leaves was investigated by Patel et al, 2013 as corrosion inhibitor for mild steel in 0.5M H₂SO₄ using conventional weight loss,

electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopic studies. The weight loss results showed that all the plant extracts act as excellent corrosion inhibitors. Electrochemical polarization data revealed the mixed nature of the inhibitors. Scanning electron microscopic studies validated the results obtained from other investigated techniques.

- The inhibitive effect of *Cuminum cyminum* extract on the corrosion of mild steel in an aqueous solution of seawater was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) and weight-loss techniques. Potentiodynamic polarization curves indicated that the plant extract behaved as an anodic type inhibitor. The inhibition efficiencies of the extract obtained from impedance and polarization measurements were in good agreement. Inhibition was found to increase with an increasing concentration of the plant extract.
- Corrosion inhibition effect of *Piper longum* fruit extract on mild steel in 1 M HCl medium has been investigated by weight loss and electrochemical techniques (Ambrish singh et al,2013). The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. Values of inhibition efficiency calculated from different techniques are in good agreement. Polarization curves reflect the mixed nature of inhibitor in hydrochloric acid. The results obtained show that the *Piper longum* fruit extract could serve as an effective inhibitor of corrosion of mild steel in HCl.
- Hui et al ,2013 reported the corrosion inhibition of mild steel in 1.0 M HCl by the *Aloes* leaves extract .The investigation was carried out using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results show that the inhibition efficiency increases with the increase of the extract concentration. The adsorption of the extract molecules on the steel surface was found to obey Langmuir adsorption isotherm. From the activation energy and other thermodynamic parameters calculated for the

inhibition process, strong interaction between inhibitor and mild steel surface was noted.

- A study on the effectiveness of acid extract of *Nicotiana tabacum* leaves on mild steel in 1M HCl was carried out using weight loss method (**Olasehinde, 2013**). Experiments were performed for varying immersion period, concentration of the inhibitor and temperature. The inhibition efficiency was found to increase with increase in concentration of *Nicotiana tabacum* leaves extract but decreased with rise in temperature and exposure time. Thermodynamic studies revealed that corrosion inhibition may be due to the spontaneous physical adsorption of the plant constituents on the surface of mild steel. Experimental data was approximated by Langmuir and Temkin adsorption isotherms. Kinetic treatment of the data followed a first order reaction.
- The inhibitive performance of leaf extracts of *Cinnamoum zeylanicum*(CZ) was tested as natural corrosion inhibitor for mild steel in 0.5 M HCl and 0.5 M H₂SO₄, respectively by gravimetric and electrochemical techniques. The results indicate that leaf extracts of CZ act as an efficient natural corrosion inhibitor in both the acid solutions. The inhibition efficiency was found to increase with increase in CZ extracts concentration and decrease with increase in temperature. Polarization measurements showed that the studied inhibitor acts as mixed inhibitor in both the acids with significant reduction of cathodic and anodic current densities. The adsorption characteristics of CZ extracts of on mild steel surface was found to obey Langmuir isotherm. The adsorption was through physical means. The electrochemical impedance studies further confirm the formation of an adsorbed film on the mild steel. (**Shivakumar and Mohana,2013**).
- Sparsioamide , a new sphingolipid, and sparsioside , a new diglyceride galactoside, have been isolated from the ethyl acetate soluble fraction of the 80% ethanolic extract of the whole plant of *Croton sparsiflorus* .Their structures were assigned by 1 H- and 13C-NMR spectra and DEPT, COSY, NOESY, HMQC, HMBC, and ESI-MS experiments. (**Rashad Mehmood et al,2013**).

- Crotosparsamide , a new cyclic nonapeptide, has been isolated from the n-butanol soluble sub-fraction of *Croton sparsiflorus* along with p-hydroxy methyl cinnamate 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.(**Mehmood R et al,2010**).
- **Raja (2007)** studied the inhibitive effect of *Daturastramonium* extract on the acid corrosion of mild steel in HCl and H₂SO₄ media at different temperatures. The anticorrosion effect was evaluated by conventional weight loss studies, electrochemical studies. The studies reveal that the plant extract acts as a good inhibitor in both the acid media and better in H₂SO₄ medium and also the potential of D. stramonium for combating corrosion may be due to the adsorption of alkaloids and other phytoconstituents.
- The crude ethanolic extract of the root of *Croton sparsiflorus* Lin. (Family-Euphorbiaceae) was evaluated for its possible phytochemical nature. Phytochemical analysis of the ethanolic extract of *C. sparsiflorus* indicated the presence of tannin, steroid & alkaloid types of compounds . (**Hemayet Hossain et al,2012**).
- **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.

- Phytochemical screening on the ethanolic extract of *C. sparsiflorus* leaves indicated the presence of carbohydrate (reducing sugars), alkaloids, steroids, flavonoids, saponin & tannins, **J. B. Harborne, 1973**

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 CSL 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 $1 \times 5 \text{ cm}^2$ have been cut from a large sheet of mild steel. A hole was drilled in the specimen, mechanically polished, degreased, washed with de ionized water then thoroughly dried and kept in desiccators for weight loss tests. The mild steel specimens used in the following percentage elemental of composition as shown in table.

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.

ELEMENTAL ANALYSIS

S.No	Elements	% Composition
1.	Carbon	0.143
2.	Manganese	0.271
3.	Silicon	0.041
4.	Phosphorous	0.035
5.	Sulphur	0.030
6.	Chromium	0.002
7.	Molybdenum	0.018
8.	Nickel	0.006
9.	Iron	the rest

3.4 SELECTION OF INHIBITORS

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

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

3.5 PREPARATION OF THE INHIBITOR

The extract was prepared by refluxing 25g of CSL 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.

3.6 TECHNIQUES EMPLOYED

- ✎ Mass Loss methods
- ✎ Electrochemical measurements

3.6.1 MASS LOSS METHODS

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

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

- ✦ Concentration (0.05% - 0.5%)
- ✦ Time of immersion (1/2 h, 1 h, 3 h & 24 h)
- ✦ Temperature (313 K – 353 K)

3.7 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,

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

Where,

W - Weight loss in g

D - Density of mild steel in g/ cm²

A - Area of the sample in cm²

T - Exposure time in hours

3.8 DETERMINATION OF PERCENTAGE OF INHIBITION AND SURFACE COVERAGE

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

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

$$\theta = \frac{w_0 - w}{w_0} \times 100$$

Where,

w_0 - Corrosion rate without inhibitor in g

w - Corrosion rate with inhibitor in g

3.9 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)

$$\log C = [\log \theta / (1 - \theta)] - \log B$$

Where,

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

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

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 .

3.10 ADSORPTION ISOTHERM

Corrosion inhibition is a surface process with specific adsorption of inhibitor on the metal surface. In recent years, attempts have been made to understand the nature of interaction between the inhibitor and metal surface in 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 [$\log (\theta / 1 - \theta)$ Vs $\log C$]

Temkin (θ Vs $\log C$)

3.11 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.

$$E_a = - 2.303 \times R \times \text{slope of the Arrhenius plot}$$

Where R-gas constant 8.314 J/mole

3.12 ELECTROCHEMICAL METHODS

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. The solartron electro chemical analyzer (model 1280 B) 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.

3.13 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,

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

I.E from LPR technique

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

Where,

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

3.14 IMPEDANCE SPECTROSCOPY

In this method an AC signal of 5 – 10 mV of frequency 10 KHz to 10MHz is applied to the system. Impedance data can be presented in the form of Nyquist or Bode plot. From the data, the R_{ct} and C_{dl} are obtained. The I.E can be calculated using the equation,

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

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.

3.14 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 specimen was immersed in 100 ml of the test solution with optimum 0.7% concentration of the inhibitor for 3 h. It was then dried with acetone and the adsorbed material was carefully scratched and the powder was taken for FTIR analysis. The powder obtained by evaporating the extract on a water bath was also subjected to FTIR 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. FTIR studies are carried out to characterize the functional groups present on the mild steel.

RESULTS & DISCUSSION

5. RESULTS AND DISCUSSION

In acidic solutions, the prime feature of the corrosion of mild steel are, that it is rapidly corroded without the formation of a passive layer of corrosion products and that the cathodic reaction consists mainly of hydrogen evolution. Acid solutions are widely used for the removal of oxide from the metallic parts before coating (acid pickling), removal of undesirable scales and rust (acid cleaning) and in several other industrial processes . Hydrochloric acid and Sulphuric acids are the most important pickling acids used for steel and ferrous alloys in industry. Inhibitors are commonly used in these processes to control the metal dissolution and acid consumption. The use of corrosion inhibitors is one of the most effective methods to protect metal surfaces against corrosion, especially in acid media. The most suitable inhibitors are the adsorptive type which adsorb immediately and have high efficiency. In this direction, the present study has been conducted to assess the inhibition efficiency that can be afforded by *Croton sparsiflorus* leaves.

