

# GREEN CORROSION INHIBITORS: REVIEWS AND APPLICATIONS



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# Green Corrosion Inhibitors: Reviews and Applications


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## Synopsis

The present work has been focused on the environmental, health as well as economic aspect and hence planned to use some of the eco-friendly corrosion inhibition behaviour of aqueous and alcoholic extract of six plants selected namely *Gloriosa Superba* Linn (GSL), *Madhuca longifolia* (ML), *Alangium lamarckii* (AL), *Holoptelea integrifolia* (HI), *Pithecellobium dulce* (PD) and *Schreabera swietenoides* (SS) on mild steel surface in 1N HCl solution were investigated by mass loss with different time of contact, various temperature and evaluated by electrochemical impedance and Tafel studies. Polarization measurement revealed that the plant extracts which can act as mixed type inhibitor. An EIS plot indicates that the increase of inhibitor concentration increased the charge transfer resistance and decreased double layer capacitance. Organic moieties present in the extract were also found responsible performance of the inhibitor which was well supported by FTIR studies. The inhibitive effect of the ML, GSL, PD, AL, HI, and SS (both extracts) could be attributed to the presence of phytochemical constituent in the plants which is absorbed on the surface of the mild steel. The nature of Protective film formed on the MS surface has been confirmed by SEM analysis. The surface coverage values were tested graphically to fit for a suitable adsorption isotherm.



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# Chapter 1

## Introduction

### 1.1 Introduction

Corrosion is “**The cancer of metal**”. All metals and alloys are susceptible to corrosion by one or more naturally available or man-made fluids. Normally metals exist in unstable form and try to get stable by reacting with the atmosphere [1-10]. Mild steel is the most versatile, least expensive and world widely used in many applications in industries like metallurgical process, chemical cleaning, fertiliser, desalination plants, bolts-nut, screw industry, storage tank, petroleum refineries, pharmaceutical industry, thermal power plant, construction material, and gas industry, sugar, paper, textile, boilers, automobiles, steam boilers, engineering purpose, mechanical purpose, chain, hinges, knives, magnets, military equipment, armour, vehicles (ships and cars) and pickling process etc., due to their stability, high strength, weld ability and good corrosion resistance [11-15].

Hydrochloric acid, sulphuric acid, phosphoric acid and organic acid like citric, oxalic, acetic acid are used to clean up the scales and rusts of the mild steel articles which are caused by corrosion of the exposed metal after the scales have been removed [16-40]. Sea water and base medium is another corrosive environment which causes drastic environmental degradation of various mild steel structures. Application of corrosion inhibitors is one of the best methods, among the various methods of mitigation of corrosion. They are generally heterocyclic organic compounds with presence of S, O or N atoms in the molecules (compounds) with a lone pair of electron, pi electron with multiple bonds. But most of the synthetic organic and inorganic inhibitor is toxic and harmful to human and other living system; this may cause temporary or permanent damage to the organ system [41-80]. Since the early 1990's in different areas of the world where platform in the sea are used to extract oil, environmental situations arise that challenge the use of corrosion inhibitor. Plant extracts have been explored as corrosion inhibitors due to their bio-degradability, non-toxicity, environmental friendly nature, easy availability, easy to handle, low cost and simple procedure [81-102]. In the present investigation, corrosion inhibition of mild steel in HCl has been studied in the presence of few green inhibitors (both in aqueous and alcoholic extract) mainly *Gloriosa superba* Linn, *Madhuca longifolia*, *Alangium lamarckii*, *Holoptelea integrifolia*, *Pithecellobium dulce* and *Schrebera swietenoides* and there are no reports in the literature on the use of these plants as corrosion inhibitors.

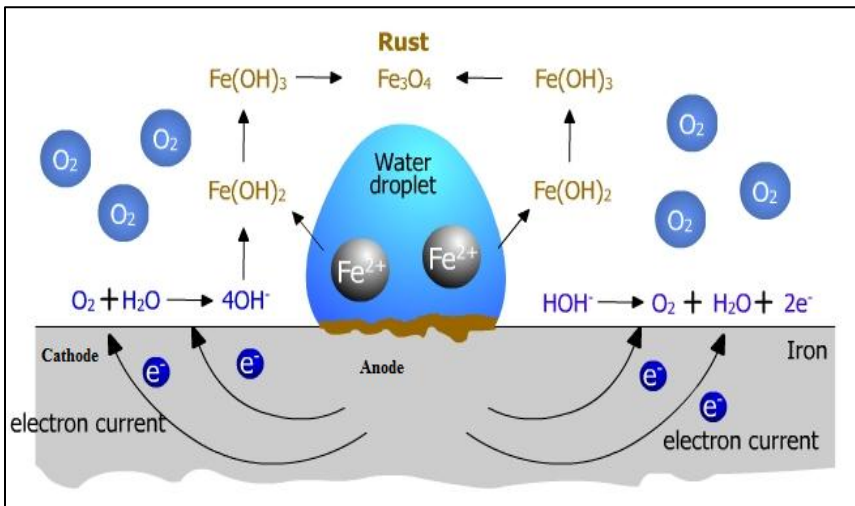
## 1.2 Basic Concept of Corrosion

Corrosion is “**Billion dollar thief**”. Corrosion has been classified as chemical and electrochemical, low and high temperature, wet and dry corrosion. Carbon and low alloy steel are widely used, mainly for economic reasons. Moreover, they may have different microstructures which influence their mechanical properties and corrosion resistance in certain environments [103].

