Inhibitive effect of leaf extract of *Durenta erecta* on Mild Steel corrosion in 1M Hydrochloric and 0.5M Sulphuric acid solution

Sowmya, B

(14PCH007)

Thesis Submitted to

Avinashilingam Institute for Home Science and Higher Education for Women,

Coimbatore-641 043

In Partial Fulfilment of the Requirements for the Degree of

Master of Science in Chemistry

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Certified as Bonafide Research work

Signature of the Supervisor

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LIST OF ABBREVIATION

DE	Durenta erecta
DEL	Durenta erecta leaf
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
MS	Mild steel
CR	Corrosion rate
IE	Inhibition efficiency
ppm	Parts per million
Mpy	Mils per year
θ	Surface coverage
I_{corr}	Corrosion current
E_{corr}	Corrosion potential
b_a	Anodic tafel slope
b_c	Cathodic tafel slope
Cdl	Double layer capacitance
Rct	Charge transfer resistance
Rp	Polarization resistance
Rs	Solution resistance
mV	Milli volt
LPR	Linear polarization resistance
EIS	Electrochemical Impedance Spectroscopy

Introduction

INTRODUCTION

Corrosion has been one of the biggest problems from time immemorial. Researches have been geared towards protecting metals from corrosion by the use of inhibitors. Corrosion inhibitors are widely used in industry to control dissolution and reduce the corrosion rate in contact with aggressive acid solution. Most of acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen in their molecule.

1.1. Definition

Corrosion is a process of formation of the compound of pure metal by the chemical reaction between metallic surface and its environment. It is an oxidation process. It causes loss of metal. Hence, disintegration of a metal by its surrounding chemicals through a chemical reaction on the surface of the metal is called corrosion.

Example: (i) Formation of rust on the surface of iron, formation of green film on the surface of copper.

(ii) Steel rusts when immersed in seawater.

The responsible factors for the corrosion of a metal are the metal itself, the environmental chemicals, temperature and the design.

"Corrosion is the deterioration or destruction 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."

Figure 1.1: Corrosion

1.2. Factors influencing corrosion

1.2.1. Effect of environment

Climate - The environmental conditions to which the metal specimens are exposed greatly affects corrosion characteristics. In a predominately marine environment, moisture-laden air is considerably more detrimental to metals than it would be if all operations were conducted in a dry climate.

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

Stress - The rate of corrosion also increases when the system is subjected to a stress (tensil, compressive etc).

Time - The extent of corrosion naturally increases with increased time.

Environmental conditions - The environmental conditions also exert a strong influence on the rate of corrosion.

1.2.2. Effect of substrate

Foreign Material - Among the controllable factors affect the consent and spread of corrosive attack is foreign material with adheres to the metal surfaces. Such foreign material includes: Soil and atmosphere dust. Oil grease and engine exhaust residues. Salt water and salt moisture condensation. Spilled battery acids and caustic cleaning solution. Welding and brazing flux residues.

- If the material produced by corrosion is insoluble and forms an impervious and tenacious layer, the corrosion reaction becomes self-limiting, as the corrosive medium can no longer diffuse through the corrosion product. A useful example of this is the oxidation of aluminum, which forms a thin protective layer of aluminum oxide, this is a good example of self-passivation.
- The corrosion product is soluble or porous, corrosion will continue until the material is depleted, and no further reaction can occur.
- Chemical and physical homogeneity of the metal surface.

1.3. Corrosion as a chemical reaction

Corrosion or destruction of a material can take place in acid and alkaline or neutral solutions.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

The corrosion of metals can also occur in fresh water, sea water, salt solution, alkaline or basic media. In all these cases corrosion will occur if dissolved oxygen is also present as the following equation shows.

$$4Fe + 6H_2O + 3O_2 \longrightarrow 4Fe\,(OH)_3 \text{ Ferric hydroxide}$$

During rusting in the atmosphere, there is an opportunity for drying and this ferric hydroxide dehydrates and forms the familiar reddish brown iron oxide (rust) as shown below.

$$2Fe(OH)_3 \longrightarrow \underset{\text{Ferric oxide}}{Fe_2O_3} + 3H_2O$$

Metals can also be corroded in solutions containing neither oxygen nor acids. The most typical of such solutions are oxidizing salts such as ferric and cupric compound as shown below.

$$Zn + 2FeCl_3 \longrightarrow ZnCl_2 + 2FeCl_2$$

$$Zn + CuSO_4 \longrightarrow ZnsO_4 + Cu$$

In the case of some metals like aluminium, the corrosion product prevents further corrosion. For example in the case of aluminium, it forms an almost invisible oxide film which protect the metal from extensive atmospheric corrosion. That is why aluminium is widely used as windows frames, gutters, automobile trims etc.

1.4. Electrochemistry of corrosion

According to the electrochemical theory, the corrosion of a metal in aqueous solution may be a two-step process, one involving oxidation and another reduction. It is known that two metals having different electrode potentials form a galvanic cell when they are immersed in a conducting solution. The emf of the cell is given by the difference between the electrode potentials. When the electrodes are joined by a wire, electrons flow from the anode to the cathode. The oxidation reaction occurs at the anode, i.e. at the anode the metal atoms lose their electrons to the environment and pass into the solution in the form of positive ions.

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

Thus, there is a tendency at the anode to destroy the metal by dissolving it as ions. Hence corrosion always occurs at anodic areas.

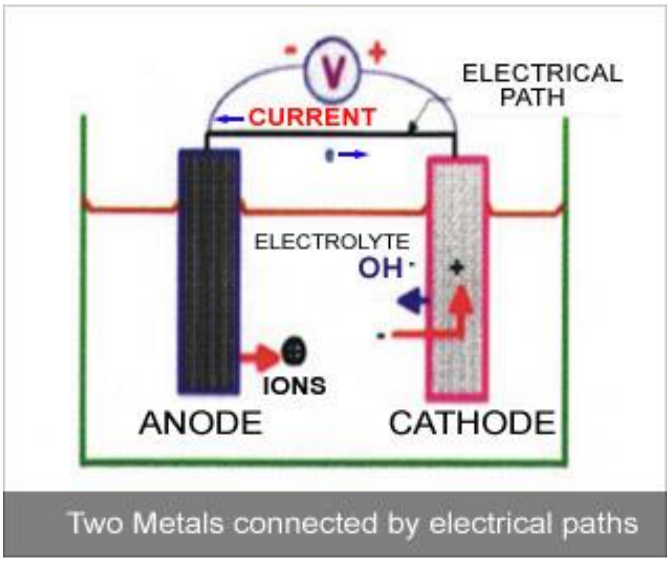


Figure 1.2: Schematic representation of electron flow from the anode to the cathode in a Galvanic cell

The electrons released at the anode are conducted to the cathode and are responsible for various cathodic reactions such as electroplating (deposition of metals), hydrogen evolution and oxygen absorption:

(i) **Electroplating:** The metal ions at the cathode collect the electrons and deposit on the cathode surface.

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

(ii) **Liberation of hydrogen:** In an acid solution, (in the absence of oxygen) hydrogen ions accept electrons and hydrogen gas is formed.

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

In a neutral or alkaline medium, (in the absence of oxygen) hydrogen gas is liberated with the formation of OH- ions.

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

(iii) **Oxygen absorption:** In the presence of dissolved oxygen and in an acid medium, oxygen absorption reaction takes place.

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

In the presence of dissolved oxygen and in a neutral or weakly alkaline medium, OH- ions are formed.

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

Thus it is clear that the essential requirements of electrochemical corrosion are as follows:

(a) Formation of anodic and cathodic areas.

(b) Electrical contact between the cathodic and anodic parts to enable the conduction of electrons.

(c) An electrolyte through which the ions can diffuse or migrate. This is usually provided by moisture.

1.5. Causes of corrosion

Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small.

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

- Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.
- Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).
- Loss of time in availability of profile-making industrial equipment.
- Reduced value of goods due to deterioration of appearance.
- Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).
- Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings.
- Loss of technically important surface properties of a metallic component.
- Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.
- Buried gas or water supply pipes can suffer severe corrosion which is not detected until an actual leakage occurs, by which time considerable damage may be done.
- In electronic equipment it is very important that there should be no raised resistance at low current connections.
- Sea water is a highly corrosive electrolyte towards mild steel. Ships suffered severe damage in the areas which are most buffeted by waves, where the protective coating of paint has been largely removed by mechanical action.

1.6. Consequence of corrosion

Some important consequences of corrosion are summarized below:

1. Plant shutdowns

Shutdown of nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.

2. Loss of products

Leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards.

It is well known that at least 25% of water is lost by leakage.

3. Loss of efficiency

Insulation of heat exchanger tubing and pipelines by corrosion products reduces heat transfer and piping capacity.

4. Contamination

Corrosion products may contaminate chemicals, pharmaceuticals, dyes, packaged goods, etc. with dire consequences to the consumers. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).

5. Nuclear hazards

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

- Loss of time in availability of profile-making industrial equipment.
- Reduced value of goods due to deterioration of appearance.
- Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

6. Over design

Corrosion is a potent force which destroys economy, depletes resources and cause costly and untimely failure of plants, equipments and components.

In the absence of adequate corrosion rate information, over design is required to ensure reasonable service life resulting in human life and safety.

1.7. Cost of corrosion

The cost of corrosion can be defined in different ways depending on what is included and who is affected. In past studies, different definitions of the cost of corrosion have been used, and have therefore arrived at different estimates. In the current study, the total direct corrosion cost for each sector was estimated and major components contributing to this cost were analyzed. In addition, preventative strategies for corrosion control were described for the individual sectors.

Corrosion is recognized as one of the most serious problem in our modern societies and the resulting losses each year are in hundreds of billions of dollars

A recent report describes the annual direct and indirect cost 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% of the 1998 U.S. gross domestic product (GDP).

The annual cost of corrosion consists of both direct costs and indirect costs.

1.7.1. Direct cost

1**.** The costs of design, manufacturing, and construction:

- Material selection, such as stainless steel to replace carbon steel,
- Additional material, such as increased wall thickness for corrosion allowance,
- Material used to mitigate or prevent corrosion, such as coatings, sealants, corrosion inhibitors, and cathodic protection, and
- Application, including the cost of labor and equipment.

2. The cost of management:

- Corrosion-related inspection, corrosion-related maintenance,
- Repairs due to corrosion, replacement of corroded parts,
- Inventory of backup components,
- Rehabilitation and loss of productive time.

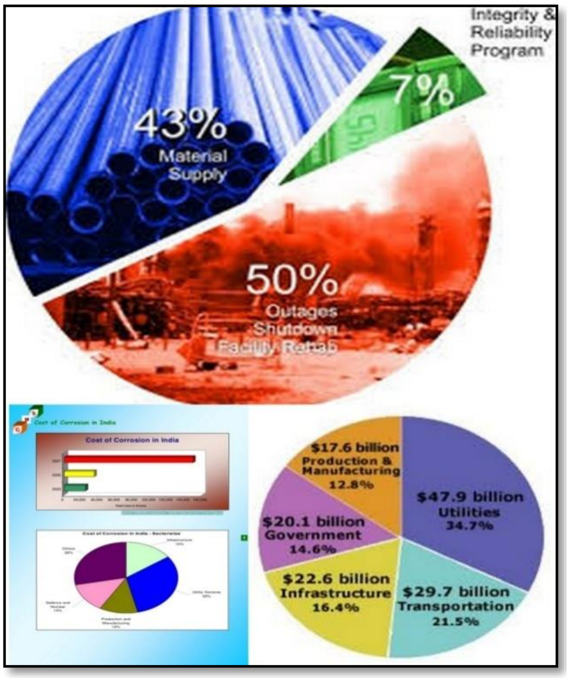


Figure 1.3: Direct cost of corrosion

1.8.2. Indirect costs

Measuring and determining the value of indirect costs are generally complex assessments; traffic delays due to bridge repairs and rehabilitation that are more difficult to turn over to the owner or operator of the structure. These become indirect costs to the user but can have a significant impact on the overall economy due to lost productivity.

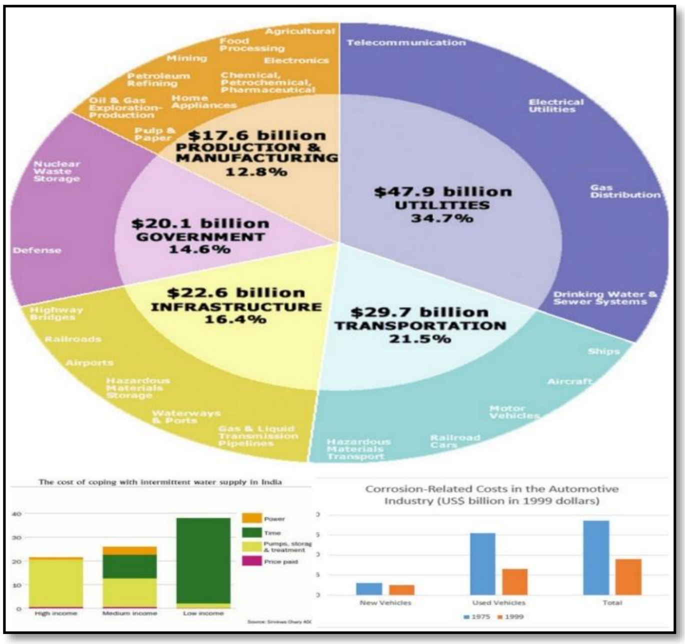
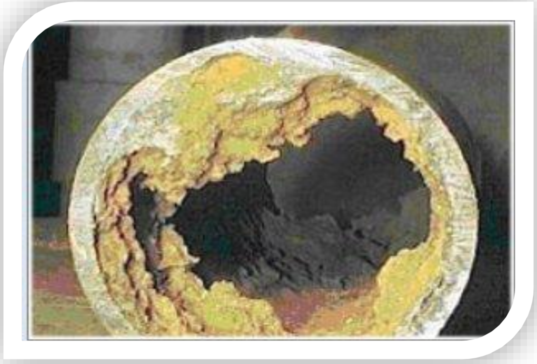
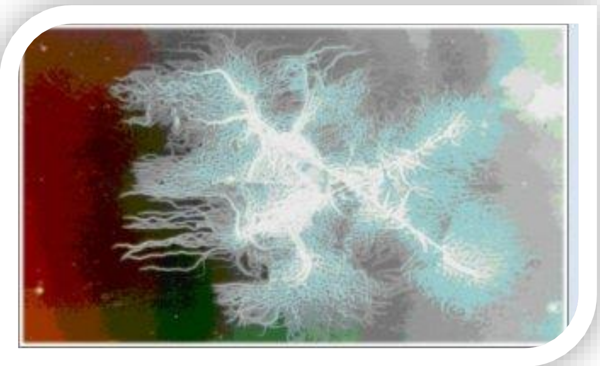
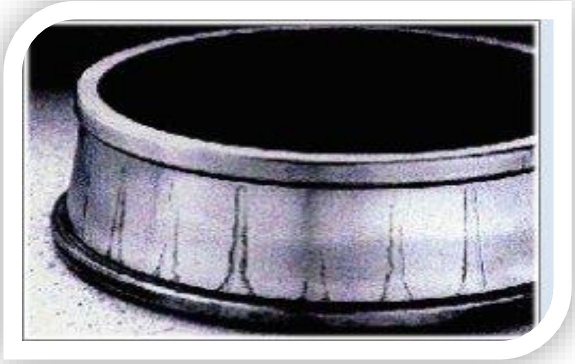


Figure 1.4: Indirect cost of corrosion

1.8. Types of corrosion

***General* Corrosion** - It damages the entire surface of the material at about the same rate, causing the metal to thin. It is a chemical attack, easily detected by its appearance.	
Galvanic Corrosion - Galvanic corrosion occurs in the presence of an electrolyte such as seawater when dissimilar types of metals join together	
Pitting corrosion - Pitting results when a small hole, or cavity, forms in the metal, usually as a result of de-passivation of a small area. This area becomes anodic, while part of the remaining metal becomes Cathodic.	
Stress Corrosion - Stress corrosion cracking (SCC) is a complex form of corrosion that occurs when brittle, dry cracks develop from the combined effects of a tensile stress.	

Corrosion Fatigue - Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment.	
Intergranular Corrosion or intercrystalline corrosion - Intergranular corrosion is a chemical or electrochemical attack on the grain boundaries of a metal.	
Crevice Corrosion - Similar to pitting, crevice corrosion occurs at a specific location. This type of corrosion is often associated with a stagnant micro-environment, like those found under gaskets and washers and clamps.	
Filiform Corrosion - Filiform corrosion occurs on painted or plated surface when moisture permeates the coating. Long branching filaments of corrosion products extend out from the original corrosion pit and cause degradation of the protective coating	

Erosion corrosion also known as flow-assisted corrosion is the process of moving a corrosive liquid against a metal surface, leading to the accelerated loss of material. For e.g., grooves gullies, waves, rounded holes, valves, pumps, propellers etc.	
Fretting Corrosion or wear oxidation, friction oxidation, chafing, and brinelling. Fretting corrosion occurs as a result of repeated wearing, weight and/or vibration on an uneven, rough surface. And impact machinery, bolted assemblies and bearings, as well as to surfaces exposed to vibration during transportation.	
Corrosion in Concrete - construction includes carbon steel, reinforcing rods, cable, and wires inside the structure. The steel that resides within the concrete structure is where corrosion can develop.	
Exfoliation Corrosion – it is a type of selective corrosion that propagates along a large number of planes running parallel to the direction of rolling or extrusion. The metal will swell, which results in the spectacular aspect of this form of corrosion.	