The results pertaining to the present investigation of corrosion inhibitive nature of *Croton sparsiflorus* leaves extract on mild steel in 1M HCl are tabulated and discussed in the light of the objective set forth.

The investigation has been carried out under the following techniques:

- Mass loss measurements
- Polarisation measurements

4.1 Evaluation of *Croton sparsiflorus* as an effective inhibitor

Croton sparsiflorus leaves extract (CSL) has been tried for its potency in the retardation of corrosion of mild steel. It has been evaluated by mass loss measurements using the following parameters.

- Effect of concentration of inhibitor
- Impact of immersion time
- Temperature effect

4.2 Effect of concentration of the inhibitor

The effect of concentration of the inhibitor plays an important role to fix a critical micellar concentration for the extract under study. The effect of CSL dosage on the dissolution of mild steel in 1M HCl medium has been investigated and the determination of the concentration of inhibitor at which maximum enhancement of inhibition efficiency is obtained by conducting the tests from the concentrations of 0.1% - 0.7% of the acidic extract and the results are illustrated in table (1) and fig (1). It is imperative from the figure that as the dosage of the inhibitor is increased, the inhibition efficiency also increased.

The increase in inhibition efficiency with increase in concentration of the extract may be attributed to the increase in the number of molecular adsorbed over the mild steel surface. This blocks the active sites in which direct acid attack proceed there by effectively protecting the metal from corrosion. [Pandian Bothi Raja et al., 2009]. In the presence of 0.7% of CSL solution, the maximum efficiency was found to be 98% for HCl acid.

4.3 Effect of Immersion Time

Efforts have been taken to find out the optimum time of immersion for the extract under investigation. The extract has been analysed for different periods of time in 1M HCl. The result obtained for the variation of IE with exposure time for the mild steel specimen immersed in 1M HCl with and without the addition of varied concentration of CSL extract are presented in table-1 and depicted in fig -1

Analysis of the table reveals that as the concentration of inhibitor increased the IE was also found to increase with all periods of immersion. A maximum IE of 98% was obtained for 6 hours at 0.7 % concentration. In the present investigation it is observed that the extract behaved as an excellent one at all periods of immersion. This proves the inhibitive nature of the adsorbed molecule on the surface of mild steel.

TABLE -1**Effect of Concentration & Time on inhibition efficiency of CSL extract in 1M HCl**

S.No	Conc (%)	Corrosion rate and Inhibition efficiency											
		½ h		1h		3h		6h		12h		24h	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	0.1	277.20	5.1	102.35	81.8	109.47	49	69.30	93.6	94.89	87.4	142.16	88.6
2.	0.2	183.38	37.2	93.83	83.3	81.08	62.2	46.20	95.7	79.25	89.5	97.73	92.1
3.	0.3	162.06	44.4	76.76	86.3	66.81	68.8	42.64	96	74.27	90.1	97.55	92.2
4.	0.4	153.30	47.3	68.23	87.8	62.55	70.8	28.43	98.1	68.94	90.8	61.83	95.0
5.	0.5	136.47	53.2	63.97	88.6	59.71	72.1	26.29	97.3	67.17	91.1	38.56	96.9
6.	0.6	127.94	56.1	55.44	90.1	54.02	74.8	20.61	97.5	62.19	91.7	36.33	97
7.	0.7	102.35	64.9	55.44	90.1	42.65	80.1	18.48	98.3	60.06	92	35.27	97.1

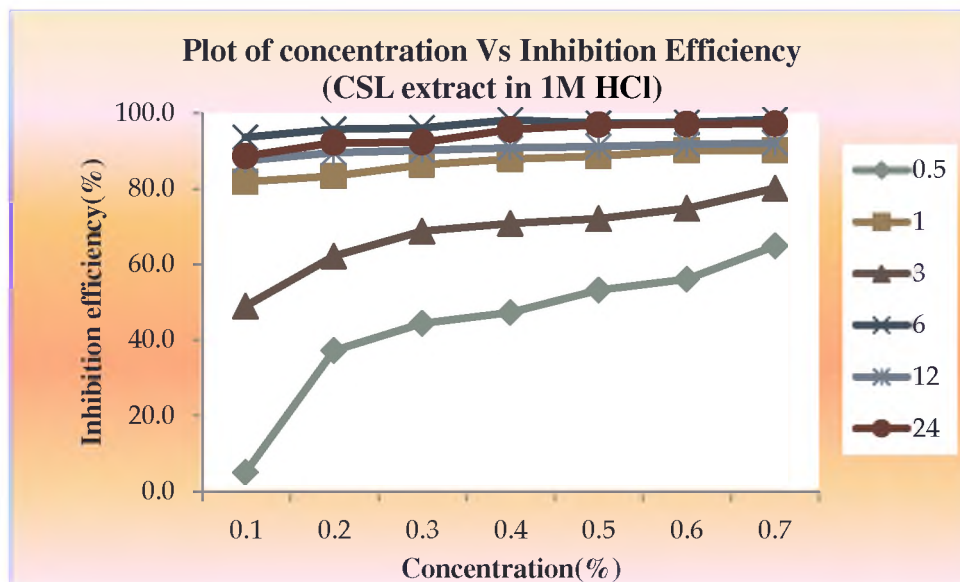


Fig-1

4.4 EFFECT OF TEMPERATURE

Temperature has a great effect on the rate of metal electrochemical corrosion. (Rajalakshmi. *et al.*, 2008). The influence of temperature on the corrosion rate of mild steel in increasing concentrations of inhibitor in 1 M HCl was studied.

To investigate the inhibition mechanism and to determine activation energy and free energy of adsorption of the corrosion process, weight loss measurements were taken in the temperature range of 303K to 353K by varying concentrations of CSL. The results are summarized in table -2 and fig -2.

The data indicated that the leaves extract was effective up to 313 K and decreased slightly thereafter. The maximum efficiency of 89 % at 313 K indicates that the inhibitor can be effectively used upto 313 K.

According to N.S Rawat and A.K Singh (1989), the above observation can be explained on the following basis adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium

exists between these two processes at a particular temperature. With the increases of temperature the equilibrium between adsorption and desorption processes is shifted leading to a high desorption rate until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperatures.

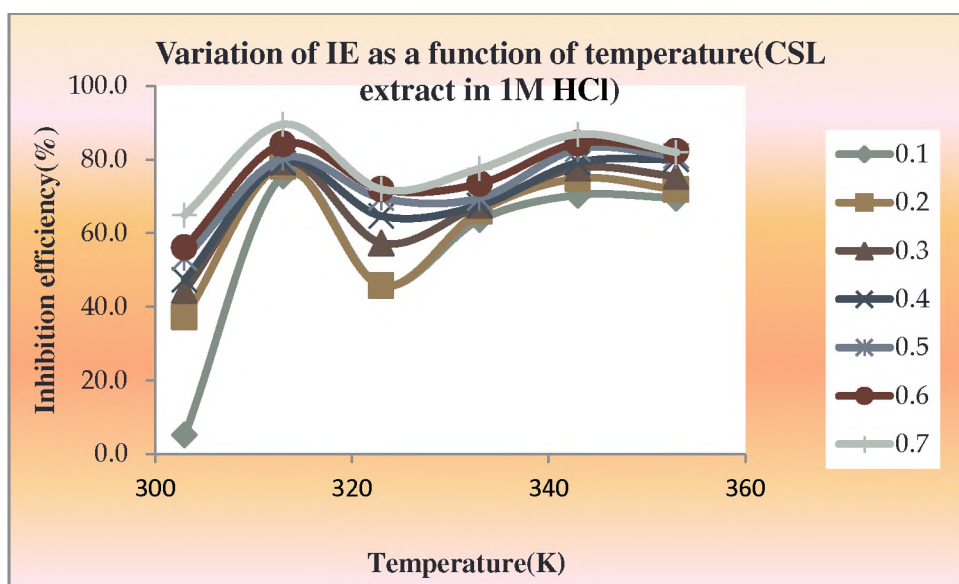


Fig-2

**TABLE – 2 EFFECT OF TEMPERATURE ON THE INHIBITION EFFICIENCY OF CSL
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	277.20	5.1	477.65	75.5	759.12	45.7	1518.2	63.6	3983.2	70.3	4392.6	69.5
2.	0.2	183.38	37.2	426.47	78.1	631.18	54.8	1424.42	65.9	3386.2	74.8	4068.5	71.8
3.	0.3	162.06	44.4	400.88	79.4	597.06	57.3	1356.1	67.5	3010.9	77.6	3539.7	75.4
4.	0.4	153.30	47.3	409.41	79	494.71	64.6	1356.1	67.5	2806.2	79.1	2874.4	80
5.	0.5	136.47	53.2	383.86	80.3	426.47	69.5	1270.8	69.5	2311.4	82.8	2755.0	80.9
6.	0.6	127.94	56.1	307.06	84.2	392.35	71.9	1108.8	73.4	2089.7	84.4	2567.3	82.2
7.	0.7	102.35	64.9	204.70	89.5	392.35	71.9	938.2	77.5	1774.1	86.8	2601.4	81.9

4.5 ADSORPTION ISOTHERMS

It has been generally accepted that 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 electrochemical reactions in the adsorption process is the adsorption isotherm. (Bockris. J. O. M, 1993) .Basic information on the interaction between the investigated inhibitor CSL and mild steel surface can be provided by the adsorption isotherms.

An adsorption isotherm gives the relation between the coverage of an interface with the adsorbed species. The degree of surface coverage θ for different concentration of the inhibitor has been evaluated from weight loss data. The values of surface coverage (θ) is calculated using the formula $\theta = IE/100$ where IE is the inhibitor efficiency obtained from weight loss measurements. The θ values for different concentrations of inhibitor for the acid solution were tested graphically by fitting to various isotherms like

Langmuir [$\log (\theta/1-\theta)$ vs $\log C$

Temkin θ vs $\log C$

4.5.1 LANGMUIR ADSORPTION ISOTHERM

A plot of $\log (\theta/1-\theta)$ Vs $\log C$ gave a straight line showing that the adsorption of CSL can be fitted to Langmuir adsorption isotherm. (Figure 3) For a reliable and linear plot, surface coverage should fall within the linear window (monolayer) for inhibitor adsorption. The strong correlation for the Langmuir adsorption isotherm plot for CSL extract confirms the validity of this approach. These results demonstrated that the inhibition of mild steel by CSL extract was attributed to adsorption of the phytochemical compounds present in the inhibitor onto the mild steel surface. (Khaled K.F, 2003).

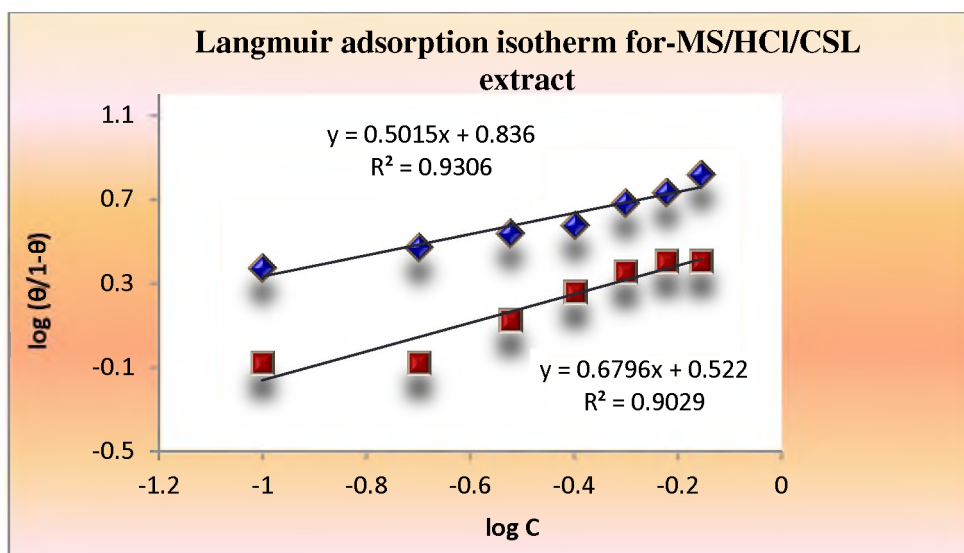


Fig-3

4.5.2 TEMKIN ADSORPTION ISOTHERM

Temkin adsorption isotherm was tested by plotting θ Vs $\log C$. A straight line obtained proves that the adsorption of the inhibitor on the surface of mild steel obeys Temkin adsorption isotherm which is pictorially represented in Figure 4.

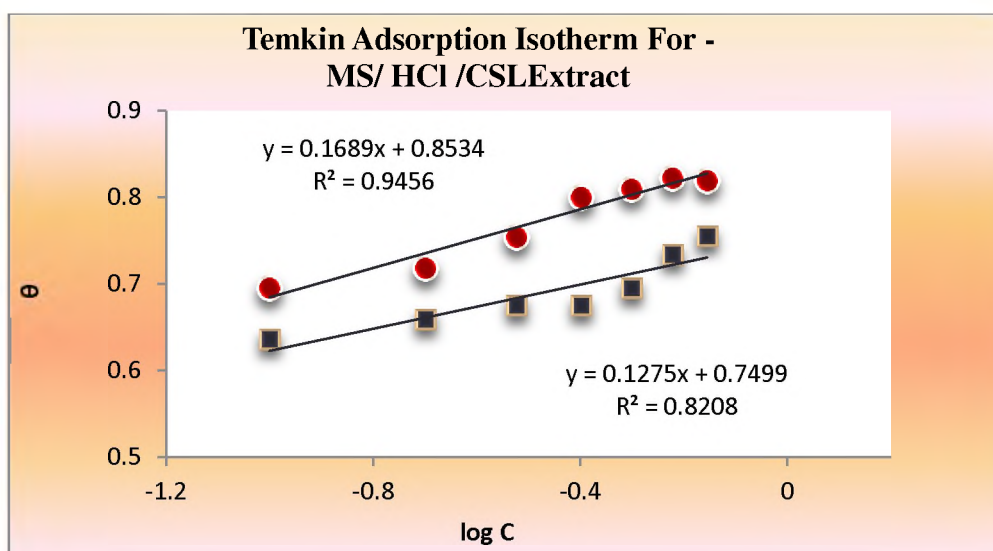


Fig-4

4.6 ACTIVATION ENERGY (E_a):

The values of corrosion rates at different temperatures make it possible to calculate the activation energy (E_a). According to Arrhenius equation,

$$\log CR = \frac{-E_a}{2.303 RT} + \text{Constant}$$

Where,

CR = Corrosion Rate

E_a = Activation energy

T = Temperature

Corrosion rates of mild steel calculated in the presence and in the absence of the inhibitor by weight loss method are plotted against the temperature ($\log CR$ Vs $1/T$) (figure 5). Activation energies were calculated from the slopes. The estimated values of E_a for mild steel in CS extract in 1M HCl are listed in the table (3). It was found that the E_a value of the blank was higher than that of the systems studied in the presence of the inhibitor.

Machu, (1938) in his studies, on the influence of temperature on inhibitor action concluded that with powerful inhibitors, the E_a was lower for the inhibited solution than that of uninhibited solutions. This type of behaviour infers that an inhibitor becomes more effective as the temperature increases as due to an increase in surface area of the metal covered by the inhibitor molecules as the temperature rises.

Experiments conducted by *Bag et.al (1996)* also reflected lower E_a values for the inhibited systems. Studies carried out by *Taha et.al (1995)* revealed that the presence of inhibitors decreased the E_a of the reaction to an extent depending on the nature of inhibitor. *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) and concluded that 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 surface and consequently the E_a can assume values greater or smaller than those calculated in the absence of the inhibitor.

In the present investigation, E_a values were found to be smaller than those calculated in the absence of the inhibitor. This can be explained by the fact that at high degree of coverage, the dissolution process is not only determined by the reaction of the metal from the blank surface but also involves the adsorbed surface. The estimated E_a in the presence of the inhibitor infer that the interaction between the metal surface and the inhibitor was found to be strong enough to prevent corrosion.

4.7 THERMODYNAMIC PARAMETERS:

4.7.1 FREE ENERGY OF ADSORPTION, CHANGE IN ENTROPY AND ENTHALPY:

The values of free energy of adsorption can be calculated by using the standard equation,

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

where,

$$C = \text{Inhibitor concentration}$$

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

The results obtained were tabulated in the table (3). From the table, it is noted that the values of ΔG are found to be negative in the presence and absence of the inhibitor. This indicates that adsorption behaviour of inhibitor is a spontaneous process under the experimental conditions. Generally values of ΔG upto -20KJ is consistent with electrostatic interaction between the charged metal (Physisorption) while those more than - 40 KJ/mole are associated with

Chemisorption. The calculated values of ΔG , indicate that the inhibitor functions by physically adsorbing onto the surface of the mild steel.