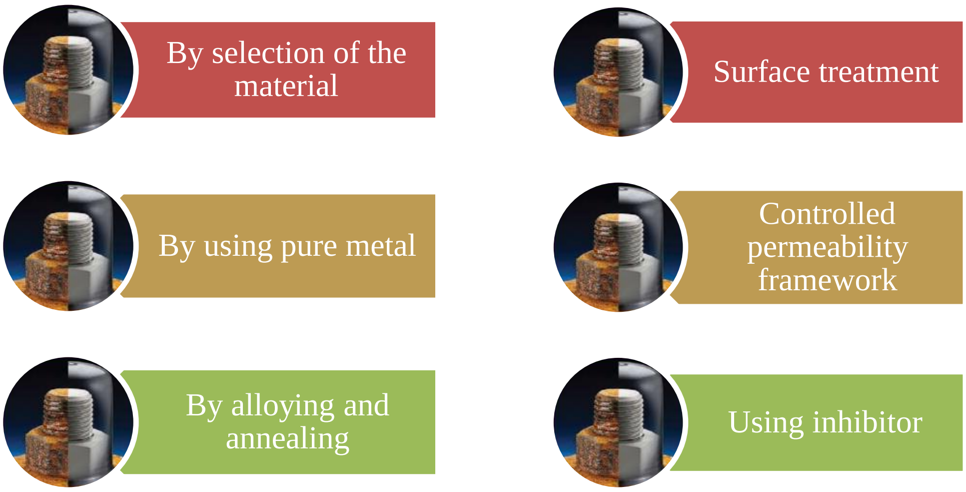
1.9. Importance of corrosion studies

It is nowadays necessary to pay more attention to metallic corrosion than was done earlier due to,

- Corrosion can lead to failures in plant infrastructure and machines which are usually costly to repair, costly in terms of cost or contaminated product, in terms of environmental damage, and possibly costly in terms of human safety.
- Increasing use of metals in all fields of technology.
- The conversion of metal resources, the world's supply of which is limited, and the wastage of which includes corresponding losses of energy and water resources accompanying the reduction and fabrication of metal structure.
- Use of rare and expansive metals whose protection requires special precautions.
- Use of new high strength alloys which are usually more susceptible to certain types of corrosive attacks.
- Increasing pollution of air and water resulting in a more corrosive environment.
- Strict safety standards of operating equipment which may fail in a catastrophic manner due to corrosion.

1.10. Corrosion prevention

Corrosion can be controlled by followings ways,



By selection of the material

By using pure metal

By alloying and annealing

Surface treatment

Controlled permeability framework

Using inhibitor

1.10.1. By selection of the material

Selection of the right type of the main factor for corrosion control. Thus, noble metals are used for surgical instruments and ornaments as they are most immune to corrosion.

1.10.2. By using the pure metals

Pure metals have higher corrosion resistance. Even minute amount of impurities may lead to severe corrosion, e.g. 0.02% iron in aluminium decreases its corrosion resistance.

1.10.3. By alloying

Both corrosion resistance and strength of many metals can be improved by alloying. E.g. stainless steel containing chromium produces a coherent oxide film which protects the steel from further attack.

1.10.4. By annealing

Heat treatment like annealing helps to reduce internal stresses and reduces corrosion.

1.10.5. Surface Treatments

Applied coating

Galvanization

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the structural material. Platings usually fail only in small sections, but if the plating is more noble than the substrate (For example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface. For this reason, it is often wise to plate with active metal such as zinc or cadmium. Painted coatings are relatively easy to apply and have fast drying times although temperature and humidity may cause dry times to vary.

Anodization

Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores, several nanometers wide, appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow.

Anodizing is very resilient to weathering and corrosion, so it is commonly used for building facades and other areas where the surface will come into regular contact with the elements. While being resilient, it must be cleaned frequently. If left without cleaning, panel edge staining will naturally occur.

Biofilm coatings

A new form of protection has been developed by applying certain species of bacterial films to the surface of metals in highly corrosive environments. This process increases the corrosion resistance substantially. Alternatively, antimicrobial-producing biofilms can be used to inhibit mild steel corrosion from sulfate-reducing bacteria.

1.10.7. Controlled permeability formwork

Cathodic protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water, and fuel pipelines and tanks; steel pier piles, ships, and offshore oil platforms.

Sacrificial anode protection

For effective CP, the potential of the steel surface is polarized (pushed) more negative until the metal surface has a uniform potential. With a uniform potential, the driving force for the corrosion reaction is halted. For galvanic CP systems, the anode material corrodes under the influence of the steel, and eventually it must be replaced. The polarization is caused by the current flow from the anode to the cathode, driven by the difference in electrochemical potential between the anode and the cathode.

Anodic protection

Anodic protection impresses anodic current on the structure to be protected (opposite to the cathodic protection). It is appropriate for metals that exhibit passivity (e.g., stainless steel) and suitably small passive current over a wide range of potentials. It is used in aggressive environments, e.g., solutions of sulfuric acid.

1.10.8. Corrosion Inhibitors

An inhibitor is a chemical compound that when added to a liquid/gas, it decreases the corrosion rate of material, typically metal or alloy.

The properties that must be met by a Corrosion Inhibitor,

a. Capability of reducing corrosion rates.

b. The active principle of the CI must be in contact with the metal to be protected.

c. Must not have side effects.

Types of corrosion inhibitors

Anodic inhibitors

Anodic inhibitor is forming a protective oxide film. Causing a large anodic shift of the corrosion potential. This shift forces the surface converted into passivation region. They are also referred to passivators. For examples: Chromates, Nitrates, Tungstates, molybdates.

Cathodic inhibitors

In acid solution, the metal is corroded because of the cathodic reaction of evolution of hydrogen at cathode,

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

Corrosion at the cathode can be controlled by,

- Decreasing the evolution of hydrogen at the cathode.
- Increasing the over voltage of hydrogen evolution.
- The evolution of hydrogen at cathode can be decreased by reducible salts of metals such as amine, nitrogen compound, urea and thiourea, heavy metal soaps, etc. For e.g., Arsenic, antimony, hetero polar organic compounds. Electrochemically, The corrosion rates can be reduced by scavengers with dissolved oxygen For e.g.., sulphite, hydrazine.

Mixed Inhibitors

Mixed inhibitors act reducing both anodic and cathodic reaction. They are typically film forming compound. This film reduces the corrosion. For e.g. silicates and phosphates.

Silicates- used to much domestic water softer to prevent the occurrence of rust water. Sodium silicates- it protects steel, copper, and brass. Phosphates- It requires oxygen for effective inhibition.

Volatile Corrosion Inhibitors

Volatile corrosive inhibitor is also called as vapour phase inhibitors. These compounds are transported in a closed environment to the site of corrosion. In boiler, volatile basic compounds such as morphine, hydrazine. The vapour phase inhibitors are usually effective, this is used in closed space such as inside packages, On the interior of machinery during shipment.

1.11. Inhibitor mechanism

The action mechanisms of CIs are,

- By adsorption, forming a film that is adsorbed onto the metal surface.
- By inducing the formation of corrosion products such as iron sulfide, which is a passivizing species.
- By changing media characteristics, producing precipitates that can be protective and eliminating or inactivating an aggressive constituent.
- It is well known that organic molecules inhibit corrosion by adsorption, forming a barrier between the metal and the environment. Thus, the polar group of the molecule is directly attached to metal and the nonpolar end is oriented in a vertical direction to the metal surface, which repels corrosive species, thus establishing a barrier against chemical and electrochemical attack by fluids on the metallic surface.

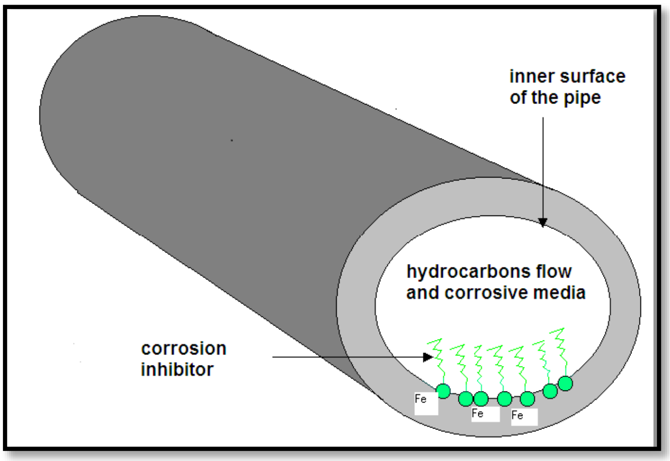


Figure 1.5: Schematic representation of inhibition mechanism

An inhibitor may be effective in one system, while in another it is not. Therefore, it is convenient to consider the following factors:

- Chemical structure of the inhibitor component.
- Chemical composition of the corrosive medium.
- Nature of the metal surface.
- Operating conditions (temperature, pressure, pH, etc.).
- Thermal stability of the inhibitor - Corrosion inhibitors has temperature limits above which lose their effectiveness because they suffer degradation of the containing components.

- Solubility of the inhibitor in the system - The solubility of the inhibitor in the system is required to achieve optimum results in the metal surface protection; this depends on the length of the hydrocarbon chain.
- The addition of surfactants to enhance the dispersibility or solubility of inhibitors.
- Modification of the molecular structure of the inhibitor by ethoxylation to increase the polarity, and thus reach its solubility in the aqueous medium.

1.11.1. The main features of an inhibitor

- Ability to protect the metal surface.
- High activity to be used in small quantities (ppm).
- Low cost compound(s).
- Inert characteristics to avoid altering a process.
- Easy handling and storage.
- Preferably with low toxicity.
- Non-contaminant.
- It should act as an emulsifier.
- It should act as a foaming agent.

1.12. Corrosion and industries

Corrosion in the electronics industry

Corrosion of device components, manufactured by the electronics industry, is a problem that has occurred during a long time. Often, especially corrosion of one or more of the metallic elements of an electronic component is the primary cause of failure in various electronic equipments. The high density of components required to reduce the size of electronic equipment, also for a better signal processing, leads to the generation of enclosed corrosion between thin metal sections.

Corrosion in the automotive industry

One of the most important elements of our daily life, which has great impact on economic activity, is represented by automotive vehicles. These vehicles are used to transport people, animals, grains, food, machinery, medicines, supplies, materials, etc. All operate mostly through the operation of internal combustion engines, which exploit the heat energy generated by this process and convert it in a mechanical force and provide traction to these vehicles.

The nuclear industry

The nuclear industry has most of corrosion problems of other industries and some that are all of its own. Right from the start, the potential for disaster was recognized and tackled head-on by adopting high grade materials in many parts of systems. For boiling water reactors and pressurized water reactors average capacity loss 5% -8% in 1982.

Corrosion in exhaust pipes and batteries

Exhaust pipes made of SS (0.6 - 0.8 mm thick) have a better resistance to chemical corrosion at high temperatures, which is why we are now using SS in many popular models. This SS resists corrosion much more than conventional CS and thus their long life covers the higher price. Another alternative is to use conventional CS tube, zinc coated or aluminum. These exhausts pipes are less expensive than stainless steel, but less resistant to corrosion.

Corrosion control in thermoelectric plants

Power plants, also called cogeneration. Generate electricity or mechanical power and useful heat, sometimes using thermal energy sources that are lost in conventional plants, because of corrosion. And there providing prevention also.

Corrosion in the paper industry

Corrosion of the infrastructure used in the pulping and paper industry, is another serious problem for corrosion specialists. The wide experience, gathered from cases of corrosion in the various infrastructure components of the paper industry, has provided an extensive literature on mechanisms, types and control of corrosion in this environment.

Figure 1.6: Corrosion and various industries

1.14. Plant description

<u>Origin</u>

Native to southern USA (i.e. Texas and southern Florida), Mexico, Central (i.e. Belize, Costa Rica, El Salvador, Guatemala, Honduras, Nicaragua and Panama), the Caribbean and South America (i.e. Surinam, Venezuela, Brazil, Bolivia, Colombia, Ecuador, Peru, Argentina and Paraguay).

<u>Cultivation</u>

A widely cultivated garden and hedge plant throughout the wetter and sub-humid regions of Australia. Several newer cultivars, which are thought to be less invasive, are still very popular in cultivation (e.g. *Duranta erecta* 'Sheena's Gold', *Duranta erecta* 'Geisha Girl', *Duranta erecta* 'Alba' and *Duranta erecta* 'Variegata').

Figure 1.7: *Durenta erecta*

Rank	Scientific Name and Common Name
Kingdom	Plantae – Plants
Subkingdom	Tracheobionta – Vascular plants
Division	Magnoliophyta – Flowering plants
Class	Magnoliopsida – Dicotyledons
Subclass	Asteridae
Order	Lamiales
Family	Verbenaceae – Verbena family
Genus	*Duranta* L. – duranta
Species	*Duranta erecta* L. – golden dewdrops

Table 1.1: Classification of the plant

Habitat

A weed of disturbed sites, waste areas, roadsides, wetter pastures, open woodlands and densely forested areas, and particularly along waterways in sub-tropical and tropical regions.

Distinguishing Features

- A slightly spiny upright shrub with drooping branches.
- Its oppositely arranged leaves are sometimes toothed towards their tips.
- Its blue or light purple (occasionally white) tubular flowers are borne in elongated clusters.
- It is most easily distinguished by its large clusters of yellow-orange mature fruit.

Habit

A upright (i.e. erect) shrub or small tree usually growing 4-6 m tall, but occasionally reaching up to 7 m in height.

Stems and Leaves

The branches can are often drooping in nature, especially when carrying large numbers of mature fruit. There are usually at least some pairs of spines along the stems, one located at the base of each of the leaf stalks (i.e. they are axillary spines).

Younger stems are green in colour and sparsely covered in close-lying (i.e. appressed) hairs.

The leaves are simple and paired (i.e. oppositely arranged) or occasionally borne in whorls of three. They have short leaf stalks (i.e. petioles) up to 1 cm long and are oval (i.e. elliptic) to egg-shaped in outline (i.e. ovate). The leaf blades (15-90 mm long and 12-60 mm wide) usually have entire margins, but sometimes they are slightly toothed (i.e. serrated) towards the pointed or rounded tips (i.e. acute or obtuse apices).

Flowers and Fruit

The blue or pale purple flowers (occasionally white) are borne in elongated clusters (5-30 cm long) at the tips of the branches and in the upper leaf stalks (i.e. in terminal and axillary racemes). These flowers (9-18 mm long) are borne on short stalks (i.e. they are sub-sessile) and each flower consists of a thin tube (about 1 cm long), made up of the fused petals, which opens into five distinct lobes (i.e. corolla lobes). The two lower petal lobes are slightly smaller and both of these has a darker stripe down its centre. Each flower also has five small green sepals (3-7 mm long), that are also fused together at the base, and four stamens. Flowering mostly occurs during summer and autumn.

The fruit are rounded (i.e. globose) 'berries' (i.e. drupes) and are usually borne in large clusters.

1.13.1. Impact on environment

Duranta (*Duranta erecta*) is regarded as an environmental weed in Queensland and northern New South Wales. It was recently listed among the top 50 most invasive species in the New South Wales North Coast environmental weed survey and among the top 100 most invasive plants in south-eastern Queensland.

Duranta (*Duranta erecta*) is also listed as an important invasive plant in China, where it causes obvious changes in natural ecosystems, and it is on the list of the most invasive horticultural plants in Hawaii. The leaves and 'berries' (i.e. drupes) are poisonous to people and animals, and are reported to have caused numerous deaths in domestic pets. Dense thickets can restrict access and reduce the productivity of pastures.

1.13.2. Objectives

- To select an eco-friendly “zero cost” inhibitor for corrosion of MS in 1M HCl and 0.5M H_2SO_4 acid medium.
- To utilize DEL extract as corrosion inhibitor for MS in 1M HCl and 0.5M H_2SO_4 acid medium
- To carryout phytochemical screening for DEL extract.
- To study the effect of concentration of the extract at room temperature on corrosion inhibition of MS in 1M HCl and 0.5M H_2SO_4 acid medium.
- To carryout immersion studies using the selected DEL extract.
- To find the stability of DEL extracts at higher temperatures.

Review of literature

REVIEW OF LITERATURE

An acquaintance with related literature of past studies is a must for any research for formulating sound methodology, which acts as a persevering force during the on set of research. From this literature new areas of research can be inferred.

The present study on **"Inhibitive effect of leaf extract of *Durenta erecta* on mild steel corrosion in 1M Hydrochloric and Sulphuric acid solution*"*** is reviewed under the following topics.