The heat of adsorption ΔH and entropy of adsorption ΔS are related to free energy of adsorption by Gibbs Helmholtz equation, $\Delta G = \Delta H - T\Delta S$

A plot of $-\Delta G$ Vs T is a straight line, which is depicted in figure (6). The values of ΔH are taken from intercept and that of ΔS from slopes. The values of ΔH and ΔS indicate that the system is enthalpic and entropic controlled.

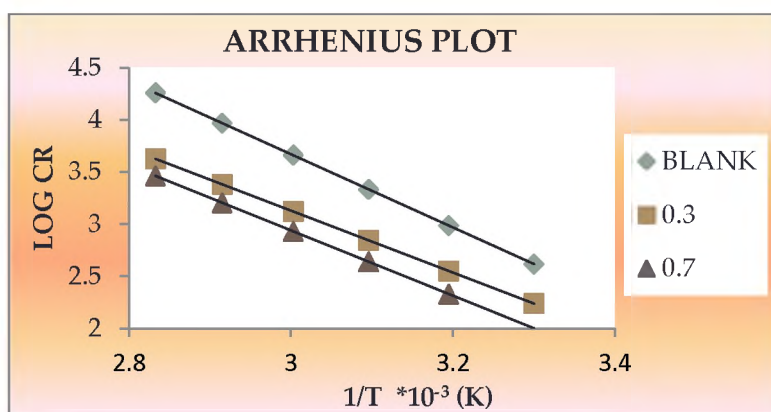


Fig-5 Arrhenius plot of corrosion rate for both blank and solution of the inhibitor

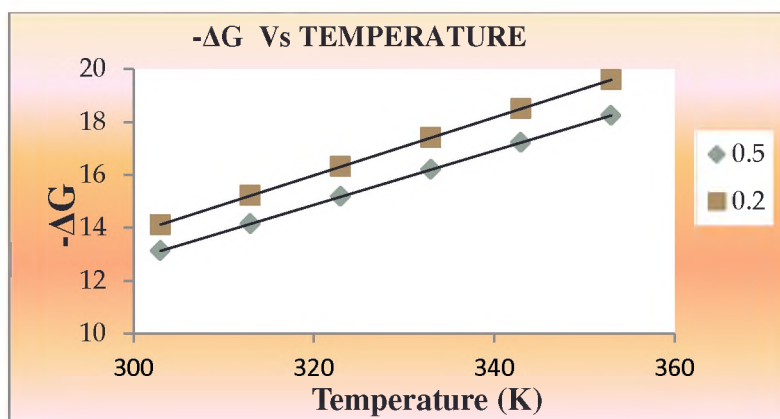


Fig-6 Temperature dependence of free energy of adsorption in 1M HCl

TABLE - 3

**VARIATION OF THERMODYNAMIC AND KINETIC PARAMETERS
WITH CONCENTRATION AND TEMPERATURE (CSL IN 1M HCl)**

S.No	-Ea (KJ/mol)	ΔG at various temperature (KJ/mol)						ΔS KJ/mole	ΔH KJ/mole
		303K	313K	323K	333K	343K	353K		
1.	62.67	8.53	19.35	16.48	19.02	15.06	20.94	-3.27	14.38
2.	49.59	12.83	17.93	14.62	17.38	19.12	19.23	-2.59	10.97
3.	53.08	12.56	17.07	14.78	16.45	18.41	18.58	-2.77	11.47
4.	52.95	12.13	16.26	14.84	15.66	17.84	18.52	-2.77	11.39
5.	50.9	12.16	15.89	14.83	15.29	17.89	18.03	-2.66	11.03
6.	51.09	11.99	16.11	14.66	15.32	17.7	17.75	-2.67	11.01
7.	51.76	12.54	16.93	14.24	15.51	17.82	17.24	-2.71	11.07

4.8 ELECTROCHEMICAL MEASUREMENTS:

Electrochemical measurements are carried out using Electrochemical Analyzer Solatron - 1284 B. Linear polarization measurements, Tafel intercept method and Electrochemical impedance measurements are carried out for mild steel acid corrosion in the presence of CSL 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 the table (4).

TABLE 4:

POTENTIODYNAMIC POLARIZATION PARAMETERS FOR THE CORROSION OF MILD STEEL IN 1M HCL WITHOUT AND WITH EXTRACT OF CSL

S.No	Conc v/v(%)	$-E_{\text{corr}}$ mV/SCE	I_{corr} $\mu\text{A}/\text{cm}^2$	b_a mV/dec	b_c mV/dec	IE (%)
1	Blank HCl	479	109.4	93.8	150.5	-
3	0.2	450	53.0	73.6	218.0	51.9
4	0.4	431	45.06	96.2	160.5	58.8
5	0.6	461	19.42	176.7	175.3	82.2

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 CSL extract are recorded in the figure (7).

TABLE 5
LINEAR POLARIZATION RESISTANCE VALUES OF MS/HCl/CSL

S.No	Conc v/v (%)	R_p Ohm/cm ²	IE (%)
1	Blank HCl	30.7	-
2	0.2	55.4	44.5
3	0.4	56.9	46.0
4	0.6	122	74.8

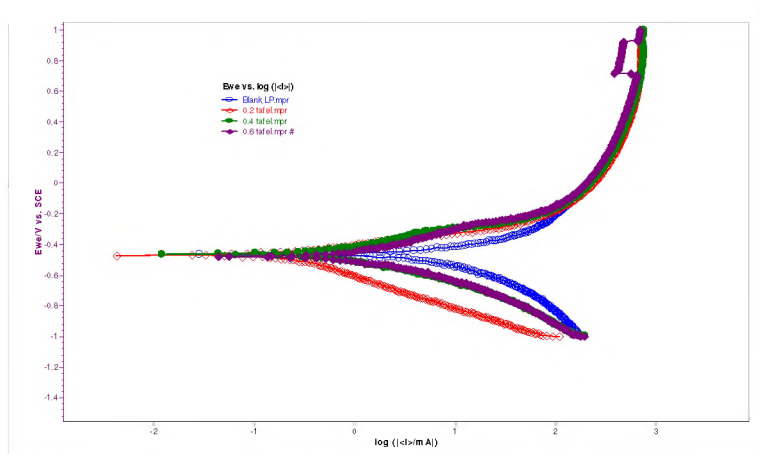


Fig- 7 Potentiodynamic curves of mild steel in 1M HCl in the presence of CSL extract

Increase in R_p value with increase in concentration of the inhibitor under study indicates the effective inhibitive action of the CSL extract. The values of R_p increases with increase in concentration of the extract. From the above experimental results the following conclusion can be drawn.

- ❖ Values of E_{corr} indicate that the CSL 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 CSL 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 74.8 % using R_p values and 82.2 % using I_{corr} values.

4.8.1 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 CSL is given in Figures 8. 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 Tables 5. The inhibitor efficiency calculated using the relationship

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

Where R_{ct} and $(R_{ct})_i$ are the charge transfer resistances without and with addition of inhibitors. Maximum inhibition efficiency using R_{ct} values was found to be 93% at 0.6%. Concentration values of C_{dl} decreases with increase in concentration of the extract indicate that the inhibition is taking place through adsorption process.

TABLE 6
IMPEDANCE PARAMETERS OF MS/CSL/1MHCl

Concv/v (%)	R_{ct} Ohm cm^2	IE(%)	$C_{dl}(\mu Fcm^{-2})$	Θ
Blank HCl	22.59	-	173	-
0.2	89.08	74.6	97.8	43.4
0.4	174.8	87	49.8	71.2
0.6	327.1	93	76.9	

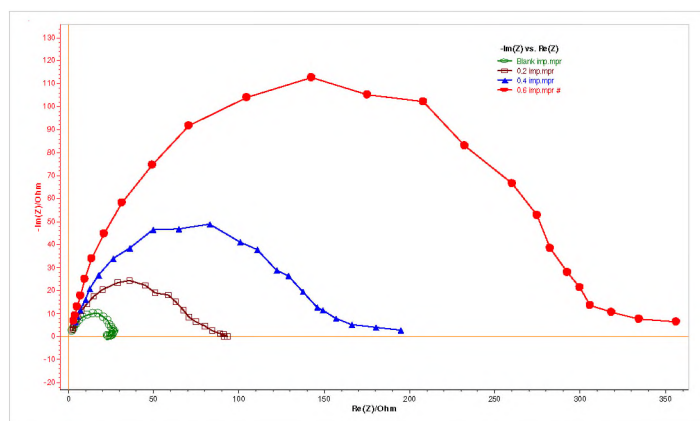


Fig-8 Nyquist diagram of mild steel electrode with and without CSL extract at E_{corr} at 30 min of time

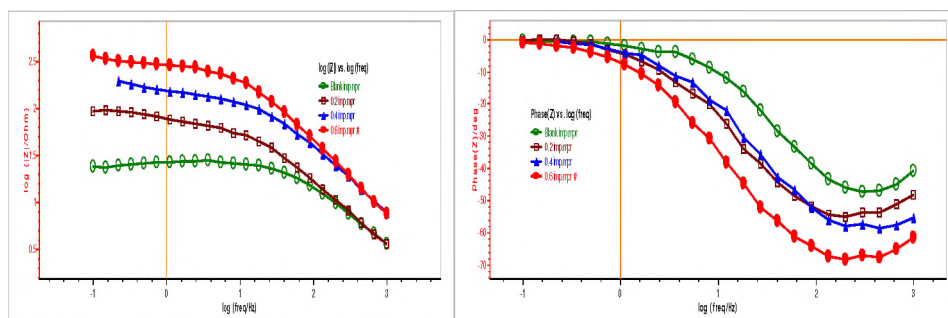


Fig- 9 Bode plot of mild steel in the presence of CSL extract in 1M HCl

4.9 SURFACE ANALYSIS

FTIR SPECTRAL ANALYSIS

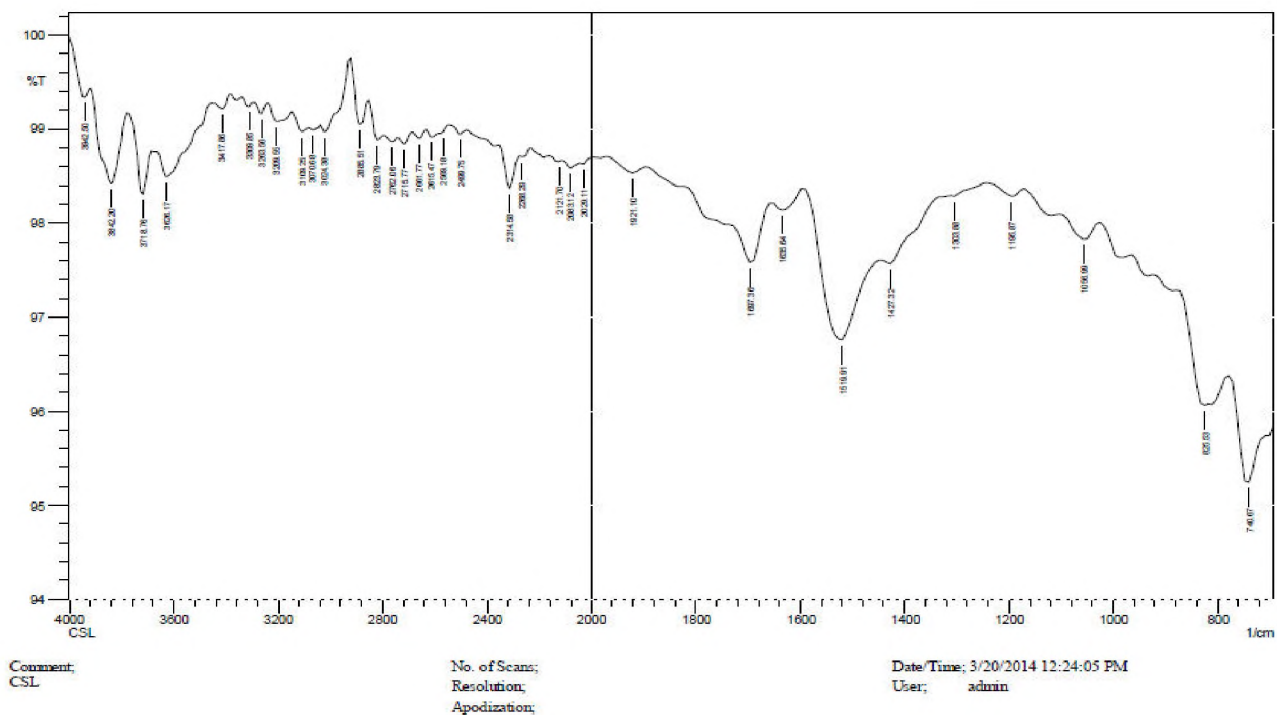
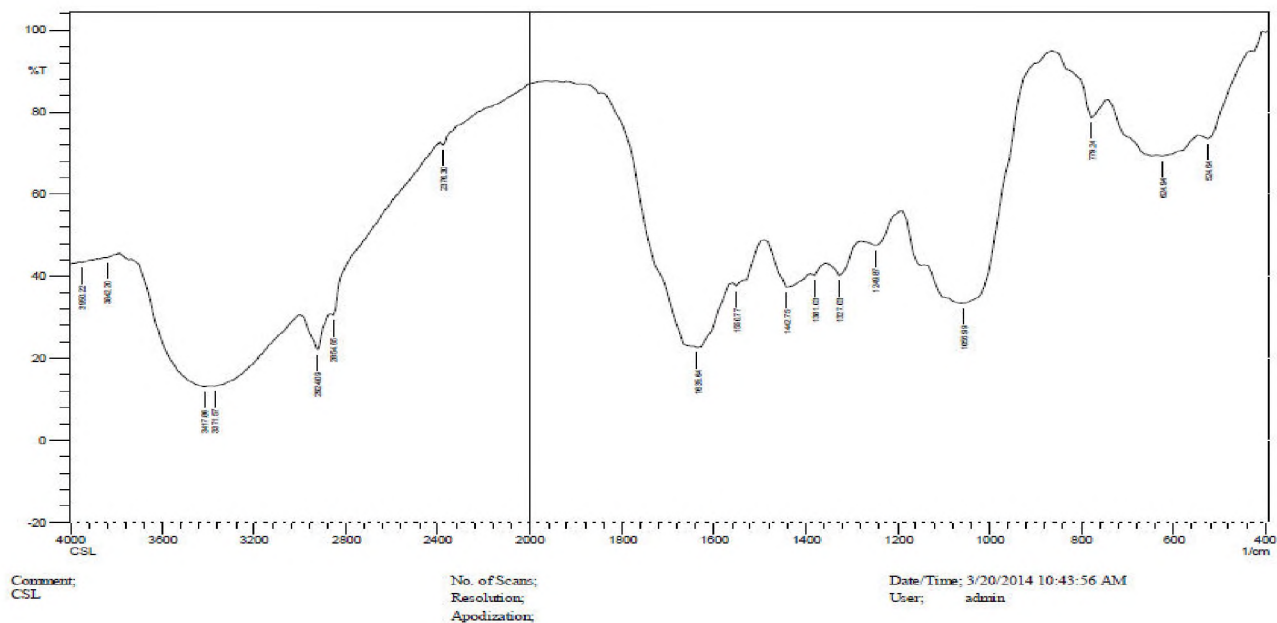


Fig- 10 IR spectrum of (a) acid extract of CSL concentrate (b) adsorbed material of MS in HCl in the presence of CSL

TABLE 7-FREQUENCIES OF IR ADSORPTION BY THE POWDERED PLANT MATERIAL AND CORROSION PRODUCT OF CSL EXTRACT

Powdered Plant material			Corrosion product of CSL		
Frequency cm ⁻¹	Assignment	Functional Groups	Frequency cm ⁻¹	Assignment	Functional Groups
3417.66	O–H stretch, H–bonded	Alcohols	3417.86	O–H stretch, H–bonded	1°, 2° amines, amides
2924.09	C–H stretch	Alkanes	-	-	-
-	-	-	2885.51	C–H stretch	Alkanes
2376.30	–C≡N stretch	Aliphatic amines	2314.58	–C≡N stretch	Aliphatic amines
1635.64	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers	1635.64	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers
1550.77	C-C in ring	aromatics	1519.91	C-C in ring	aromatics
1442.75	C–H bend	Aliphatic amines	1427.32	C–H bend	Aliphatic amines
1381.03	C–O-C stretch	Ethers	1303.88	C–O-C stretch	Ethers
1249.87	C-O stretch	carboxylic acids	1195.87	C-O stretch	carboxylic acids
1056.99	C-O stretch	carboxylic acids	1056.99	C-O stretch	carboxylic acids
779.24	O–H bend	alcohols	740.67	O–H bend	Alcohols
624.94	C-H “oop”	alkynes	-	-	-

In the presence of the inhibitor, IR spectrum of the corrosion product revealed that the –OH stretch (341786 cm⁻¹) was shifted from 3417.56 cm⁻¹. From the spectra, it is observed that the C–H stretch of alkanes and C–C stretch (in–ring) of aromatics are at 2885.51 cm⁻¹ and 1519.91 cm⁻¹. From the Figure (10a & 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 1635.64 cm^{-1} and 1056.99 cm^{-1} . From the crude plant extract to the corrosion product of CSL₂, absorption shifts of $\text{-C}\equiv\text{N}$ stretch (2376.30 cm^{-1} to 2314.58 cm^{-1}), C-H bend (1442.75 cm^{-1} to 1427.32 cm^{-1}) and C-O-C stretch (1381.03 cm^{-1} to 1303.88 cm^{-1}). The shift in the absorption frequencies of the inhibitor on the metal surface strongly support 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 $\gamma\text{-Fe}_2\text{O}_3$ (540.07 cm^{-1}). Some missing bonds are there in corrosion products indicating that there is interaction (Fe-CSL complex formation) between the leaves extract of CSL and the surface of mild steel.