1) Natural products as inhibitors

2) Organic compounds as inhibitors

3) Corrosion behaviour of mild steel with varying parameters

- Effect of concentration of the inhibitor
- Influence of exposure time
- Temperature effect

4) Kinetic analysis

5) Polarization behaviour

2.1. Natural products as inhibitors

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

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

- ***Orubite and Oforka (2004)*** reported the inhibition of corrosion of mild steel in HCl solution using the leaves of ***Nypa fruticans wurmb*** by weight loss and hydrogen gas evolution methods. Maximum inhibition efficiency of 75.11% was observed with ***Nypa fruticans*** wurmb extract.
- ***Oguzie et al., (2005)*** investigated the efficiency of ***Telfaria occidentals*** extract as a corrosion inhibitor for mild steel in 2M HCl and 1M H_2SO_4

solutions using hydrogen gas evolution technique. The results showed that the inhibition efficiency increased with increasing extract concentration.

- An evaluation of the effective performance of ***Artemisia oil***, extracted from Artemisia Herba Alba, as corrosion inhibitor for steel in 0.5 M H_2SO_4 using electrochemical impedance spectroscopy and weight loss methods was carried out. The inhibition efficiency was found to increase with increasing oil content to attain 74% at 1 g/L ***(Ouachikh et al.,)***.
- Natural oil extracted from ***Pennyroyl Mint*** *(Mentha eulogiums, PM)* was evaluated as corrosion inhibitor of steel in molar HCl by ***Bouyanzer et al., (2006)*** using weight loss, electrochemical polarization and EIS methods**.**The inhibition efficiency was found to increase with increasing oil content to attain 80% at 2.76 g/ L.
- The leaves extract of ***Datura stramonium*** was studied as a possible source of green inhibitor for corrosion of mild steel in HCl and H_2SO_4 media using weight loss and electrochemical techniques. The studies revealed that the plant extracts act as a good inhibitor in both the acid media and had better inhibitive capacity in H_2SO_4 medium (***Raja et al., 2007).***
- ***Oguzie (2008)*** studied the corrosion inhibiting properties of extracts of ***Occimum vridis, Telferia occidentails, Azadirachta indica*** and ***Hibiscus sabdariffa*** as well as extracts from the seeds of ***Garcinia kola*** on the corrosion of mild steel in 2M HCl and 1M H_2SO_4 using gasometric techniques and reported that inhibition efficiency increased with increase in extract concentration
- ***Chauhan and Gunasekaran (2006)*** investigated the inhibitive action of ***Zenthoxylum alatum*** plant extract on the corrosion of mild steel in 5% and 15% aqueous HCl, using weight loss and EIS methods and reported that corrosion inhibition efficiency increases on increasing plant extract concentration till 2400 ppm. The Plant extract was found to reduce the corrosion of steel more effectively in 5% HCl than in 15% HCl.
- Investigations of ***Rosliza et al., (2010)*** using natural honey as corrosion inhibitors revealed that natural honey acted as a very good inhibitor towards corrosion of Al-Mg-Si alloy in sea water.
- ***Farooqi et al.,(1997)*** investigated the inhibitive effect of aqueous extracts of *Jasminum auriculatum* (leaves), *Momordica Charantia* (Fruits) and

Hibiscus (flower) on the corrosion of mild steel for cooling water system, using 3% NaCl water. The inhibition efficiencies of the extracts were compared with that of HEDP. All the extracts were found to inhibit corrosion and their inhibition efficiencies were HEDP (93%), Jasminum auriculatum (80%), Momordica charantia (79%), and Hibiscus (76%).

- Corrosion inhibition effect of the extract of black pepper on mild steel (MS) in 1 M H_2SO_4 media revealed that the corrosion rate significantly reduced with increasing concentration of the extract. ***Pandian Bothi Raja and Mathur Gopalakrishnan Sethuraman (2008).***
- ***Chaieb et al., (2004) Minhaj et al.,* (1999)** investigated the inhibitive effects of aqueous extracts of Eucalyptus (leaves), Hibiscus (flowers), and Agaricus on the corrosion of mild steel for cooling- systems using tap water by weight loss and polarization methods. The results showed that all the plant extract inhibited corrosion of mild steel and their inhibitive efficiencies were in the order: Agaricus (85%) > Hibiscus (79%) > Eucalyptus (74%).
- ***Loto and Mohammed (2000)*** investigated the inhibitive effect of the barks, nuts and apples of the cashew tree on the corrosion inhibition of mild steel in HCl medium using weight loss and electrochemical measurements. The apple juice extract was found to exhibit good corrosion inhibition efficiency.
- ***El-Etre and Abdallah (2000)***, evaluated the inhibitive action of natural honey on the corrosion of C-steel, used in manufacture of petroleum pipelines, in high saline water. The inhibition efficiency was calculated using weight loss measurements and potentiodynamic polarization technique. It was found that, natural honey exhibited a very good performance as inhibitor for steel corrosion in high saline water.
- Aqueous extracts of Henna *(Lawsonia inermis)* leaves powder was evaluated as corrosion inhibitors for steel and commercial aluminum in saline, acidic and alkaline waters by ***Al-Sehaibani(2000)***. Weight loss measurements showed that the extracts can inhibit efficiently the corrosion of steel for 37days in HCl with 96% efficiency and for aluminum in NaOH up to 99.8% while no inhibition occurred for steel or aluminum in NaCl solutions.

- ***Loto et al.,(2001)*** investigated the corrosion inhibition effect of *Bitter* leaf (*Vernonia Amygdalina*) solution extract on the corrosion mild steel in 0.5M HCl and H_2SO_4 at ambient temperature of 28°C and elevated temperature 80°. The work was performed using the weight loss method. Studies revealed that bitter leaf acted as a very good inhibitor.
- ***Sahoo et al., (2001)*** observed the corrosion inhibition of mild steel in aqueous environment by Neem extract through electrochemical and weight loss measurements. Experimental results indicated that the inhibition efficiency increased with increasing inhibitor concentration.
- *Nerium oderum (flower), Lantana camara (leaves), Aglemermolus* extracts were studied by ***Mohan et al., (2001),*** as corrosion inhibitor for mild steel in 10% HCl by using weight loss measurements. The results inferred that inhibition increases with increase in concentration and decreases with temperature. The maximum efficiency reported for these extracts are as follows *Lantana camara* (100%), *Nerium oderum* (flower 100%), *Aeglemer mould* (90%).
- ***Sethuraman et al.,(2001)*** observed the effect of *solonum triblobatum* extract on corrosion of mild steel in 5% HCl by weight loss measurement. It was found that inhibitor efficiency increased with increase in concentration and temperature. The presence of solanaces alkaloid in the plant was found to be responsible for the inhibition of mild steel.
- The acid corrosion of *Andiographis Paniculata* was tested for its corrosion inhibitive nature by weight loss method, Tafel polarization method and impedance studies by ***Ramesh et al., (2001)***. The results revealed that this plant extract had the potential to serve as corrosion inhibitor.
- ***Rajalakshmi et al., (2002)*** investigated the performance of acid extracts of *Ficus benghalensis* bark on the corrosion inhibition of mild steel in 1M HCl and 0.5M H_2SO_4 by weight loss and electrochemical techniques. The presence of anthrocyanin compounds, flavanoidal compounds and reducing sugars in the bark extract may be responsible for the inhibitive action. The efficiency of the inhibitor was noticed to increase with increase in concentration of the inhibitor.
- The Biocidal and inhibitive effects of aqueous extract of *Azardiracta indica* on mild steel in fresh water environment was noticed by ***Mohanan et al.,***

(2002) using weight loss measurements. The retardation of corrosive effect depended on the concentration and stability of the extract. The inhibition activity is due to the adsorption of natural compounds.

- ***Fabrizio Zucchi and Ibrahim Hashi Omar (2002)*** studied the effect of various plant extracts like *Papaia, Poincianaz pulcherima, Cassia occidentalis, Datura stramonium seeds, Caltropis procera B, Azydracta indica, Autrpio turkiale sap* on dissolution of mild steel in HCl by electrochemical and weight loss measurements. It was noted that the inhibitive action was due to the products of hydrolysis of the protein content of these plants.
- The effects of various plant extracts such as papaya, *Poinciana pulclcherrima, cassia occident ails* and *Datura stramonium* seeds and papaya, *calotropis procera B, Azydracta indica* and *Auforpia turkiala* sap. On the dissolution of mild steel in HCl solution was evaluated.The study revealed that all extracts except those of *Auforpio turkiale* and *Azydracta indica* reduced the corrosion with an efficiency of 88%-96% in 1N HCl**. *[Fabrizio Zucchi and Ibrahim Hashiomar(1984)].***
- Methanolic extract of *Artemisa pallens* was tested as corrosion inhibitor for mild steel in 4N HCl and conc. HCl. FI.IR studies were carried out in conc.HCl. The inhibition efficiency was found to be 93% at 1.5 g 1-1 in 4N HCl and 96% at gl –1 in conc. HCl**. *[Patchaiah kalaiselvi et al.,(2010)].***
- Water extracts from leaves of ***date palm, phoenix dactylifera, henna, lawsinia inermis, corrozea mays*** were tested as corrosion inhibitors for steel, aluminium, copper and brass in acid solutions using weight loss, solution analysis and potentiodynamic studies by ***Rehan (2003)***. ***Date palm*** and ***henna*** extracts were found to be highly effective in reducing the corrosion rate of steel in acid chloride solutions and aluminum in NaOH solutions.
- The effectiveness of ***Khillah (Ammivisnaga) seeds*** on the corrosion of S × 316 steel in HCl solution was determined using weight loss measurements as well as potentiostatic technique by ***El –Etre (2005).*** The inhibition efficiency increased as the extract concentration increased.
- ***El – Etre (2007)*** investigated the inhibitive action of the aqueous extract of the root of ***shirsh el zallouh (Ferula harminis)*** toward the corrosion of C-

steel in HCl solution. The addition of the extract was found to enhance the inhibition efficiency with increasing extract concentration.

- Corrosion inhibition effect of *Justiciia gendarussa* extract on mild steel in HCl medium was investigated by weight loss and electrochemical techniques. Inhibition efficiency of 93% was achieved with plant extract at 25^0C. AFM and ESCA confirmed the adsorption of justiciia gendarussa extract on mild steel surface ***Satapathy et al.,(2009)***
- Inhibition of the corrosion of mild steel by ethanol of *Musa acuminate* peel has been studied using thermometric method of monitoring corrosion. Inhibition efficiency of the extract was found to vary with concentration, temperature, period of immersion, P^H and electrode potentials. Physical adsorption mechanism was proposed for the adsorption of the inhibitor. ***Eddy, et al.,(2008).***

2.2. Organic compounds as inhibitors

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

methylbenzimidazole ($2CH_2$-Br) and 2-mercaptobenzimidazole was investigated using potentiodynamic polarization technique. Result obtained show that the benzimidazole derivatives retard both the cathodic and anodic reactions in both acidic media, by virtue of adsorption on the carbon steel surface. ***Alijourani, et al.,(2010)***

- The inhibition for performance of mebendazole, a drug on mild steel in molar HCl acid solution was studied by weight loss and electrochemical methods. A maximum inhibition efficiency 96.25% was observed in presence of 2.54*10-4 M inhibitor ***Ishtiaque Ahamad and Quraishi et al.,(2009)***
- ***Solomon et al.,*** **(2011)** investigated the corrosion inhibition of mild steel in 1 M H_2SO_4 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.
- ***Rosliza et al.,*** **(2010)** measured the effect of *tapioca* starch to improve the corrosion resistance of AA6061 alloy in seawater by gravimetric, potentiodynamic polarization, linear polarization resistance and electrochemical impedence measurements. The results showed that the tapioca starch significantly decreases the corrosion rates, corrosion current densities (i_{corr}), and double layer capacitance (C_{dl}), simultaneously increases the values of polarization resistance (R_p). The results revealed that the inhibition efficiency increased with increasing concentration. Langmuir adsorption isotherm well fitted with the experimental data.
- ***Aisha et al.,*****(2012)** investigated *Plectranthus tenuiflorus (Shara)* plant as safe (green) inhibitor on the corrosion of mild steel in 2.0 M H_2SO_4 solution using weight loss and hydrogen gas evolution technique. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with rising temperature. The inhibition was attributed to adsorption of the inhibitor molecules on mild steel surface. Adsorption

characteristics of the aqueous extract of *Shara* plant were approximated by Langmuir adsorption isotherm. Effect of temperature was studied in the range (30-70) ° C and activation parameters was determined.

- ***Rajalakshmi et al.,* (2008)** studied the role of seed extract 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%.

2.3. Corrosion behaviour of mild steel with varying parameters

2.3.1. Effect of concentration of the inhibitor

- The influence sodium dodecyl benzene sulfonate on the corrosion behaviour of an elaborated annealed Fe1lTi-20 alloy has been investigated in 0.5 M H_2SO_4 solution using electrochemical techniques. The inhibition occurs through adsorption of a surfactant on the metal surface without modifying the mechanism of corrosion process. The studied surfactant acts predominately as cathodic inhibitors by blocking effect on the cementite cathodic sites. The inhibition efficiency increased with increasing surfactant concentrations and decreased with increasing temperature. Maximum inhibition was observed at concentration above its critical micelle concentration ***Kellou –Kerkouche et al.,2008***
- *Calotropis procera* was found to exhibit significant corrosion inhibitive effect in sulphuric acid medium on mild steel. Inhibition was through adsorption of the Phytoconstituents on mild steel followed temkin adsorption isotherm. ***Raja, Sethuraman(2009).***

2.3.2. Influence of exposure time

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

to 0.5 % w/v) and immersion time (1 hr – 24 hr). Good inhibition efficiency was found at 0.5% (w/v) concentration of the inhibitor for 2 hours (94.67%).

2.3.3. Temperature Effect

- The inhibitive action of leaf extracts of *Sansevieria trifasciata* on aluminium corrosion in 2M HCl and 2M KOH solutions was studied using gasometric technique and the studies revealed a decrease in efficiency with rise in temperature ***Oguzie,(2006).***
- The inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in aqueous orthophosphoric acid was investigated by weight loss and electrochemical impedance spectroscopy (EIS). The plant extract exhibited a maximum of 88% inhibition efficiency on corrosion inhibition of mild steel. ***Gunasekaranand , Chauhan (2004)***.
- Corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by leaf extracts of *Occimum viridis* (OV) was studied using the geometric technique at temperatures of 30 and 60 °C. The extracts inhibited the corrosion process in both acid media and inhibition efficiency increased with increasing of the extract concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives namely KCl, KBr, KI. ***Emeka Oguzie (2006)***
- The inhibitive action of the root of ginseng on aluminium corrosion in HCl using weight loss method at 30-60^{0}C. Corrosion rate was found to decrease in the presence of inhibitor compared to the free acid solution .The inhibition efficiency increased with increase in concentration of the inhibitor but decreased with increase in temperature. A mechanism of physical adsorption of the root components on the surface of the metal is proposed for the inhibition. ***Obot, Obi-Egbedi et al.,(2006).***

2.3.4. Kinetic analysis

- According to ***Obot et al., (2009)*** the inhibition of corrosion for mild steel in H_2SO_4 by 2,3-diphenylbenzoquinoxaline was found to obey Langmuir adsorption isotherm equation suggesting that the inhibition efficiency increased with increase in the concentration of the inhibitor.
- The aqueous extract of the leaves of henna (lawsonia) was tested as corrosion inhibitor of C-steel, nickel and zinc in acidic, neutral and alkaline solutions. Degree of inhibition depended on the nature of metal and the type

of the medium. It was found that this adsorption followed Langmuir adsorption isotherm. ***El-Etre , Abdallah and El-Tantawy (2004)***

- The corrosion inhibitive effect of the extract of Aloe Vera leaves on zinc surface in 2M HCl solutions was carried out the inhibition efficiency decreased with increase with increasing the temperature. A. Vera extract obeyed the Langmuir adsorption isotherm. A first-order kinetic relationship with respect to zinc was obtained with and without the extract from the kinetics treatment of the data. ***Olusegum Abiola and James(2010)***

2.3.5. Polarization measurement

- According to ***de Souza and Spinelli*** *(2008)* the naturally occurring biological molecule caffeic acid acted as an excellent inhibitior on the corrosion of mild steel in 1 M H_2SO_4 by decreasing the cathodic reaction area and modifying the activation energy of the anodic reaction.
- Berberine extracted from *Coptis chinensis* was tested for corrosion of mild steel in 1 M H_2SO_4 From the Potentiodynamic curves, it can be seen that berberine suppressed both cathodic and anodic processes. The polarization resistance increased with the increasing inhibitor concentration. ***Yan Li, Peng ZhaoQiang Liang and Baorong Hou- (2005)***
- Quinine was tested as corrosion inhibitor for low carbon steel corrosion in 1M HCl solution using ESI and potentiodynamic polarisation method. The corrosion of steel was controlled by a charge transfer process and a maximum efficiency of 96% was obtained at 20^0C**.** ***Mohamed Ismail Awad(2006)***
- The inhibition effect of bis-thiadiazole (BTDS) derivatives against the corrosion of mild steel in 1M HCl solution was studied by weight loss, electrochemical impedance spectroscopy [EIS] and potentiodynamic polarization methods. All the BTDS exhibited >90% inhibition efficiency at concentration as low as 40 ppm. Polarization curves indicate that they are mixed type of inhibitors. ***Ashish kumar singh and Quraishi (2009).***
- Corrosion inhibition of mild steel by the extracts of *Pongamia glabra* and *Annona squamosa* in HCl and H_2SO_4 media was studied by ***Sakthivel et al*****., (1999).** Weight loss, polarization, hydrogen permeation and impedance studies were carried out at various temperatures. Polarization studies

inferred that, *Pongamia glabra* and *Annona squamosa* acted as mixed and cathodic inhibitors respectively.