4.10 PERFORMANCE EVALUATION OF CSL EXTRACT USING CONVENTIONAL WEIGHT LOSS METHOD AND ELECTROCHEMICAL MEASUREMENTS:

Performance evaluation of CSL extract using weight loss and electrochemical methods are pictorially represented in figure (11). Inhibition efficiency values obtained from electrochemical studies for different concentration of extract under investigation do not show an absolute agreement with those obtained from weight loss measurements. These observations can be explained in the following ways.

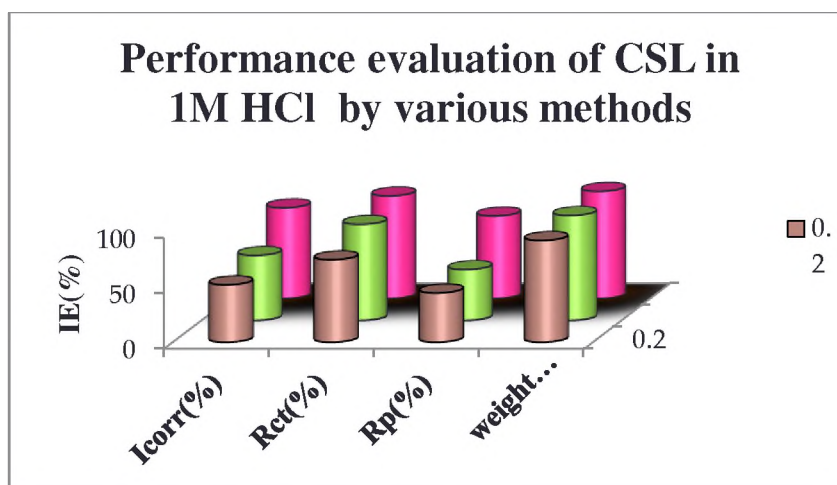


Fig-11

The values of inhibition efficiency calculated from electrochemical measurements are lower than those obtained from weight 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.

4.11 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 the figure 12. The inhibitor acts 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.

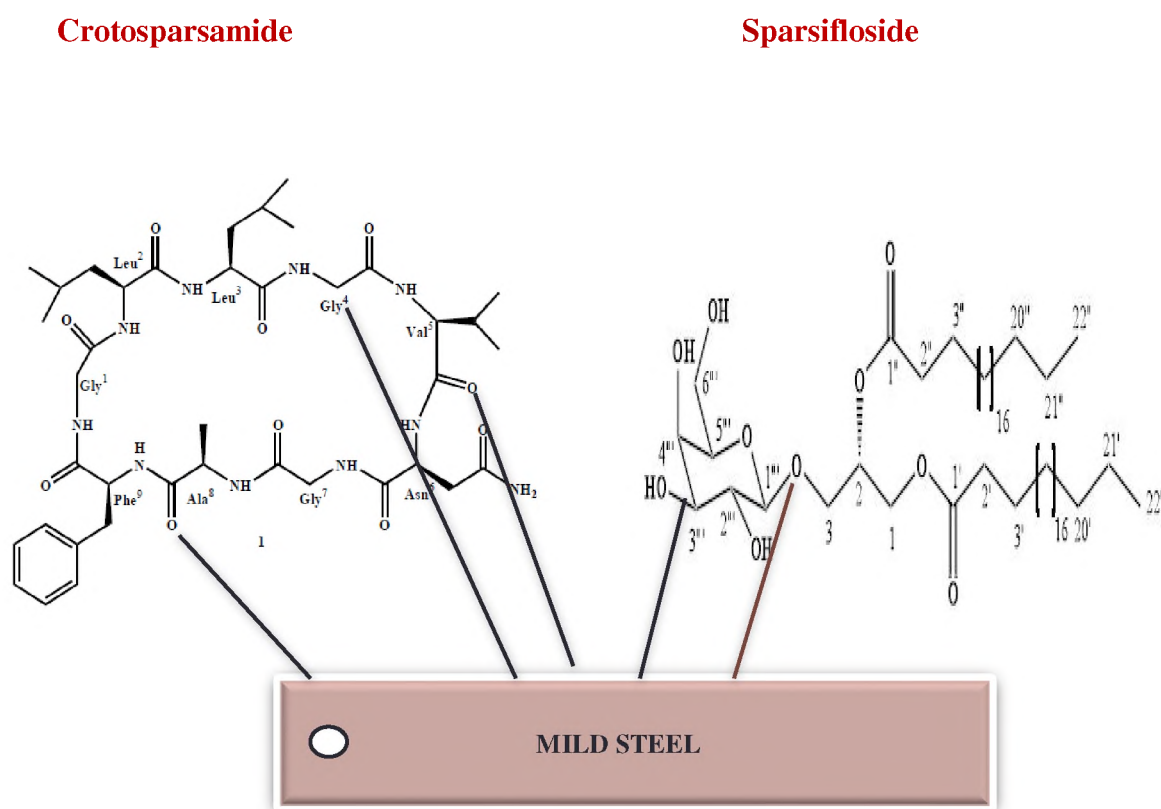


Fig-12 Schematic Adsorption model of onto the MS surface

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 leaves extract of CS on corrosion of mild steel in 1 M HCl by weight 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 98 % inhibition efficiency was obtained for 0.7% concentration of leaves extract of CS.

- * The leaves extract of CS 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 CS 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 CSL extract is adsorbed on the mild steel surface and inhibition process is by monolayer adsorption.
- * Inhibition Efficiency by weight loss methods was found to be greater than electrochemical measurements.
- * CSL 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 leaves extract of CS play a major role in reducing the metal dissolution and protect the MS surface from corrosion.

BIBLIOGRAPHY

6. BIBLIOGRAPHY

- **Ambrish Singh , Ishtiaque Ahamad , V. K. Singh , Mumtaz Ahamed Quraishi.** Inhibition effect of environmentally benign *karanj* (*Pongamia pinnata*) seed extract on corrosion of mild steel in hydrochloric acid solution, J Solid State Electrochem. 2010; 6.
- **Anantkrishnan S. V., Aravamuthachari S., Govindarajan V. S.** A 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.
- **Ananda Louis Sathiyathan . R, Maruthamuthu.S, Selvanayagam.M Mohanan.S, Palaniswamy .S.** Corrosion inhibition of mild steel by ethanolic extracts of *Ricinus communis* leaves, Indian Journal of Chemical Technology, Vol 12, May 2005, pp 356-360.
- **Abiola O.K, N.C. Oforika, E.E Ebenson, N.M. Nwinuka, and M.Saadawy,** "The role of acid anion on the inhibition of the acidic corrosion of steel by *lupine* extract", Corrosive science, 51(5), 2009, 1038, 1042.
- **Amit, Jain; Paras, Sharma; Kaushik, Sunil,** Evaluation of phenolic & flavonoid profile and screening of antioxidant activity of plant croton sparsiflorus by bio-autographic method, Journal of Pharmacy Research; May 2010, Vol. 3 Issue 5, p1146.
- **Ambrish Singh, V. K. Singh, M. A. Quraishi .** Aqueous Extract of *Kalmegh* (*Andrographispaniculata*) Leaves as green inhibitor for Mild Steel in Hydrochloric Acid Solution. International Journal of Corrosion .2010; 1-10.
- **Anand . B., Balasubramanian.V,** Corrosion behaviour of mild steel in acidic medium in presence of aqueous extract of *Allamandablanchetii*. E-Journal of Chemistry. 2011; 8(1):226-230.
- **Ashok Kumar S. L., Iniyavan P, Saravana Kumar M., Sreekanth A.,** "Corrosion Inhibition Studies of *Ecbolium Viride* Extracts on Mild Steel in HCl, J. Mater. Environ. Sci. 3 (3) (2012) 461-468.

- **Bag S.K., Chakraborty S.B. and Chaudri,** Journal Indian Chem.Soc.,73, pg:113-118, 1996.
- **Bouyanzer .A, Hammouti. B. And Majidi. L.;** pennyroyal oil from *Mentha pulegium* as corrosion inhibitor for steel in 1 M HCl, Materials letters, 60,2006, 2840-2843.
- **B Singh, S Singh, Surender Singh, L .Ali, Ritu Mahajan,** Ethnobotanical Significance and Antimicrobial Activity of *Blumea lacera* (Roxb.) International Journal of Pharmaceutical & Biological Archives 2010; 1(3):314 - 316.
- **Chauhan L.R. and Gunasekaran. G.,** Corrosion inhibition of mild steel *Zenthoxylum alatum* plant extract in dilute HCl medium, Corrosion science,49,(3),(2006)1143-1161.
- **Chaieb.E, Bouyanzer.A, Hammouti. B, Benkaddour.M,** “Inhibition of corrosion of steel in 1M HCl by *Eugenol* derivatives”, Applied surface science, (246), (2005), 199-206.
- **De Souza F.S, and Spinelli A.,”Caffeicacid** as green corrosion inhibitor for mild steel”, Corrosion science, 51(3), 2009, 642-644.
- **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.
- **Eddy N. O., Odoemelam S. A., Odiongenyi A. O..** Joint effect of halides and ethanol extract of *Lasianthera africana* on inhibition of corrosion of mild steel in H₂SO₄. J Appl Electrochem. 2009; 39:849–857.

- **Elyn Amira W.A.W., A.A. Rahim, H. Osman, K. Awang, P. Bothi Raja.**
Corrosion Inhibition Of Mild Steel In 1 M HCl Solution By *Xylopi Ferruginea* Leaves From Different Extract And Partitions, Int. J. Electrochem. Sci. 2011; 6: 2998 – 3016.
- **El-Etre A.Y,** *Khillah* extract as inhibitor for acid corrosion of SX 316 steel, Appl. Surf. Sci. 252 (2006) 8521.
- **Emeka E. Oguzie** .Studies on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel .Materials Chemistry and Physics.2006; 99:441–446.
- **Emeka E. Oguzie.**, Evaluation on the inhibitive effect of some plant extracts on the acid corrosion of mild steel; Corrosion Science, 50(11),2008,2993-2998.
- **Ehteram A.Noor;** Aqueous extracts for *fenugreek* leaves and seeds as green inhibitors for mild steel corrosion in acidic solution ; JCSE Volume 10, Preprint 39 submitted 15 July 2007.
- **El-Etre A.Y. ;(2006),** *Khillah* extract as inhibitor for acid corrosion of SX 316 steel, Applied surface science, 252, (24), 8521-8525.
- **El-Etre A.Y. ;(2007)** Inhibition of acid corrosion of carbon steel using aqueous extract of *olive* leaves, Journal of Colloid and Interface Science, 314,(2)78-583.
- **El-Etre A.Y. and Abdallah.M.** Natural *honey* as corrosion inhibitor for metals and alloys. II. C-steel in high saline water, Corrosion Science, Vol: 42, Pg: 731-738, April 2000.
- **Emeka E. Oguzi.**, Corrosion Inhibitive Effect and Adsorption behaviour of Hibiscus sabdariffa extract on Mild Steel in Acidic Media. Portugaliae Electrochimica Acta. (2008) 26: 303-314.
- **de Souza F.S., Spinelli A..Caffeic acid** as a green corrosion inhibitor for mild steel. Corrosion Science 2009; 51: 642–649.
- **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 2012Mar 12.

- **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.
- **Harborne J. B.**, Phytochemical Methods: A guide to modern techniques of plant analysis, Chapman and Hall, New York, (1973) 279.
- **J. B. Harborne, 1973**, Phytochemical Methods: A guide to modern techniques of plant analysis, Chapman and Hall, New York, (1973) 279.
- **Hemayet Hossain, Md. Sariful Islam Howlader, Shubhra Kanti Dey , Arpona Hira, Arif Ahmed, Dalim Kumar Tanchangya** Evaluation Of Phytochemical Screening And Antinociceptive Property Of The Ethanolic Extract Of *Croton Sparsiflorus* Roots ,International Journal of Pharmascholars ijps/July-Sept. 2012/Vol.1/Issue 2 Page 109.
- **Janaina cardozo da rocha, Jose Antoxio da conha ponciano, Gomes and Eliane D'elia**, corrosion sci., 2010., 2341-1297. Ashish kumar singh and Quraishi M.A., Corrosion sci., 2011., 1288-1297 Fabriziozucchi and Ibrahim Hashi omar, surface technology., 1985., 396-399.
- **Jain Amit Kumar, Paras Sharma, Mukesh S. Sikarwar**, Evaluation of Anti-Inflammatory and Anti-pyretic activity of total alcoholic extract of *Croton sparsiflorus* and its fractions, Journal of Pharmacy Research. 2010.
- **Jassbi AR, Zamanizadehnajari S, Tahara S.** Chemical constituents of *Euphorbia marschalliana* Boiss. Z Naturforsch C. 2004 Jan-Feb;59(1-2):15-8
- **Karthikaiselvi. R, Subhashini S, Rajalakshmi R.**, “ Biodegradable Green inhibitor (*Myristica Frangans*) as a corrosion inhibitor of mild steel in 1M HCl”, The journal of corrosion science and Engineering, 12 , (2009), preprint 33.
- **Khalid Hasan, S., and Pinky Sisodia.**, Paniala (*Flacourtia jangomas*) plant extract as eco friendly inhibitor on the corrosion of mild Steel in acidic media, Rasayan journal of Chemistry, 4(3), 2011a ;548-553

- **Khamis. E., Professor, Hefnawy.A, El-Demerdash. A.M.**; Acid cleaning of steel using *Arghel* Echo Friendly, Corrosion inhibitor 38, 2007,232.
- **Khamis. E.**, The effect of temperature on the acidic dissolution of steel in the presence of inhibitors; Corrosion, Vol: 46, No: 6, Pg: 476-483, 1990.
- **Kiran Iqbal, Sarfraz Ahmad Nawaz, Abdul Malik, Naheed Riaz, Naveen Mukhtar, Pir Mohammad, M Iqbal Choudhary** ,Isolation and lipoxigenase-inhibition studies of phenolic constituents from *Ehretia obtusifolia*, Chem Biodivers. 2005 Jan ;2 (1):104-11 17191923.
- **Loto C. A., Loto R. T. and Popoola A. P. I.**, “Corrosion and plants extracts inhibition of mild steel in HCl”, International Journal of the Physical Sciences Vol. 6(15), pp. 3689-3696, 4 August, 2011.
- **Loto C.A.and Popoola A.P.I.**, “Effect of *Cola Acuminata* and *Camellia Sinensis* Mixed Extracts on the Corrosion Inhibition of Mild Steel in 0.5M Sulphuric Acid, Int. J. Electrochem. Sci., 7 (2012) 2983 – 2996.
- **Mehmood R, Malik A**,Isolation and characterization of crotosparsamide, a new cyclic nonapeptide from *Croton sparsiflorus*, Nat Prod Commun. 2010 Dec;5(12):1885-8.
- **Manohari.G and Rajalakshmi R.**, Ninth Seminar proceedings, Tamilnadu state council for science and technology, (2001), India 318.
- **Muhammad Shahid**, “Corrosion protection with eco-friendly Inhibitors”, Adv. Nat. Sci.: Nanosci. Nanotechnol. 2 (2011).
- **Nnabuk. O. Eddy.** Ethanol Extract of *Phyllanthus amarus* as a Green Inhibitor for the Corrosion of Mild Steel in H₂SO₄. Portugaliae Electrochimica Acta. (2009) 27(5): 579-589.
- **Nnabuk O. Eddy; Stevens A. Odoemelam; Ibiam N. Ama.** Ethanol extract of *Ocimum gratissimum* as a green corrosion inhibitor for the corrosion of mild steel in H₂SO₄, Green Chemistry Letters and Reviews. 2010; 1_8, iFirst.
- **Okafor. P.C.I.E.Uwah, U.J.Ekpe, O.O.Ekerenam**, “*Combretum bracteosum* extract as Eco-friendly corrosion inhibitor for mild steel in acidic medium”, Pigment & Resin Technology, 38 (4), 2010, 236-242.