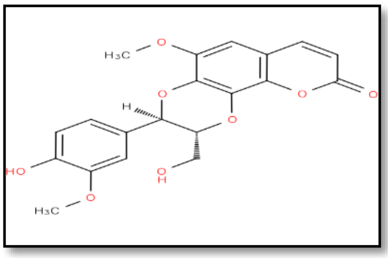
- The effect of extracts of Chamomile (*Chamaemelum mixtum* L.), Half bar (*Cymbopogon proximus*), Black cumin (*Nigella sativa* L.), and Kidney bean (*Phaseolus vulgaris* L.) plants on the corrosion of steel in aqueous 1 M sulphuric acid were investigated. Potentiodynamic polarization curves indicated that the plant extracts behaved as mixed-type inhibitors. ***Abdel-Gaber et al.,(2006)***
- According to ***Solomon et al., (2010)*** the adsorption of the carboxymethyl cellulose on to the mild steel surface followed Langmuir and Dubin Radush Kevich adsorption isotherm models. The inhibition mechanism was further corroborated by the values of activation parameters obtained from the experimental data
- ***Rajalakshmi. et al., (2008)*** studied the role of seed extracts of *Phaseolus aureus* on corrosion of mild steel in 1M HCl by weight loss method and potentiodynamic polarization technique. The Potentiodynamic polarization results reveal that the seed extract behaved like mixed type inhibitor. Maximum inhibition efficiency of Phaseolus aureus in 1M HCl was found to be 93%.
- Evaluation of the performance of acid extract of Ficus Benghalensis bark on the corrosion inhibition of mild steel in 2N, 3N, and 4N HCl medium at different temperature were studied by ***Subhashini. et al., (2008).*** Weight loss, electrochemical polarization and impedance measurement techniques were conducted. The efficiency of the inhibitor was noticed to increase with increase in concentration of the inhibitor.
- 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.

2.3.6. Phytochemical constituents of Durenta erecta leaves

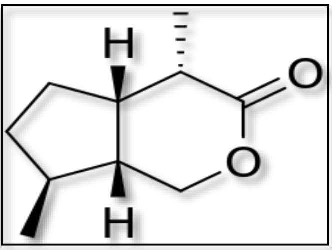
Methanolic extract of the leaves of ***Durenta erecta*** Lin.(Family- Verbenaceae) was evaluated for its possible phytochemical nature (group determination of plant constituents). Phytochemical analysis of the ethanolic extract of *Durenta erecta* indicated the presence of steroid, carbohydrate, alkaloids, flavanoids, saponin and tannin types of compounds.

From n-butanol soluble fraction of the leaves, four new iridoid glucosides, cleomiscin a, oleanolic acid, cinnamic acid, lamiide, durentosides A, I, III were isolated together with known compounds by combination of silica gel chromatography reversed phase HPLC. Their structures were assigned by ^{13}C NMR, ^{1}H NMR, FAB mass spectrum, HRFAB mass spectrum, HPLC.

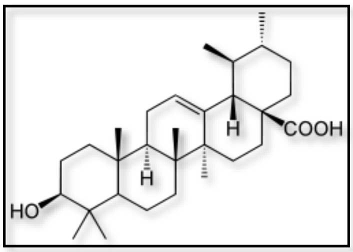
Cleomiscin a



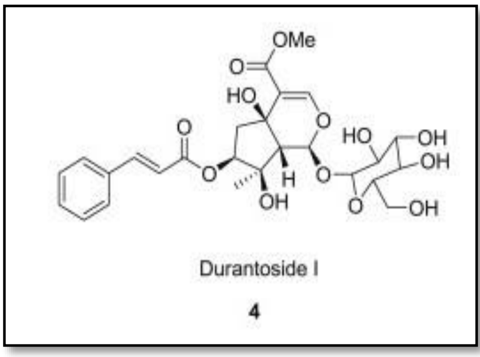
Iridoids



Ursolic acid

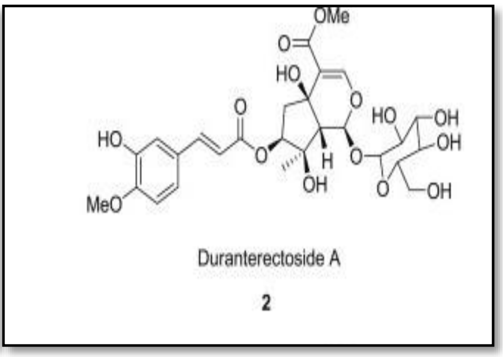


Durenta erectoside



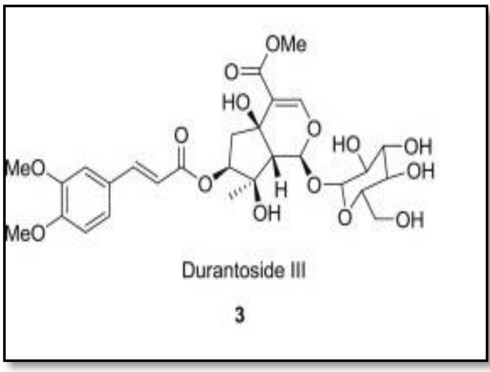
Durantoside I

4



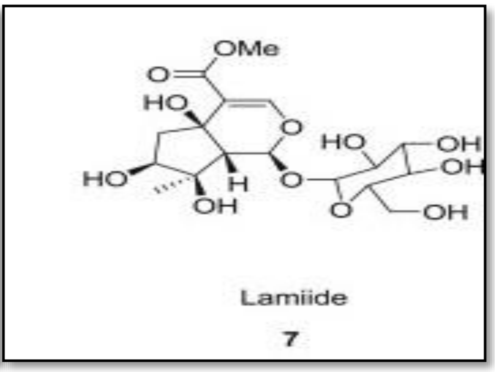
Duranterectoside A

2



Durantoside III

3



Lamiide

7

The plant identified for the current investigation had abundant phyto constituents which will aid as corrosion inhibitor for metals. Thus this overview justifies the choice of the plant source selected as an inhibitor for mild steel. Further investigations are warranted to prove its role in the corrosion inhibition of mild steel in acid media.

Materials & Methods

MATERIALS AND METHODS

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

3.1. Selection of sample

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

3.2. Preparation of sample

Regular sample of area 1x5 cm^2 have been cut from a large sheet of mild steel. A hole was drilled in the specimen, mechanically polished, degreased, washed with de ionized water then thoroughly dried and kept in desiccators for weight loss tests. The mild steel specimens used in the following percentage elemental of composition as shown in Table 3.1.

Figure 3.1: Elemental of composition

3.3. Test medium

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

3.4. Selection of inhibitor

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

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

3.5. Preparation of the inhibitor

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

3.6. Phytochemical screening

Phytochemical examinations were carried out for all the extracts as per the standard methods.

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

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

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

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

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

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

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

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

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

3. Detection of glycosides: Extracts were hydrolysed with dil. HCl, and then subjected to test for glycosides.

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

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

5. Detection of saponins

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

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

6. Detection of phytosterols

a) Salkowski's Test: Extracts were treated with chloroform and filtered. The filtrates were treated with few drops of Conc. Sulphuric acid, shaken and allowed to stand. Appearance of 2golden yellow colour indicates the presence of triterpenes.

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

7. Detection of phenols

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

8. Detection of tannins

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

9. Detection of flavonoids

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

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

10. Detection of proteins and aminoacids

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

b) Ninhydrin Test: To the extract, 0.25% w/v ninhydrin reagent was added and boiled for few minutes. Formation of blue colour indicates the presence of amino acid. **(*Prashant Tiwari ,et al,* Jan-March 2011).**

3.7. Techniques employed

- Mass loss methods
- Electrochemical measurement

3.7.1. Mass loss methods

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

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

- ✓ Concentration (0.1% - 0.7%)
- ✓ Time of immersion (1/2 h, 1h, 3h, 6h, 12h & 24h)
- ✓ Temperature (313K-353K)

3.7.1.1. Determination of corrosion rate

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

$$\textbf{C.R (mpy)} = 543 \times W / D \times A \times T \text{ ……………….. } (3.1)$$

Where,

W-Weight loss in g

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

A-Area of the sample in cm^2

T-Exposure time in hours

3.7.1.2. Determination of percentage of inhibition and surface coverage

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

$$\text{I.E } (\%) = w_o - w/w_o \times 100 \text{ …………………… } (3.2)$$

$$\theta = w_o - w/w_o \times 100 \text{ …………………………… } (3.3)$$

Where,

w_o - corrosion rate without inhibitor in g

w – Corrosion rate with inhibitor in g

Determination of thermodynamic parameters,

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

$$\text{Log } C = [\log \theta / (1-\theta)] - \log B \text{ …………………… } (3.4)$$

Where,

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

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

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

$$\Delta G = \Delta H - T\Delta S \text{ ………………………… } (3.5)$$

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

3.7.1.3. Adsorption isotherm

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

Langmuir [log (θ / 1-θ) Vs log C]

Temkin (θ Vs log C)

3.7.1.4. Activation energy (E_a)

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

$$E_a = -2.303 \times R \times \text{slope of the Arrhenius plot} \qquad \ldots\ldots\ldots\ldots (3.6)$$

Where,

R is the gas constant 8.314 J/mole

3.7.1.5. Activation Parameters

An alternative formulation of Arrhenius equation is

$$CR = (RT/\,Nh)\exp(\Delta Sa/\,R)\,\exp(\Delta Ha/\,R) \qquad \ldots\ldots\ldots\ldots (3.7)$$

Where,

h is Planck’s constant

N is Avagadro number

ΔSa is entropy of activation

ΔHa is enthalpy of activation

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

3.7.2. Electrochemical measurements

3.7.2.1. Polarization techniques

Electrochemical studies were carried out using conventional three electrode cell with large area of platinum foil as counter electrode saturated calomel electrode

(SCE) as reference electrode and sample was as working electrode. Electrochemical measurements were done by using Biologic EC Lab version 10.23.

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

3.7.2.2. Tafel plot

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

The inhibitor efficiency was calculated using the following equation,

$$\mathbf{I.E\ (\%) = \frac{I_{corr}\,(blank) - I_{corr}\,(inhibited)}{I_{corr}\,(blank)} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3.8)}$$

I.E from LPR technique,

$$\mathbf{I.E\ (\%) = \frac{R_p(inhibited) - R_p(blank)}{R_p(inhibited)} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ (3.9)}$$

Where,

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

3.7.2.3. Impedance spectroscopy

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

$$\mathbf{I.E\ (\%) = \frac{R_{ct}(inhibited) - R_{ct}(blank)}{R_{ct}(inhibited)} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ (4.0)}$$

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

$$\theta = \frac{1 - C_{dl}\ (\text{inhibited})}{C_{dl}\ (\text{blank})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$

Where,

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

3.8. Surface analytical techniques

3.8.1. FT-IR

The samples for FT-IR studies were prepared by finely mixing the extract with spectroscopically pure KBr and then pressed by using a die so as to get a fine transparent pellet. The FT-IR spectrum was recorded for stem and leaves of DEL extract with a frequency ranging from 4000 to 400 cm^{-1} using **Perkin Elmer FT-IR spectrophotometer** with the **SOFTWARE – OPUS version 6.5**.

FT-IR Spectral Analysis

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

3.8.2. Scanning Electron Microscope

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

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

3.8.3. UV Spectrophotometric measurement

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

3.8.4. Laser Profilometer

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

Results & Discussion

RESULTS AND DISCUSSION

The present study entitled **“Inhibitive effect of leaf extract of *Durenta erecta* on mild steel corrosion in 1M Hydrochloric and Sulphuric acid solution”** deals with the assessment of corrosion inhibitive nature of DEL for mild steel in 1M HCl and 0.5 M H_2SO_4 acid medium. The inhibitive action as anticipated depended on the concentration of the inhibitor, period of immersion and temperature of the attacking acid. The results obtained from the study are dealt under the following sections.

a) Mass loss measurements

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

b) Electro chemical measurements

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

c) Surface Analytical Techniques

1. FT-IR
2. 3 D Laser Profilometer
3. SEM
4. UV

4.1 Characterisation of *Durenta erecta* leaf extract

4.1.1 Phytochemical Screening

The investigated *Durenta erecta* leaf (DEL) extract was screened for the presence of flavonoids, alkaloids, terpenoids, saponins, tannins, reducing sugar, polyphenols, and anthraquinones using standard procedure **(Harborne, 1973).**

Table 4.1

Phyto chemical screening of crude DEL extract

Phyto constituents	Alkaloids	Reducing sugars	Flavonoids	Saponins	Saponins	Steroids	Gums	Tannins	Carbohydrates	Terpenoids
Results	+	-	+	+	+	+	-	+	+	-

+ present ; - absent

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

4.1.2 FT-IR

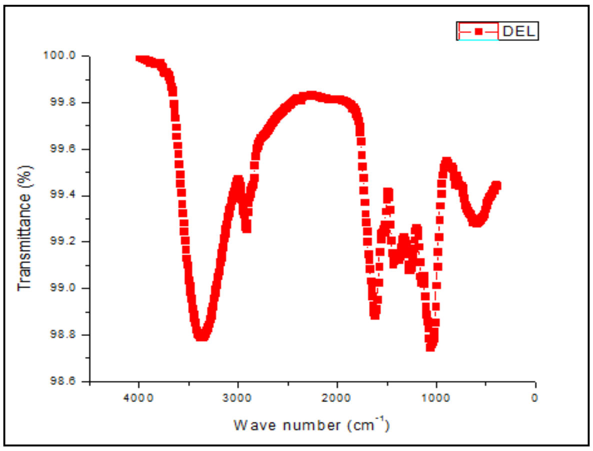


Figure 4.1: FT- IR spectral peak of crude DEL extract

Figure 4.1, shows the FT-IR spectrum of crude DEL extract. A very strong broad band at 3379.29 cm^{-1} is attributed to O–H stretching. The absorption band at 2924 cm^{-1} is related to –CH asymmetrical stretching vibration **(Li *et al*, 2009)**, and a strong band at 1627 cm^{-1} corresponds to the C=O stretching vibration. Hence, it can be inferred that DEL contains oxygen and nitrogen atoms in functional groups (O–H, N–H, C=O, C–O, C=C), aromatic ring, which meets the general structural consideration of the corrosion inhibitors.

4.2. Mass loss measurements

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

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

4.2.1. Effect of concentration of the inhibitor in 1M HCl

The concentration of the inhibitor plays an important role to fix an effective concentration for the extract under study. The effect of inhibitor on the dissolution of mild steel in 1M HCl media has been investigated by conducting the tests with various concentration of the extract (0.7% extract). The results were illustrated in Table 4.2 and Fig 4.2 & 4.3. The data showed that the corrosion rate of mild steel decreased with increase in concentration. The inhibition efficiency increased from 70.3% to 90.4% with 0.7% concentration of DEL extract.

From the data, the maximum enhancement of inhibition was noted with 0.7% of the extract. 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].**

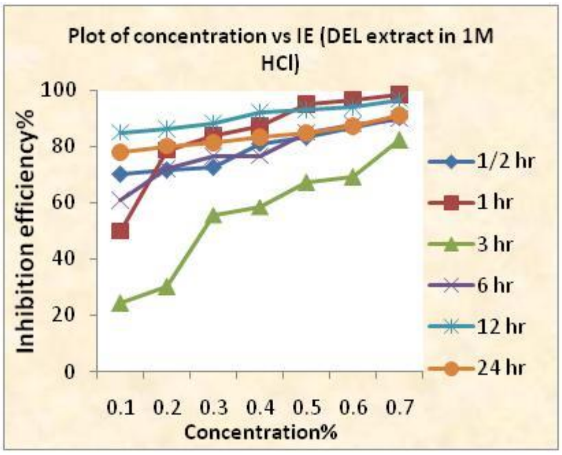


Figure 4.2

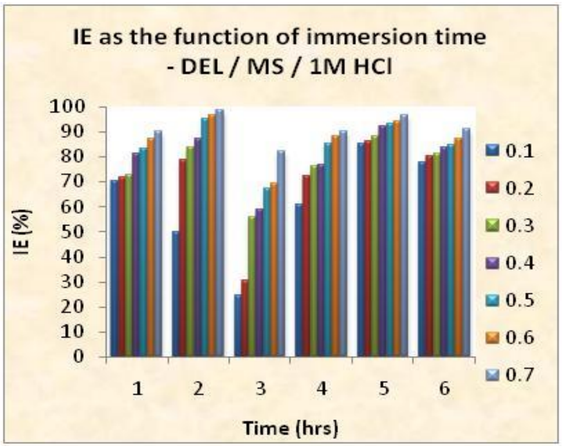


Figure 4.3

4.2.2. Impact of immersion time

To evaluate the impact of immersion period on the inhibition efficiency, mass loss studies were carried out in 1M HCl for immersion periods of 1/2, 1, 3, 6, 12, and 24 h and the results were tabulated in Tables 4.2 & 4.3.

From Tables 4.2 & 4.3, it can be seen that inhibition efficiency increased with increasing concentration of the inhibitor at all periods of immersion. From the results, it can be inferred that as the time of immersion increase, the inhibitor molecules gets coated on the surface of mild steel there by decreasing the mild steel dissolution effectively. A maximum of 98.6% of inhibition was obtained at 0.7% of extracts. In the present investigation it was also observed that the extract behaved as an excellent one at all periods of immersion. This proved the inhibitive nature of the adsorbed molecules on the surface of mild steel.

Table 4.2: Role of concentration of DEL extract on MS in 1M HCl

S. No	Conc (%)	Corrosion rate and inhibition efficiency											
		½ h		1 h		3 h		6 h		12 h		24 h	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	849		845		338		456		435		101	
2.	0.1	252	70.3	423	49.9	256	24.3	178	60.9	65	85	22	77.9
3.	0.2	240	71.7	179	78.7	236	30.2	126	72.2	59.3	86.3	19	80.2
4.	0.3	232	72.6	135	83.9	149	55.8	107	76.4	50.1	88.4	19	81.4
5.	0.4	160	81.1	106	87.4	139	58.8	106	76.7	33.7	92.2	17	83.5
6.	0.5	141	83.4	42	95	111	67.2	68	85	29.4	93.2	15	84.9
7.	0.6	110	87	27	96.7	104	69.3	55	88	24.8	94.2	13	87.1
8.	0.7	81	90.4	11	**98.6**	60	82.3	45	90	13.8	96.8	9	91.1

4.2.3. Effect of temperature

Temperature can influence the interaction between mild steel and the acid in the presence and absence of the inhibitors. To determine the activation energy and the energy of adsorption of the corrosion process, mass loss studies were conducted using DEL extract at various temperatures ranging from 303K to 353K. Inhibition efficiency of mild steel at various temperatures were listed in the Table 4.3 and depicted in Figure 4.4 &4.5.

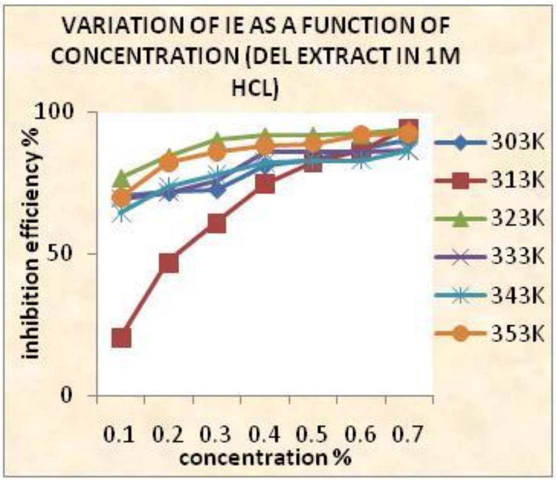


Figure 4.4

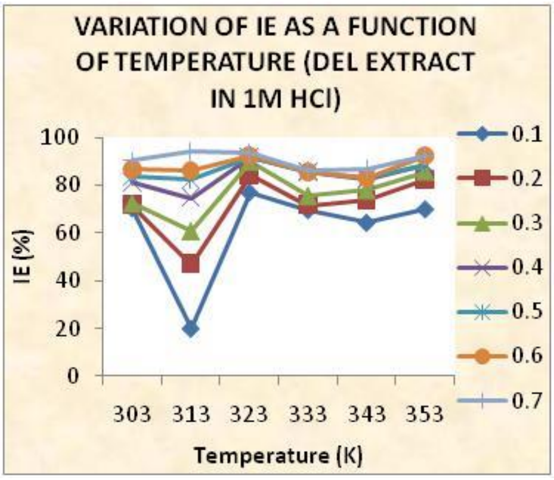


Figure 4.5

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

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		303K		313K		323K		333K		353K		363K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	849		1689		2951		4504		8222		25298	
2.	0.1	252	70.3	1348	20.2	682	76.8	1373	69.5	2943	64.2	7634	69.8
3.	0.2	240	71.7	896	46.9	461	84.3	1271	71.7	2158	73.7	4461	82.3
4.	0.3	232	72.6	665	60.9	290	90.1	1092	75.7	1800	78.1	3565	85.9
5.	0.4	160	81.1	426	74.7	247	91.6	648	85.6	1450	82.3	2943	88.3
6.	0.5	141	83.4	299	82.3	239	91.9	640	85.7	1390	83.0	2772	89.0
7.	0.6	110	87	230	86.3	222	92.4	631	85.9	1373	83.2	1962	92.2
8.	0.7	81	90.4	94	**94.4**	179	93.9	614	86.3	1083	86.8	1859	92.6

From Table 4.3, it can be seen that the IE increased upto 313K and then a gradual decrease was observed for the extract in 1M HCl medium. A maximum efficiency of 94.4% at 313K for DEL extract was noticed.

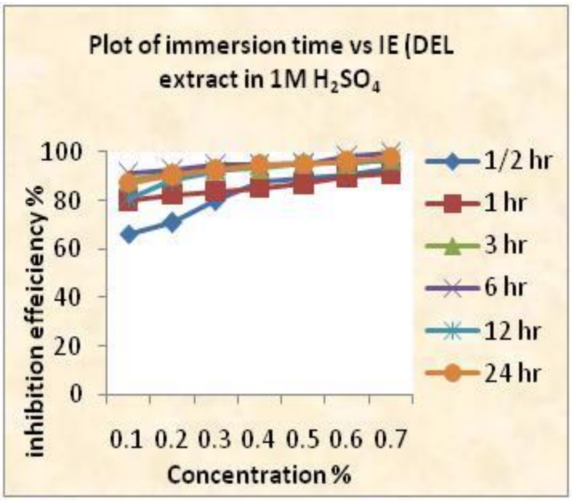
According to N.S Rawat and A.K Singh (1989), the above observation may be explained on the following basis adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between these two processes at a particular temperature. With the increases of 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.

4.2.4. Effect of concentration of the inhibitor in 0.5M H_2SO_4:

The effect of using different concentration of the extract is shown on the Table 4.4, and Figure 4.6 & 4.7, as the concentration of the inhibitor increased, the inhibition efficiency also increased. This could be result of the fact that as the inhibitor increases, more surface of the metal was covered by the inhibitor molecular. **Dahmani *et al.,(2010)*** reported that increase in inhibitor concentration led to a decrease in the concentration rate. A highest efficiency of 93.2% was obtained at 0.7 concentration of the extract.

Table 4.4: Role of concentration of DEL extract on MS in 0.5M H_2SO_4

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		½ h		1 h		3 h		6 h		12 h		24 h	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	1399		1207		1888		2085		1877		2084	
2.	0.1	469	66.4	243	79.8	215	88.6	183	91.2	354	81.1	264	87.3
3.	0.2	409	70.7	213	82.3	166	91.1	153	92.6	214	88.5	204	90.2
4.	0.3	281	79.8	196	83.7	134	92.9	107	94.4	151	91.9	158	92.4
5.	0.4	171	87.8	179	85.1	125	93.3	115	94.6	93	95.0	112	94.6
6.	0.5	154	89.0	158	86.9	90	95.2	112	94.8	90	95.2	104	95.0
7.	0.6	128	90.8	124	89.7	84	95.5	41	98.0	83	95.5	84	95.9
8.	0.7	94	93.2	107	91.1	55	97.0	10	**99.5**	64	96.5	45	97.8



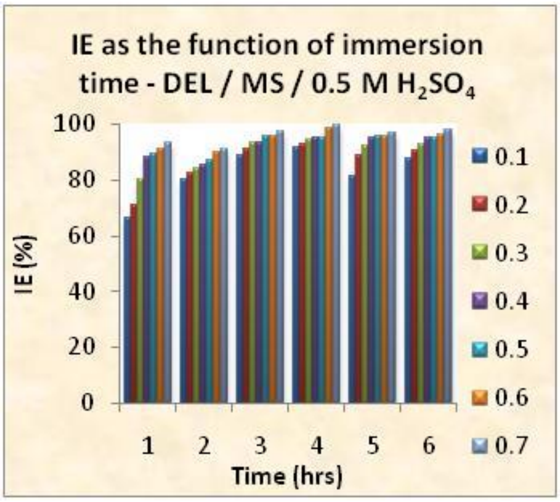


Figure 4.6

Figure 4.7

4.2.5. Impact of immersion time:

The influence of duration of immersion on the IE of MS system is given in Table 4.5. When the immersion period increased, the inhibition efficiency decreased and the corrosion rate increased. This shows that the protective film formed on the metal surface, was broken by the corrosive environment and the film was dissolved.

In the present study, results indicated the increase in IE with increase in time of immersion till 6h. At 6h, inhibition efficiency was maximum 99.5% and then decreased to 70.0% at ½ h. The best performance of the DEL extract was perceived at 313K of immersion period with the entire concentration of the inhibitor. The variations of inhibition performance of DEL extract with time at various concentrations are shown in Figure 4.8 & 4.9.

Table 4.5: Role of temperature on Corrosion of MS in the presence of various concentration of DEL extract in 1M H_2SO_4

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		303K		313K		323K		333K		343K		353K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	1399		4700		11634		9493		31721		51740	
2.	0.1	469	66.4	529	88.7	2994	74.2	3634	61.7	17008	46.3	43321	16.2
3.	0.2	409	70.7	469	90.0	1399	87.9	2047	78.4	12786	59.6	28446	45.0
4.	0.3	281	79.8	392	91.6	1160	90.0	1578	83.3	10542	66.7	19362	62.5
5.	0.4	171	87.8	358	92.3	1083	90.6	1365	85.6	4904	84.5	14935	71.1
6.	0.5	154	89.0	316	93.2	938	91.9	1271	86.6	4828	84.7	12018	76.7
7.	0.6	128	90.8	273	94.1	614	94.7	989	89.5	4239	86.6	11344	78.0
8.	0.7	94	93.2	222	**95.2**	597	94.8	819	91.3	4043	87.2	9579	81.4

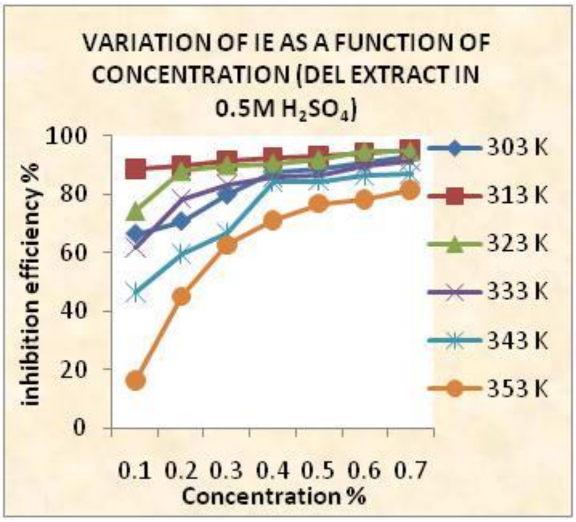


Figure 4.8

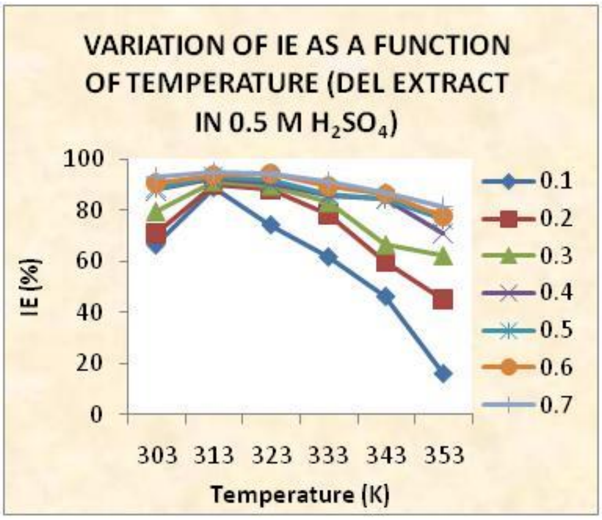


Figure 4.9

4.3. Adsorption behaviour

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metal has been deduced in terms of adsorption characteristic of the inhibitor. The inhibition data are used for constructing experimental adsorption isotherms. Adsorption isotherms provide a clue to the mode and mechanism of adsorption. It is assumed that the inhibition efficiency is comparable to the degree of surface coverage of the inhibitor on the metal surface.

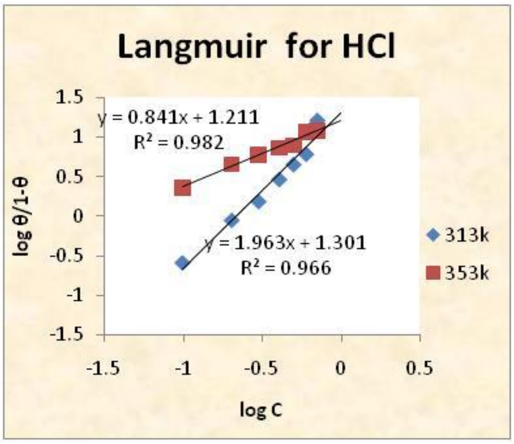


Figure 4.10

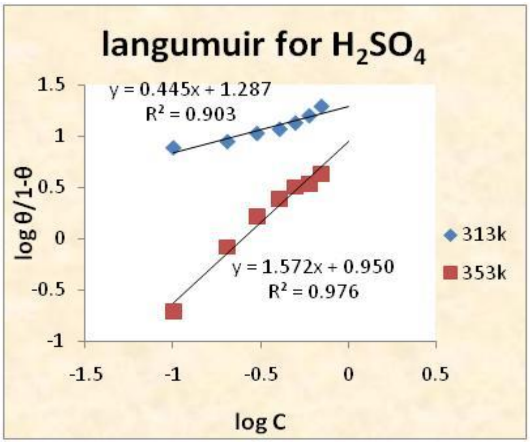


Figure 4.11

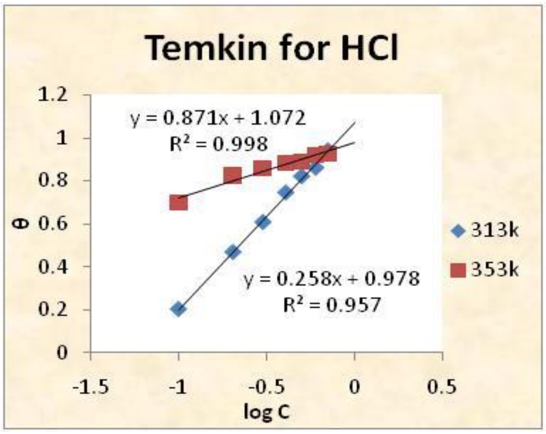


Figure 4.12

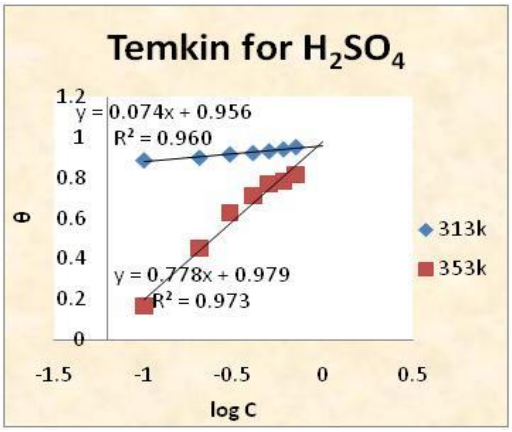


Figure 4.13

The surface coverage (θ) values for different concentration of the inhibitors in acid medium were evaluated from the mass loss data. Attempts were made to fit the data obtained from mass loss measurement into different adsorption isotherms like Langmuir and Temkin. An assumption of Langmuir adsorption isotherm relate concentration of inhibitor in the bulk electrolyte and the degree of surface coverage by the following equation,

$$\mathbf{Log\ [\theta/1\text{-}\theta] = log\ K + log\ C\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4.1)}$$

From the above equation, if the assumptions of Langmuir are obeyed, a plot log (θ/1-θ) Vs log C should give a straight line. Langmuir plots for the corrosion reaction of mild steel in the presence of are shown in figure 9 & 10. The fact that the lines obtained were linear confirmed that Langmuir adsorption isotherm was applicable to the present study. It also confirmed the monolayer adsorption.

A straight line was obtained when the surface coverage was plotted against log C vs θ for the inhibitor. This shows that the adsorption of the inhibitor at the mild steel acidic solution interface obeys Temkin adsorption isotherm. Plots of θ Vs log C for the inhibitors are shown in Fig 4.12 & 4.13.

4.4. Statistical analysis of adsorption isotherm

Comparing the linearity of Langmuir and Temkin adsorption isotherm, the correlation co-efficient values were calculated. The correlation co-efficient obtained for the fitness of the data to adsorption models were furnished in the **Table 4.6**. From these findings, it may be inferred that DEL was adsorbed on MS surface obeying both Langmuir and Temkin isotherms. The values of correlation co-efficients for the isotherms tested are given in Table 4.6.