- **Okafor, Peter C., Ebenso, Eno E., and Ekpe, Udofot J.,** *Azadirachta indica* Extracts as Corrosion Inhibitor for Mild Steel in Acid Medium, International Journal of Electrochemical Science, 5: 2010, 978 – 993.
- **Oguzie. E.E.,** (2005), “Inhibition of acid corrosion of mild steel by *Telfaria occidentalis*” Pigment & Resin Technology, 34(6): 321 – 326.
- **Odiongenyi A.O., Odoemelam S.A., Eddy N.O.** Corrosion inhibition and adsorption properties of ethanol extract of *Vernonia amygdalina* for the corrosion of mild Steel in H₂SO₄. Portugaliae Electrochimica Acta .2009; 27(1):33-45.
- **Ostovari.A, S.M.Hoseineih, M.Peikari, S.R. Shadizadeh and S.J. Hashemi,** “Corrosion inhibition of mild steel in 1 M HCl solution by *henna* extract”, 51(9), 2009, 1935-1949.
- **P. Arora, S. Kumar, M. K. Sharma and S. P. Mathur,** Corrosion Inhibition of Aluminium by *Capparis decidua* in Acidic Media, E-Journal of Chemistry, Vol. 4, No. 4, pp. 450-456, October 2007.
- **Pandian Bothi Raja, Sethuraman M.G,** “Inhibition of corrosion of mild steel in sulphuric acid medium by *Calotropis procera*”, Pigment & Resin Technology, 38(1), 2009, 33-37.
- **Patchaiah Kalaiselvi, Subbiah Chellammal, Seeni Palanichamy and Gopalan Subramanian** “*Artemisia pallens* as corrosion inhibitors for mild steel in HCl medium”, Corrosion science, (1202-3), 2010, 643-648.
- **Patel N. S., Jauhari S., and. Mehta G. N.** Mild steel corrosion inhibition by *Bauhinia purpurea* leaves extract in 1N sulphuric acid. The Arabian Journal for Science and Engineering. 2009;34 : Number 2C.
- **Pandian Bothi Raja and Mathur Gopalakrishnan, Sethuraman** Inhibitive effect of *black pepper* extract on the sulphuric acid corrosion of mild steel, Materials Letters, Article in Press, 2008.
- **Pongsak Lowmunkhong, Dusit Ungthararak and Pakawadee Sutthivaiyakit** “ *Tryptamine* as a corrosion inhibitor of mild steel in HCl” Corrosion science, 52(1)2010, 33-37.

- **Quraishi M.A., Ambrish Singh, Vinod Kumar Singh, Dileep Kumar Yadav, Ashish Kumar Singh.** Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves. *Materials Chemistry and Physics* .2010; 122: 114–122.
- **Quraishi, M.A., Dileep Kumar Yadav and Ishtiaque Ahamad.,** Green Approach to Corrosion Inhibition by Black Pepper Extract in Hydrochloric Acid Solution, *The Open Corrosion Journal*, 2: 2009;56-60.
- **Radojic, K.Berkovic, S.Kovac and J.Vorkapic-Furac,** “*Natural honey and black Radish juice* as tin corrosion inhibitors” *Corrosion science*, 50(5), 2008, 1498-1504.
- **Raja, P.B., and Sethuraman, M.G.,** Studies on the inhibitive effect of *Datura stramonium* extract on the acid corrosion of mild steel, *Surface Review and Letters*, 14: 2007; 1157-1164
- **Rajalakshmi .R, Subhashini S, Leelavathy.S. and Femina Mary R.,** “Efficacy of sprouted seed extracts of *Phaseolus aureus* on the corrosion inhibition of mild steel in 1M hydrochloric acid”, *Oriental Journal of Chemistry*, 24(3), (2008),P.No- 1085-1090.
- **R. Rajalakshmi, S. Subhashini, A. Prithiba .** Acid extracts of *Ervatamia coronaria* leaves for corrosion inhibition of mild steel. *Asian Journal of chemistry* .(2010) 22 (7):5034-5040.
- **Rajiv Prakash, Gopal, J.L., Sudhish Kumar Shukla., Priyanka Dwivedi.,and Shanthi Sundaram.,** Inhibitive Effect of *Argemone mexicana* Plant Extract on Acid Corrosion of Mild Steel, *Industrial & Engineering Chemistry Research*, 50, 2011;11954–11959
- **Rashad MEHMOOD, Amna BIBI, Abdul** New secondary metabolites from *Croton sparsiorus* Morong *Turk J Chem* (2013) 37: 110-111 *Turkish Journal of Chemistry*.
- **Sanjana S.D., Sheth N.R., Patel Dhaval, Patel Biraju,** Characterization And Evaluation Of Antioxidant Activity Of *Portulaca Oleracea*, *International Journal of Pharmacy and Pharmaceutical Sciences* 01/2009;

- **Satapathy A.K., Gunasekaran. G, Sahoo S.C, Kumar Amit and Rodrigues P.V.,**”corrosion inhibition by *Justicia gendarussa* plant extract in HCl”,51(12),2009,2848-2856.
- **Sangeetha M., S. Rajendran, T.S. Muthumegala, A. Krishnaveni,** Green corrosion inhibitors – An Overview, *Zastita Materijala* 52 (2011) broj 1, 3- 19.
- **Sribharathy V., Susai Rajendran, Sathyabama J.,** “Inhibition of mild steel corrosion in sea water by *Dacus carota*”,*International Journal of Chemical Science and Technology* (ISSN: 2248-9797),2011.
- **Subhashini S, Rajalakshmi .R, and Safina.A.S,** “Biodegradable *aquatic waste* – *fish* scales as corrosion inhibitor for mild steel in acid medium”, *Material Science Research India*, 5(2), (2008), P.No- 375-382.
- **Shuduan Deng and Xianghong Li,** “Inhibition by Ginkgo leaves extract of the corrosion of steel in HCl and H₂SO₄ solutions,scidirect February 2012, Pages 407–415.
- **Shyamala,M., and Arulanantham,A.,** (2009), "*Eclipta alba* as Corrosion pickling inhibitor on mild steel in hydrochloric acid", *Journal of Material Science Technology*, 25:5, 633-636.
- **Subha.R., Saratha.R.,** Naturally occurring substance (*Calendula officinalis* flower) as a corrosion inhibitor of mild steel in 1 M HCl solution; *JCSE*, Vol:10, Preprint 9, 3rd Sep 2010.
- **Subhashini S, Rajalakshmi .R, Elakkiya. T, Srimathi.M.,** “ Evaluation of extract of *Ficus Benghalensis* as corrosion inhibitor of mild steel in HCl medium at different pH”, *Ultra Chemistry*, 4(2),(2008) 159 – 164.
- **Santhi T., Manonmani S.** Adsorption and inhibitive properties of ethanol extracts of *Muntingia calabura*as a green corrosion inhibitor for mild steel in acidic media. *Journal of Applied Sciences Research*. 2010; 6(12): 2264-2268.
- **Udayaprakash N.k. Bhuvanewari .S., Aravind .R, Kaviyarasan .V, Kalaivanan.K and sekar babu hariram .a** comparative study on antibacterial

activity of common weeds, International Journal of Pharma and Bio Science Vol2/issue1/jan-mar-2011.

- **Umoren S.A., Eduok U.M., Solomon M.M., Udoh A.P.** Corrosion inhibition by leaves and stem extracts of *Sida acuta* for mild steel in 1 M H₂SO₄ solutions investigated by chemical and spectroscopic techniques. Arabian Journal of Chemistry .2011;doi:10.1016/j.arabjc.2011.03.008.
- **Umoru L.E., Fawehinmi I.A., Fasasi A.Y.** Investigation of the inhibitive influence of *Theobroma Cacao* and *Cola acuminata* Leaves extracts on the Corrosion of a Mild Steel in Sea Water. Journal of Applied Sciences Research. (2006)2 (4): 200-204.
- **Urvija Garg, R K. Tak** ,Inhibition of the Corrosion of Mild Steel in Acid Media by Naturally Occurring *Acacia senegal* ,E-Journal of Chemistry.2010;7(4): 1220-1229.
- **Vinod Kumar K.P., Narayanan Pillai M.S., Rexin Thusnavis G.** Pericarp of the Fruit of *Garcinia mangostana* as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium. Portugaliae Electrochimica Acta 2010; 28(6) :373-383.