Table 4.6

Values of correlation coefficient obtained for Langmuir and Temkin Adsorption isotherm

TEMPERATURE (K)	CORRELATION VALUES (R^2)			
	IM HCl EXTRACT		0.5M H_2SO_4 EXTRACT	
	LANGMUIR	TEMKIN	LANGMUIR	TEMKIN
303	0.791	0.834	0.931	0.953
313	0.967	0.998	0.905	0.960
323	0.972	0.944	0.952	0.898
333	0.858	0.876	0.983	0.944
343	0.98	0.978	0.933	0.946
353	0.984	0.957	0.977	0.973

The correlation values are almost 1 showing that the data obey both Langmuir and Temkin isotherms.

4.5. Kinetic parameters

4.5.1. Activation energy (Ea)

Energy of activation for different concentration of the inhibitor in 1M HCl and 0.5 M H_2SO_4 was calculated by plotting log C.R Vs 1/T (Fig 4.14 & 4.15). The dependence of logarithm of the C.R on the reciprocal values of the absolute temperature gave a straight line. The values of the slope of these straight lines permit the calculation of activation energy Ea by the application of following equation.

$$\mathbf{C.R = A.e^{(-Ea/RT)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (4.2)$$

Where,

A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature (Kelvin). Thus Ea can be evaluated from the rate constant at any temperature. The estimated values of Ea for MS in leaf extract of DEL extract in 1M HCl and 0.5 M H_2SO_4 are listed in the Tables 4.8. From the Table, it can be understood that energy of activation changes in the presence of the inhibitors. The estimated Ea in the presence of inhibitors infer that the interaction between the metal surfaces was strong enough to prevent corrosion.

This may seem surprising and paradox, but Riggs *et al.,* (1967), reported that in the presence of the inhibitor, the dissolution of the metal proceeds with two distinct processes corresponding to the covered area and the bare metal surface 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 inhibitor and consequently the E_a can assume values greater or smaller than those calculated in the absence of the inhibitor.

As far as the present study is concerned the above said explanation aptly suits the result obtained for the extracts of DEL in 1M HCl and 0.5M H_2SO_4. It has also been pointed out by Khamis *et al.,* (1990) that a corrosion inhibitor greatly enhances the activation energy of the corrosion.

Experiment conducted by Bag *et al.,* (1996) also reflected lower Ea values for the inhibited system. The studies carried out by Taha *et al.,* (1995) revealed that the presence of inhibitors decrease the Ea of the reaction to an extract depending on the nature of inhibitors.

It was also found that the activation energies of the acid medium in the presence of the inhibitors were lower (higher for higher concentrations of DEL in 1M

HCl and 0.5 M H_2SO_4) than the values in the absence of the extract The higher Ea values in the presence of inhibitor compared to the blank solution indicates that the inhibitor will be effective at low temperatures, but efficiencies will diminish at higher temperatures (Umoren *et al*, 2006) there by confirming that the adsorption of the extract of DEL in 1M HCl and 0.5 M H_2SO_4 occurred through the mechanism of physical adsorption.

4.5.2. Activation parameter

An alternative formulation of Arrhenius equation is,

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

Where,

h is Planck's constant
N is Avagadro number
ΔSa is entropy of activation
ΔHa is enthalpy of activation

A plot of log (CR/T) Vs 1/T gave a straight line with a slope of -ΔHa /2.303R and an intercept of log(R/Nh + ΔSa/2.303R) from which the values of ΔHa and ΔSa were calculated and listed in **Table 4.7.** The values of ΔHa & Ea were nearly the same and are higher in the presence of the inhibitors. This indicates that the energy barrier of the corrosion reaction increased in the presence of the inhibitors without changing the mechanism of dissolution. The positive values of ΔHa for both corrosion processes with and without the inhibitors and reveal the endothermic nature of the steel dissolution process and indicate that the dissolution of steel is difficult. The large negative value of ΔSa for mild steel in acid medium implies that the activated complex is the rate determining step, rather than the dissolution step. In the presence of the inhibitors, the value of ΔSa increased and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes.

Table 4.7: Values of Ea, ΔHa and ΔSa of MS in Various Concentrations of DEL 1M HCl / 0.5M H_2SO_4

S.No	Conc V/V (%)	Activation energy -Ea kJ/mol		ΔHa kJ/mol		-ΔSa kJ/mol	
		HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4
1.	Blank	55.96	60.08	53.01	57.30	14.93	5.95
2.	0.1	50.58	83.55	47.96	80.91	39.13	69.32
3.	0.2	45.99	78.77	43.31	76.18	55.79	51.71
4.	0.3	45.03	78.77	42.29	75.99	60.73	48.84
5.	0.4	48.07	76.70	45.32	74.00	54.13	40.22
6.	0.5	51.58	76.37	48.67	73.67	44.78	38.31
7.	0.6	52.30	78.35	49.72	75.59	42.92	42.52
8.	0.7	60.88	81.08	58.26	78.36	19.20	49.60

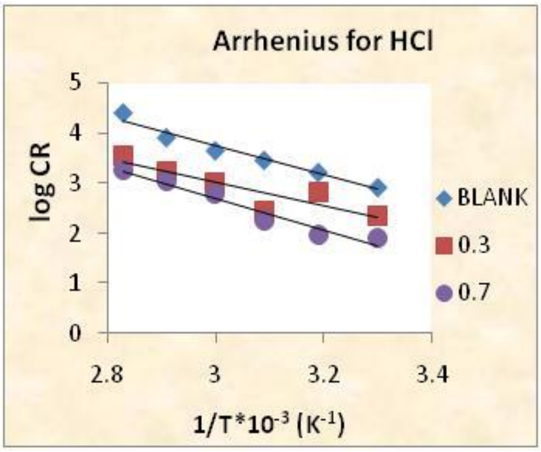


Figure 4.14

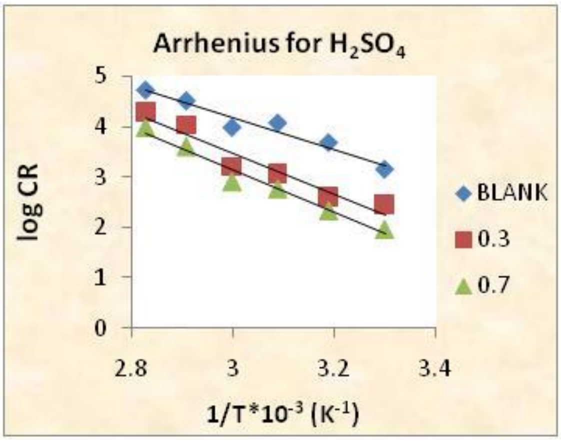


Figure 4.15

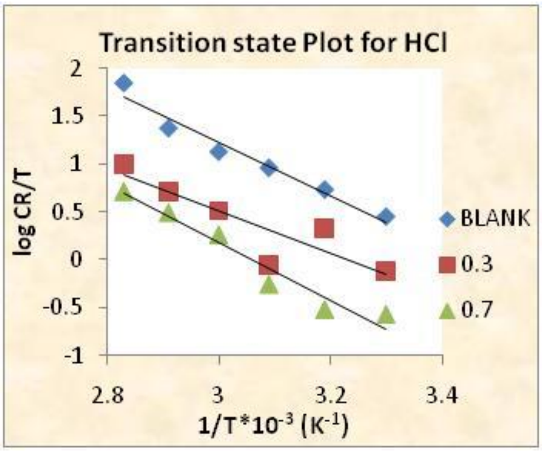


Figure 4.16

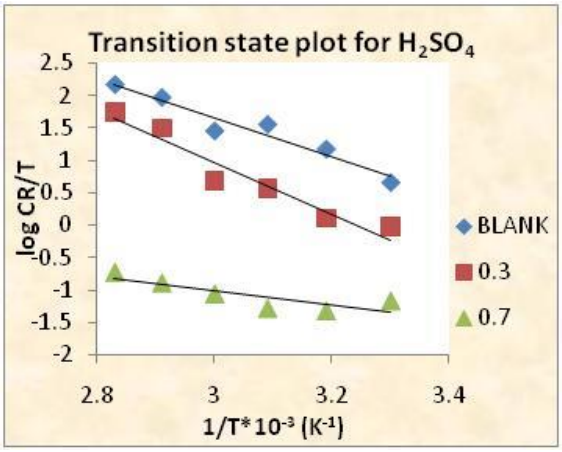


Figure 4.17

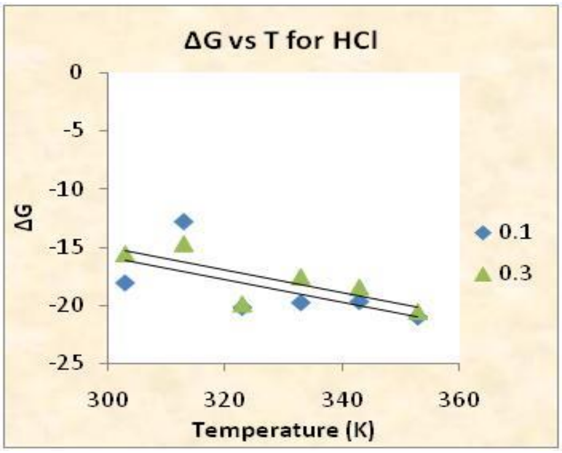


Figure 4.18

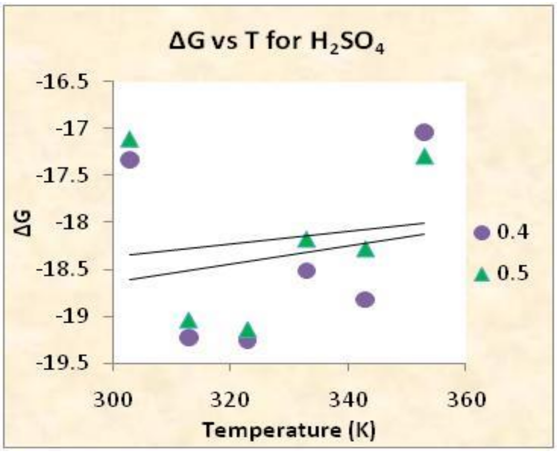


Figure 4.19

Table 4.8: Values of -ΔG, ΔH and -ΔS of MS in various concentration of DEL in 1M HCl and 0.5M H_2SO_4 medium

S.No	Concentration of inhibitor V/V (%)	Free energy of adsorption -ΔG (kJ/mol)						-ΔS (J)	ΔH (kJ/ mol)
		303K	313K	323K	333K	343K	353K		
1M HCl									
1.	0.1	18.06	12.84	20.16	19.75	19.66	20.97	98.8	13.84
2.	0.2	16.44	14.24	19.54	18.06	18.89	20.93	99.9	14.75
3.	0.3	15.56	14.69	19.90	17.55	18.46	20.57	97.2	14.09
4.	0.4	16.02	15.58	19.59	18.51	18.37	20.32	82.3	8.92
5.	0.5	15.90	16.22	19.14	17.96	17.92	19.92	68.6	4.66
6.	0.6	16.16	16.53	18.83	17.50	17.43	20.49	65.9	3.77
7.	0.7	16.61	18.67	19.03	17.14	17.78	20.19	38.03	-5.76
0.5M H_2SO_4									
1.	0.1	17.61	21.78	19.78	18.79	17.57	13.69	157.4	-60.78
2.	0.2	16.31	20.28	20.35	19.06	17.06	15.83	144.8	-56.46
3.	0.3	16.57	19.76	19.87	18.85	16.82	16.77	149.2	-57.82
4.	0.4	17.33	19.23	19.25	18.51	18.82	17.03	141.1	-55.51
5.	0.5	17.10	19.03	19.14	18.17	18.27	17.28	142.2	-55.72
6.	0.6	17.13	18.95	19.86	18.43	18.19	16.96	145.5	-56.92
7.	0.7	17.56	19.10	19.48	18.56	17.88	17.10	153.1	-59.37

4.5.3. Thermodynamic parameters

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

The results obtained were tabulated in Table (4.8). From the table, it is noted that the values of ΔG were negative in the presence and absence of the inhibitors. This indicates that adsorption behaviour of inhibitor is a spontaneous process under the experimental conditions. This negative value also indicates the strong interaction between the metal surface and the inhibitors molecules.

Generally, values of ΔG around -20 kJmol-1 or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption); those around -40 kJmol-1 or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) (Khamis *et al*, 1994). In the present work, the calculated ΔG_{ads} values are almost slightly less negative than -21 $kJmol^{-1}$ ranging from -13to -21 $kJmol^{-1}$. Hence it may be assumed that the adsorption of the inhibitor molecules is obeying physical adsorption however chemical adsorption may not be excluded due to the complex nature of the corrosion inhibiting process (Ahamad *et al,* 2010).

4.5.4.ΔH and –ΔS

A plot of ΔG Vs T was a straight line as depicted in Fig 4.18 & 4.19. The values of ΔH and ΔS are taken from intercept & slope respectively. The values of ΔH and ΔS indicate that the system was enthalpic and entropic controlled. From Table 4.8, the leaves extract of DEL in 1M HCl and 0.5M H_2SO_4 on MS shows positive value for ΔH suggesting that the dissolution process was an endothermic phenomenon and that the dissolution of steel was difficult which in turn proves the corrosion inhibition effect of the plant extracts. Also the entropy ΔS widely decrease with the content of the inhibitors. This means the formation of an ordered stable layer of inhibitors on the steel surface.

4.6. Electrochemical measurements

Electrochemical studies will be helpful to predict the nature of the inhibitors - anodic, cathodic or mixed type inhibitors and to predict a suitable mechanism for the inhibition process. The values of corrosion kinetic parameters corrosion current

(E_{corr}), corrosion current density (I_{corr}), Tafel slopes (ba and bc), linear polarization resistance (R_p) are recorded in Tables 4.9.

4.6.1. Potentiodynamic studies

The anodic and cathodic polarization curves of MS electrode in 1M HCl and 0.5M H_2SO_4 medium in the absence and presence of various concentrations of DEL extracts in at 303K are shown in Fig 4.20. The electrochemical polarization parameters for mild steel in 1M HCl and 0.5 M H_2SO_4 medium without and with different concentrations of DEL extract in 1M HCl and 0.5 M H_2SO_4 were listed in Table 4.9.

The electrochemical parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves depicted in Fig 4.20 and tabulated in Table 4.9. It was clear from Fig 4.20 that, the presence of DEL extract decreases both cathodic and anodic slopes with increasing concentration. That is DEL extract affected both the cathodic and anodic parts of the curves indicating that the extract influence the dissolution of MS and the hydrogen evolution processes, implying that DEL extract functioned as a mixed-type of inhibitor.

Corrosion current (Icorr) was found to decrease with increasing concentration, indicating the increased inhibition efficiency with the increase in the concentration of the inhibitors. This confirmed the inhibitive nature of the extract and also the adsorption of the plant extracts on metal surface.

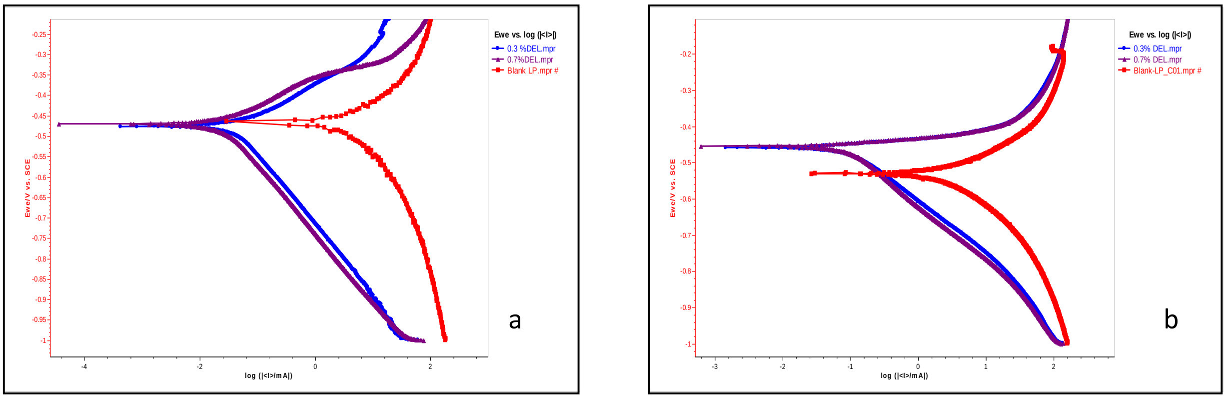


Figure 4.20: Potentiodynamic polarization plots for MS in (a) 1M HCl and (b) 0.5M H_2S0_4 in the presence and absence of DEL extract.

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

S.No	Conc V/V (%)	E_{corr} mV/SCE	I_{corr} μA/cm^2	b_a mV/dec	B_c mV/dec	IE (%)	R_p (Ω/cm^2)	IE (%)
1M HCl								
1	Blank	-479.7	530.7	93.8	150.5	-	55.4	-
2	0.3	-488.7	45.6	84.4	165.4	91.4	160	65.37
3	0.7	-443.3	16.6	162.4	162.4	96.8	476	88.36
0.5M H_2SO_4								
4	Blank	-584.8	4973.2	171.7	185.8		10.2	
5	0.3	-647.3	2284.9	244.8	143.7	54.05	53.2	80.8
6	0.7	-654.8	1944.4	239.6	158.1	60.90	126	91.9

The values of IE are found to be increasing with increase in concentration of inhibitors. A maximum of 96.8% and 60.4% of inhibition for DEL extract in 1M HCl and 0.5M H_2SO_4 was obtained with 0.7% concentration.

No significant change in E_{corr} values in the presence of inhibitors was noticed indicating the mixed nature of the inhibitors. It was found that, the values of E_{corr} shifted toward more positive by increasing the concentrations of inhibitors. This is due to the dissolution of metal is retarded by the film formed on the metal surface. Generally, an inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential (E_{corr}) in the presence of the inhibitor were more than 85 mV with respect to that in the absence of the inhibitors. From the results, the changes of E_{corr} are less than 85 mV for studied inhibitors, which indicate that inhibitors act as a mixed type inhibitors for the corrosion of MS in 1M HCl and 0.5 M H_2SO_4 acid medium. (C.B. Pradeep Kumar, K.N. Mohana., 2014).

Rp values were found to increase with increasing concentration of the inhibitor in both acidic solutions. A maximum of 88.36% and 91.9 % efficiency was obtained for DEL extract in 1M HCl and 0.5M H_2SO_4 respectively.

The inhibition action of DEL extract in 1M HCl and 0.5M H_2SO_4 was attributed to adsorption and formation of barrier film on the metal surface that separates the metal surface from the corrosive medium.

4.6.2. Impedance Spectroscopy

The Nyquist plot of the impedance behavior of mild steel in 1M HCl and 0.5 M H_2SO_4 in the presence of various concentrations of the inhibitor is shown in Figs 4.21 & 4.22. The impedance analysis of mild steel in 1M HCl and 0.5 M H_2SO_4 shows one depressed capacitive loop (one time constant Bode-phase representation). All experimental plots have a depressed semicircular shape in the complex impedance plane, with the centre the real axis (Fig 4.21 & 4.22) .A clean electrode without a passive film especially in the case of corroding electrode immersed in acid solutions gives rise to an impedance spectrum consisting of perfect semicircle. This behaviour is typical for solid metal electrodes that show frequency dispersion of the impedance data and has been attributed to roughness and inhomogeneties of the solid surface.

The R_{ct} value is a measure of electron transfer across the surface and inversely proportional to C.R. It was found that, as the concentration of the inhibitor increases, R_{ct} values increase (radius of semicircle increases), and the C_{dl} values tend to decrease due to the adsorption of inhibitors on the MS surface. The size of the semicircle increases with increasing inhibitor concentration, indicating the charge transfer process is the main controlling factor of the corrosion of MS.

Decrease in the capacitance of interface (C_{dl}) with increasing charge transfer resistance is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the inhibitor acts via adsorption at the metal/solution interface.

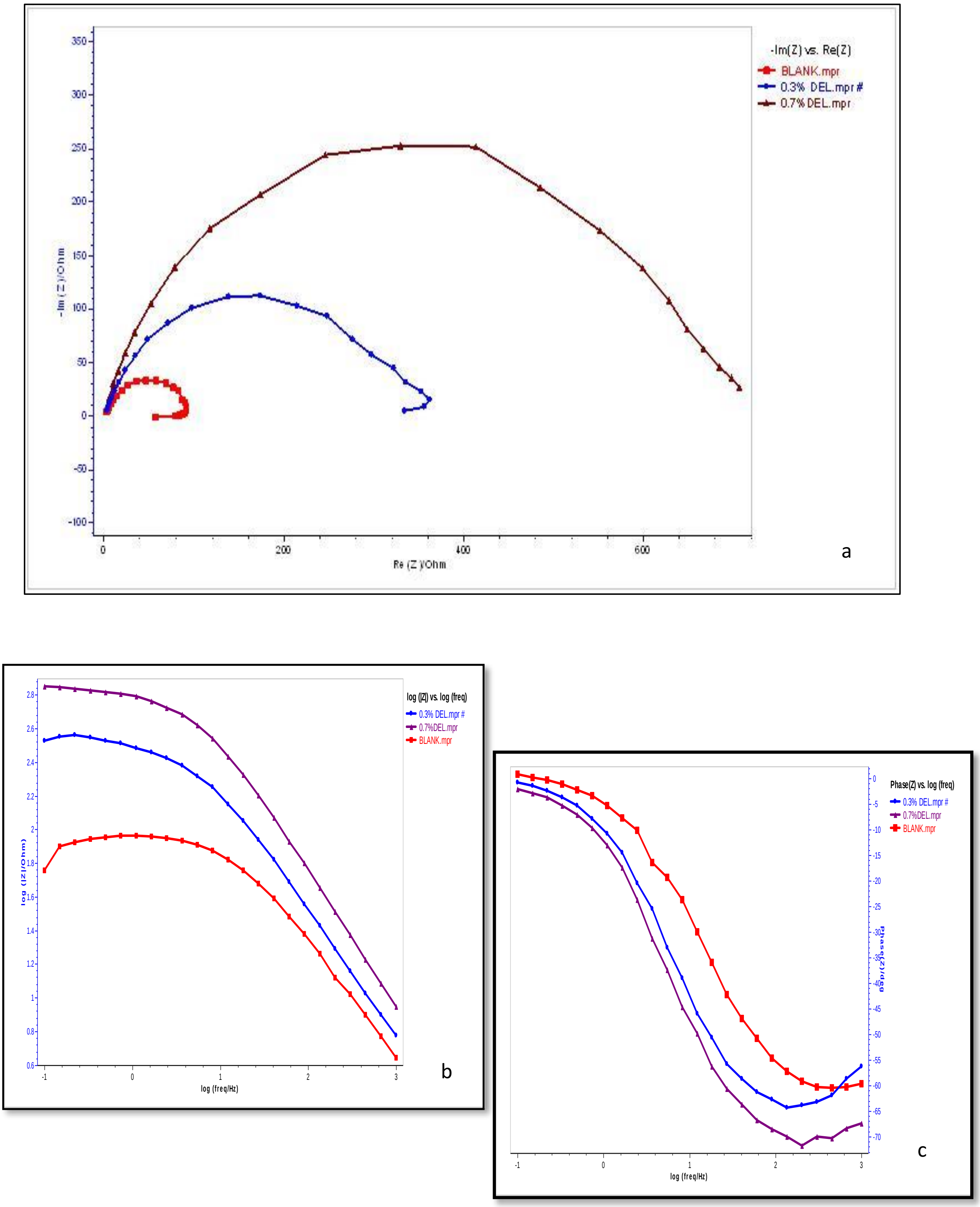


Figure 4.21: Impedance plots in Nyquist and Bode format for MS in 1M HCl (a-c) in the presence and absence of DEL extract

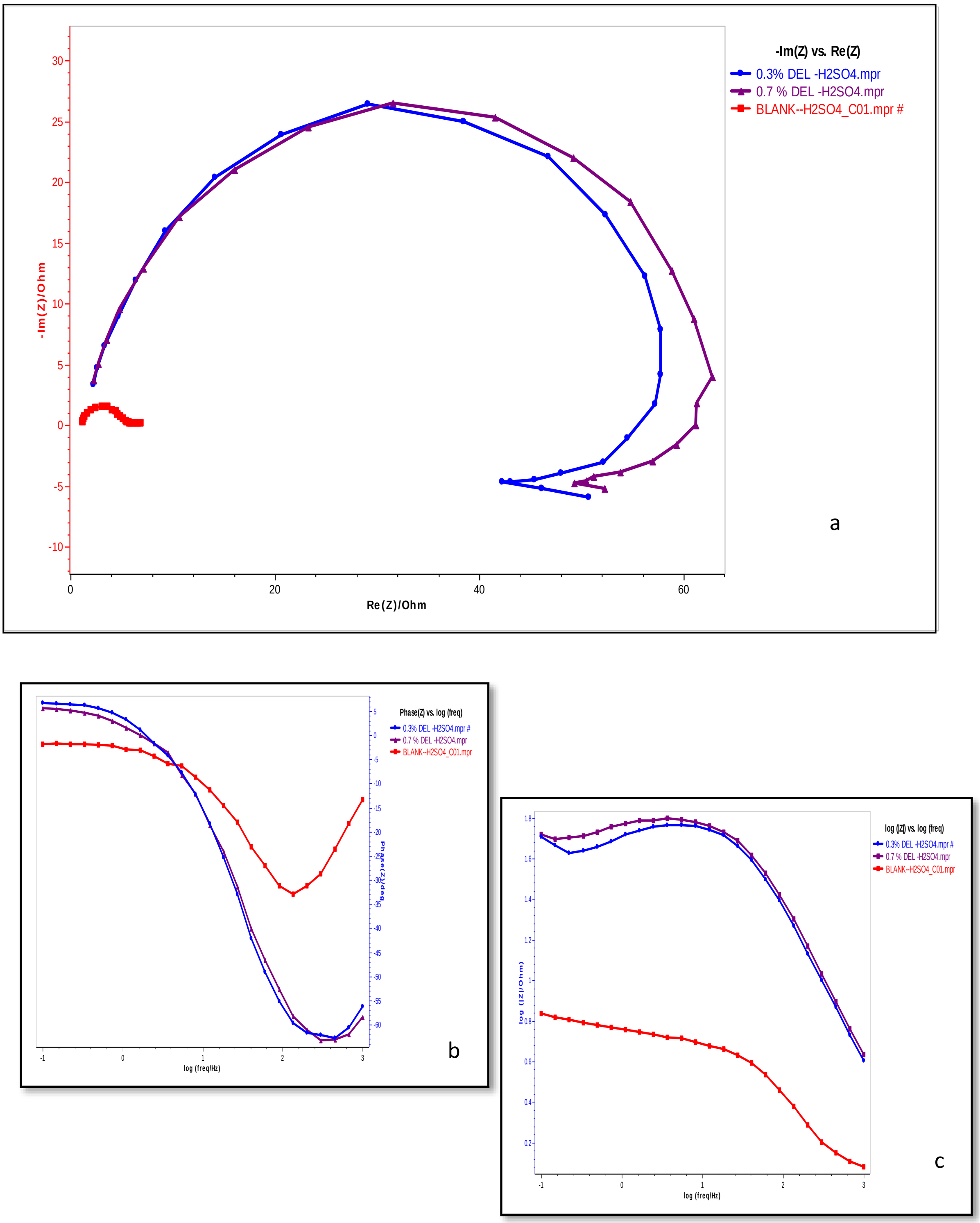


Figure 4.22: Impedance plots in Nyquist and Bode format for MS in 1M H_2SO_4 (a-c) in the presence and absence of DEL extract

Table 4.10: Impedance plots in Nyquist and Bode format for MS in 1M HCl / 0.5M H_2SO_4 in the presence and absence of DEL extract

S.No	Conc.(v/v) %	R_S	Rct (Ω/cm^2)	IE (%)	Cdl (μ F cm^{-2})	θ
1M HCl						
1.	Blank	6.281	81.1	-	107	-
2.	0.3	-2.182	356.1	77.2	81.4	0.238
3.	0.7	-3	702.6	88.4	41.2	0.614
0.5M H_2SO_4						
4.	Blank	0.90	5.26	-	498	-
5.	0.3	6.82	45.8	88.5	85.6	0.828
6.	0.7	5.82	51.7	89.8	75.8	0.847

From the impedance parameters, it can be seen that as the concentration increases, R_{ct} values were found to increase. Figures 4.21 and 4.22, illustrates that the charge transfer resistance is found to increase with increase in concentration of the inhibitor. This indicates the dissolution of the metal and the corrosion of mild steel is controlled by charge transfer process. The charge transfer reactions are known to take place at the metal solution interface. Consequently the high R_{ct} values of inhibited electrodes can be explained by the buildup of protective layers and the effective barrier behaviour of adsorbed layers. The LF inductive loop may be attributed to the relaxation of adsorbed compound on electrode surface (Noor 2008).A maximum of 88.4% (in 1M HCl) and 89.8% (in H_2SO_4) was obtained for 0.7% of DEL extract.

The C_{dl} values tend to decrease with increase in concentration of 0.3 and 0.7. Decrease in C_{dl} can result from a decrease in local dielectric constant or an increase in thickness of the electrical double layer, suggests that the inhibitors function by adsorption at the metal solution interface (Mc. Cafferty.,1972).

4.7. Comparison of Mass loss and electrochemical methods

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

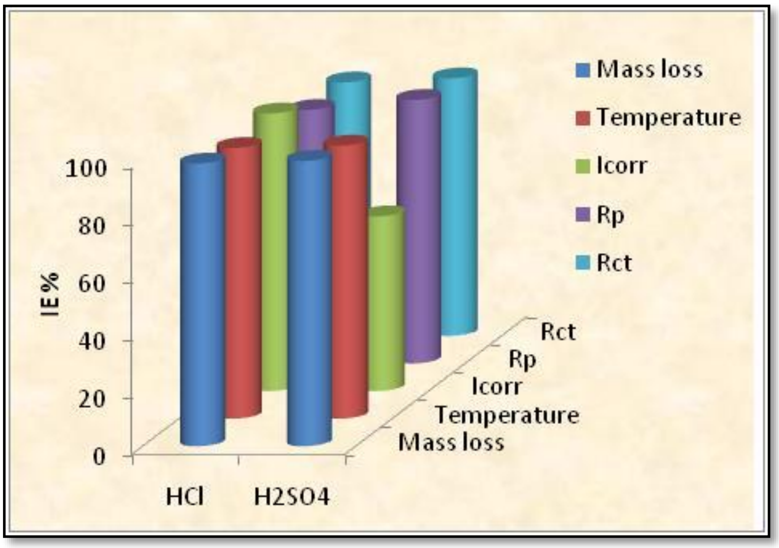


Figure 4.23: Performance of DEL extracts by mass loss and electrochemical measurements.

4.8 Surface Analysis

4.8.1 FT- IR Spectral Analysis

In the presence of the inhibitor, IR spectrum of the corrosion product **(Figure 4.24)** revealed that the –OH stretch (3379.23 cm^{-1}) was shifted from (3363.86 cm^{-1}). From the spectra, it is observed that the C–H stretch of alkanes and C–C stretch (in–ring) of aromatics from the absorption bands at 2924.09 cm^{-1} and 2924.09 cm^{-1}. From the Figure (4.24) the IR spectrum of the phytochemical compounds adsorbed on the metal surface reveal the presence of functional group peaks whose absorption frequencies correspond to carbonyl groups at 1627.92cm^{-1} and 1689.64cm^{-1}.

From the crude plant extract to the corrosion product of DEL absorption shifts of –C ≡ N stretch (2376.30cm^{-1} to 2314.58 cm^{-1}), C-H bend (1442.75cm^{-1} to 1543.05cm^{-1}) and C-O stretch (1064.71cm^{-1} to 1018.41 cm^{-1}). The shift in the absorption frequencies of the inhibitor on the metal surface strongly supports the interaction between the phytochemical compounds of the inhibitor and metal surface. The band at 450 cm^{-1}to 700 cm^{-1}probably originates mainly from γ -Fe_2O_3 (670.07cm^{-1}). Some missing bonds are there in corrosion products indicating that there is interaction (Fe - complex formation) between the leaves extract of and the surface of mild steel.

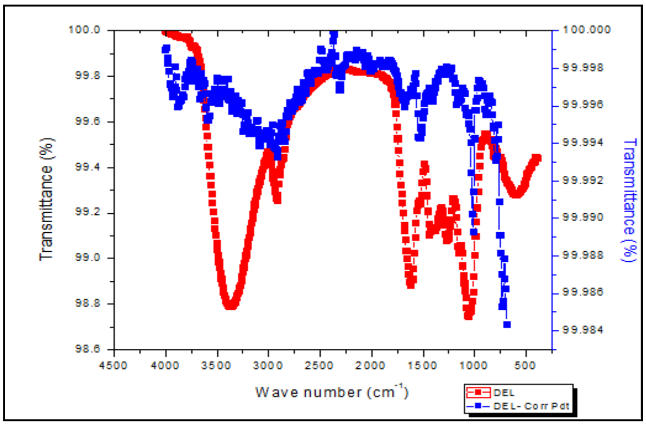


Figure 4.24: IR spectrum of extract and corrosion products in 1M HCl

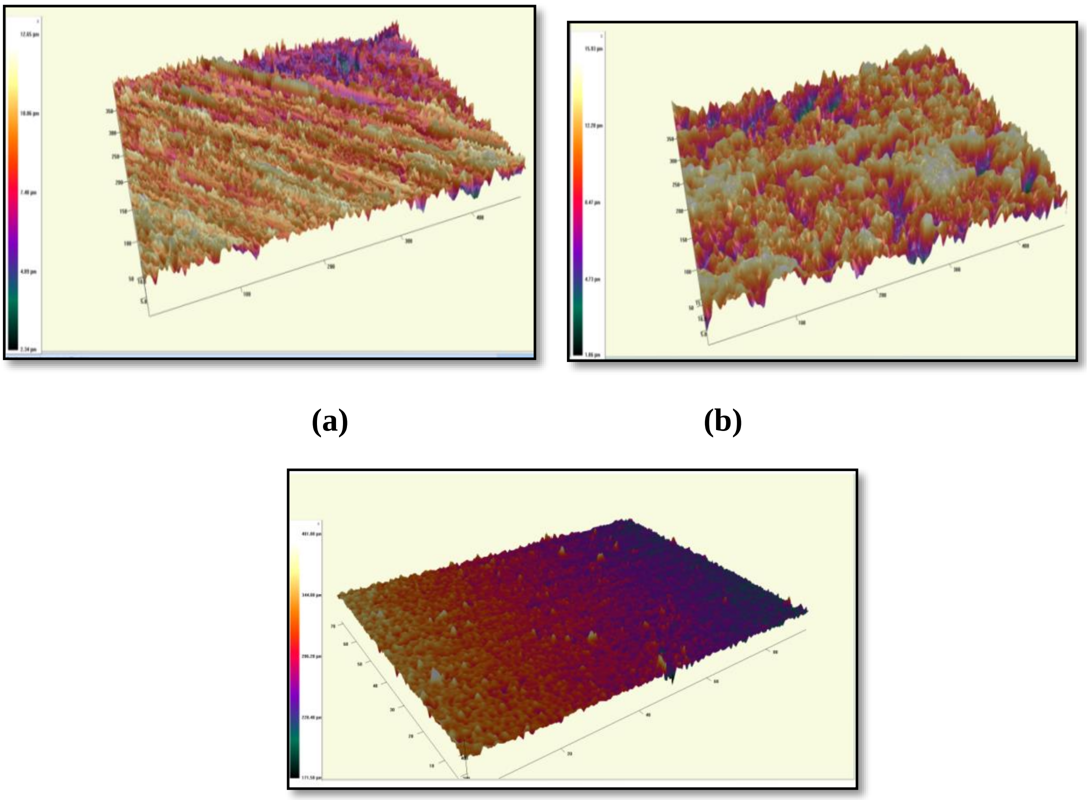
Table 4.11: IR spectrum of (a) acid extract of concentrates (b) adsorbed material of MS in the presence of HCl extract of DEL as an inhibitor

Powdered Plant material			**Corrosion product of DEL**		
Frequency cm^{-1}	**Assignment**	**Functional Groups**	**Frequency** cm^{-1}	**Assignment**	**Functional Groups**
3379.23	OH stretch	Alcohol	3363.86	O–H stretch, H–bonded	1°, 2° amines, amides
2924.09	C–H stretch	Alkanes	2924.09	C–H stretch	Alkanes
-	-	-	-	-	-
2376.30	-C ≡N Stretch	Aliphatic amines	2314.58	–C ≡N stretch	Aliphatic amines
1627.92	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers	1689.64	C=O stretch	Carbonyl groups, carboxylic acids, esters, ethers
1442.75	C–H bend	Aliphatic amines	1543.05	C-C in ring	Aromatics
1381.03	C–O-C stretch	Ethers	1411.89	C–H bend	Aliphatic amines
1273.02	C-O stretch	carboxylic acids	-	-	-
1064.71	C-O stretch	carboxylic acids	1018.41	C-O stretch	carboxylic acids
810.10	O–H bend	Alcohols	802.39	O–H bend	Alcohols
			671.23	- γ -Fe_2O_3	-

4.8.2. 3D Laser profilometer:

3D Laser Profilometer image analysis was performed to obtain the average roughness, Ra, (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, Rq, (the average of the measured height deviations taken within the evaluation length and measured from the mean line).

In Figure 4.25 (a) the surface topography of uncorroded metal surface is shown. The value of Rq, Ra for the polished mild steel surface reference sample are 3.140 µm, 2.558 µm respectively.



(a) (b)

(c)

Figure 4.25: (a) Plain MS (b) MS in 1M HCl (c) 1M HCl +0.7% DEL

Figure 4.25 (b) show the corroded metal surface in the absence of the inhibitor in 1M HCl. The (Rq), (Ra) height values for the mild steel surface are 22.35 µm, 17.28 µm respectively. These data suggest that mild steel surface immersed in 1M HCl has greater surface roughness than the polished metal surface due to the corrosion of the mild steel.

Figure 4.25 (c) show the mild steel surface after immersion in 1M HCl in the presence of 0.7% DEL. The (Rq), (Ra) for the mild steel surface are 11.1 µm, 8.48

µm respectively. The (Rq), (Ra) are considerably less in the inhibited environment compared to the uninhibited environment.

These parameters confirm that the surface of MS in the presence of the inhibitor is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} -DEL complex on the metal surface thereby inhibiting the corrosion of mild steel.

Table 4.12: Roughness Parameters for MS/1M HCl/DEL

Samples	**Average Roughness Ra (µm)**	**Root Mean Square Roughness Rq (µm)**
Plain MS	2.558	3.140
MS in 1M HCl	17.28	22.35
MS in 1M HCl + 0.7% DEL	8.48	11.1

4.8.3. Scanning Electron Microscopy (SEM)

SEM morphologies of MS after immersing in 1M HCl for 3h in the absence and presence of DEL were shown in Fig 4.26 (a). Fig 4.26 (b), shows the general appearance of MS in HCl without DEL. No obvious corrosion products present on the sample. That is the corrosion attack in 1M HCl is more uniform in character and there is little tendency towards local enrichments of products on the surface.

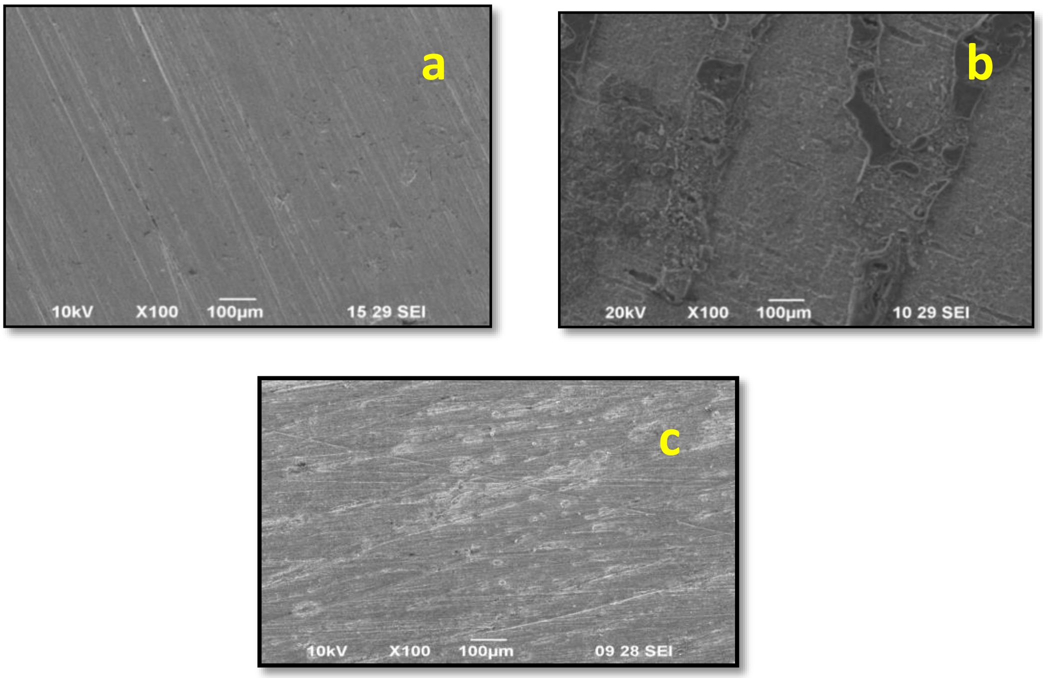


Figure 4.26: (a) Plain MS (b) Blank (MS in 1M HCl) (c) 1M HCl +0.7% DEL

In addition, parallel features which can be associated with abrading scratches are also observed. Fig 4.26 (c) shows the SEM morphologies of MS in HCl in the presence of 0.7% DEL.

4.8.4. UV- Visible Spectroscopy

UV-Visible spectroscopy provides a strong evidence for the formation of a metal complex (Quraishi *et al*, 2012). From Figure 4.27, a deviation is shown in absorbance values and their intensities.

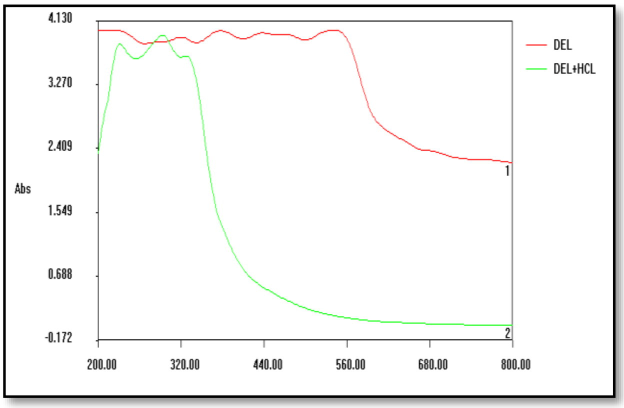


FIGURE 4.27: UV analysis of DEL extract and 1M HCl+0.7% DEL

There is an increase in absorbance after mild steel immersion for the investigated plant extract. These bands may arise due to π-π* and n- π* transitions with a considerable charge transfer character. After 3h immersion of mild steel change in the position of absorption maximum or change in the values of absorbance indicate the formation of a complex between Fe^{2+} and the phytoconstituents of the plant extract. The displayed UV spectral data reveal that the band in the region of 300-332 nm is due to the carbonyl groups which are held up in the complex with Fe. It is clearly seen that the band maximum of the n- π* and π -π* transition underwent a blue shift, indicating that the carbonyl group are held up in the complex with Fe. (Abboud *et al*, 2007).

Table 4.13: UV Visible spectral details of DEL extract and 1M HCl +0.7% DEL

Inhibitor	**Absorption bands (nm)**	
	Crude plant extract	**Mild steel+1M HCl+ inhibitor**
DEL	545.6	336.8

Formation of this complex may be responsible for the observed deviation in the absorbance and its intensity value and this may be responsible for plant extracts anti-corrosion activity. Similar assertion has been reported by Bothi Raja and Sethuraman, 2009 a,b.

4.9. Mechanism of Inhibition

In most inhibition studies, the formation of donor-acceptor surface complexes between π-electrons of an inhibitor and the vacant d-orbital of metal were postulated (Zucchi, *et al.,* 1996). The presence of lone pairs of electrons on the active centers of phytochemical components delocalized and thus produced a delocalization energy that stabilized the compound. It is also known that the adsorption of the inhibitor can be influenced by the nature of the anions in acidic solution. The presence of anions in the solution should be mentioned. They are characterized with strong absorbability on the metal surface which brings about a negative charge favouring the adsorption of cation type inhibitors ***(Antropov, et al., 1981).***

These studies showed that the larger the substance was adsorbed, the more effectively it protects surface. In the current investigation DEL works out to be a good inhibitor for mild steel corrosion. Phytochemical screening of DEL and phytochemical components in DEL collected from literature are listed in Table 4.6. The phytochemical components form Fe complex with mild steel and the adsorption model is depicted in Figure 4.28. Adsorption is the primary step in achieving inhibition in acid solutions. This is a consequence of the fact that the corroding metal surface to be inhibited is usually oxide-free allowing the inhibitor ready access to retard the cathodic and/or the anodic electrochemical processes of corrosion. Once the inhibitor was adsorbed on the metal surface it can then affect the corrosion reactions in a number of ways: by offering a physical barrier to the diffusion of ions or molecules to or from the metal surface; direct blocking of anodic and cathodic reaction sites; interaction with corrosion reaction intermediates; change the make-up of the electrical double layer which develops at the metal/solution interface and so affect the rate of electrochemical reactions **(Graeme Wright, 1998).**

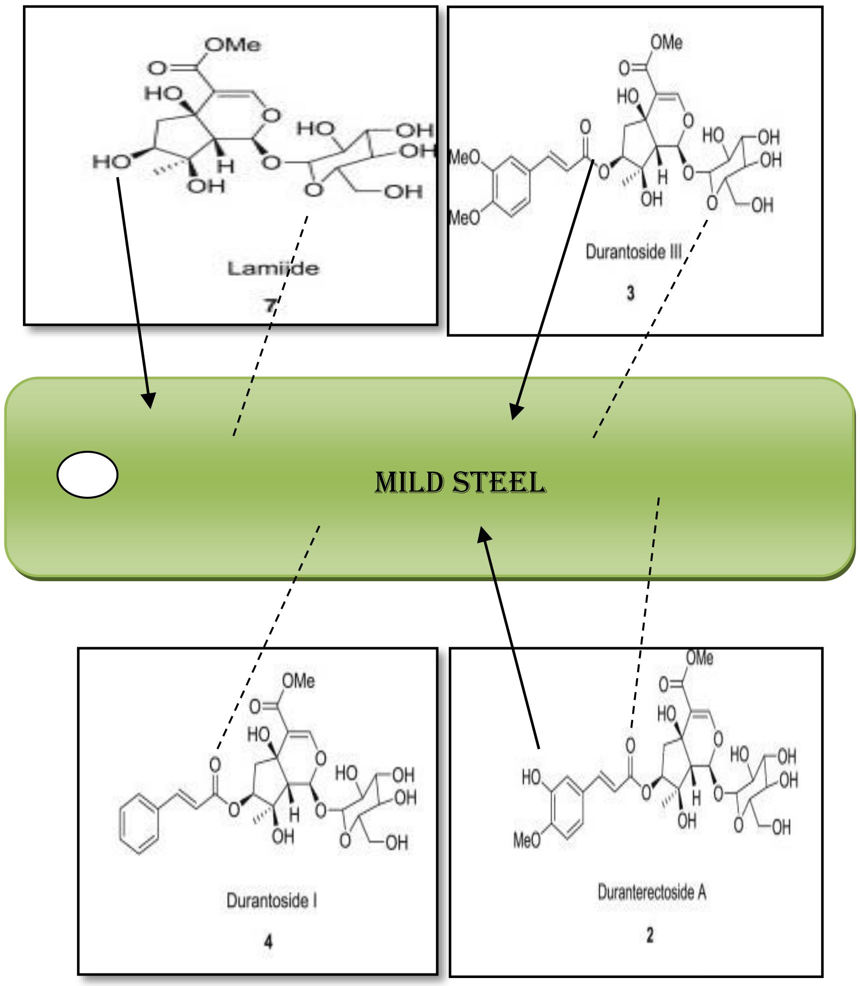


Figure 4.28: Skeletal representation of adsorption of inhibitor molecules of DEL on the surface of MS

Summary & Conclusion

SUMMARY AND CONCLUSION

The use of inhibitors is one of the best options for protecting metals against corrosion. Several inhibitors in use are either synthesized from cheap raw materials or chosen from compounds having hetero atoms on their aromatic or long chain carbon system However, most of these inhibitors are toxic to the environment. This has prompted the search for green corrosion inhibitors. Corrosion control methods, especially the use of inhibitors, have gained monumental importance in the present scenario of expunging corrosion and the quest for natural products as inhibitors for ecofriendly reasons continues. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds and so they are environmentally friendly. In this direction, to arrive at inexpensive non-toxic ecofriendly inhibitors formation the present study **"Inhibitive effect of leaf extract of *Durenta erecta* on Mild Steel corrosion in 1M Hydrochloric and 0.5M Sulphuric acid solution"** leaves has been carried out by the classical mass loss measurements and polarization measurements.

- The acid extracts of DEL could bring out a maximum inhibition of 98.6% in 1M HCl and 99.5% in 0.5M H_2SO_4 acid.
- The extracts were temperature resistant in nature and the inhibition efficiency varied from 98.6%, at room temperature to 82.3% for DEL in1M HCl and 99.5%, at room temperature to 91.1% for 0.5M H_2SO_4 extract
- The inhibitors used in the current study followed Langmuir and Temkin adsorption isotherm which indicated the mono layer formation with heterogeneity in the surface of the electrode.
- Thermodynamic parameters calculated could reveal the physisorption process, spontaneity of adsorption and there is interruption of solvent entropy. Thus a suitable mechanism could be predicted.
- Increase in Rp and Rct values and decrease in I_{corr} and C_{dl} value confirm that DEL is adsorbed on the mild steel surface and inhibition process is followed by monolayer adsorption.
- Maximum efficiency of 96.8% in 1M HCl and 60.9% in 0.5M H_2SO_4 from icorr and of from Rp were obtained.
- Results from the polarization techniques such as Tafel and impedance spectroscopy could be comparable with the classical mass loss methods.

- The eco friendly inhibitors under study behaved as mixed type inhibitors.
- Cost effective and non-toxic to the environment.
- In the current investigation the *Durenta erecta* leaves extracts play a major role in reducing the metal dissolution as well as hydrogen evolution and protect the mild steel surface from corrosion.
- Thus the *Durenta erecta* leaves extract has proved to be zero cost, eco-friendly and highly economical inhibitor.

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