## 1.3 Definitions

**Ulick R. Evans** the “**Father of Corrosion Science**” has said that corrosion is largely an electro chemical phenomenon, may be defined as deterioration of metals and alloys in the presence of an environment by chemical or electrochemical means.

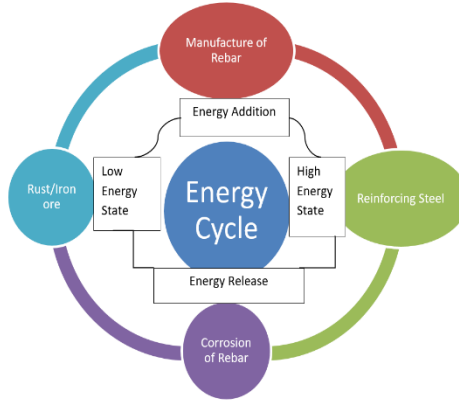
In simple terminology, corrosion is an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with environmental species [104-105].



**Fig. 1.** Formation of Rust

For environments with water present, including moisture in the air, the electrons consume metal converting oxygen and water to hydroxide ions. All metal and alloys in those hydroxide ions in turn combine with iron ions to form  $[\text{Fe}(\text{OH})_2]$ . Subsequent reactions form a mixture of **magnetite ( $\text{Fe}_3\text{O}_4$ )** and **hematite ( $\text{Fe}_2\text{O}_3$ )**. This **red-brown** mixture of iron oxides is called as **rust** [106-108].

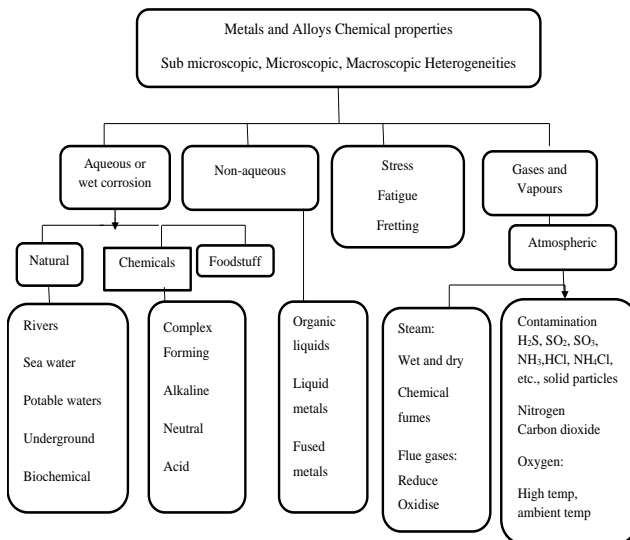
## 1.4 The energy cycle of Iron



**Fig. 2.** The energy cycle of iron

## 1.5 Factor influencing corrosion

Environmental effects such as the role of various micro organisms present in **soil and water bodies, oxygen and other oxidizers, changes in flow rates (velocity), temperature, reactant concentrations and pH** would influence the rate of anodic and cathodic reactions. The definition for corrosion needs to be further widened and to be included in microbial influenced factors.

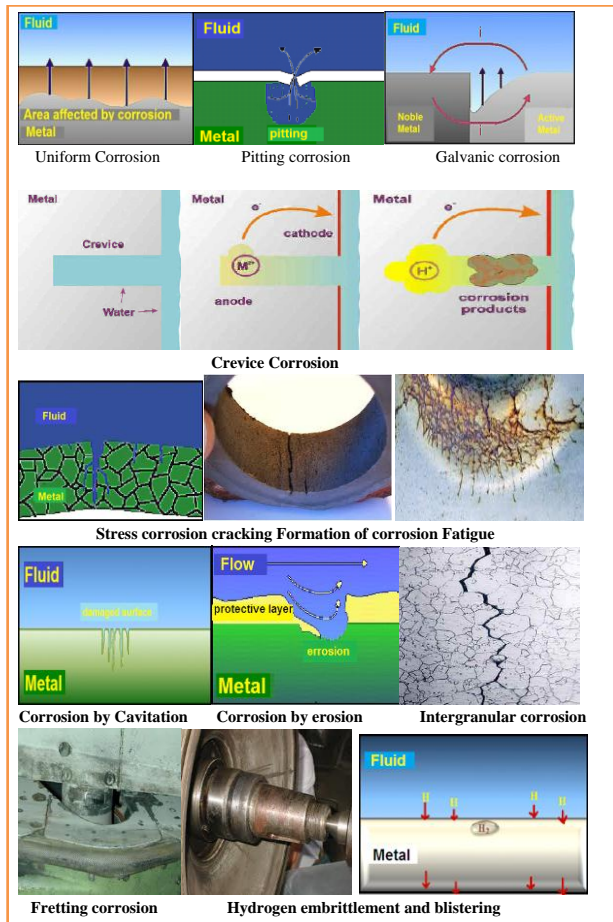


**Fig. 3.** Factors of various corrosion formations

## 1.6 Types of corrosion

The most important types of corrosion are

- General corrosion
- Localized corrosion
- Pitting corrosion
- Crevice corrosion
- Filiform corrosion
- Galvanic or bi-metal corrosion
- Environmental cracking
- Stress corrosion cracking
- Corrosion fatigue
- Corrosion fatigue
- Flow-Assisted corrosion
- Cavitation corrosion
- Erosion
- Intergranular corrosion
- De-Alloying
- Exfoliation
- Fretting corrosion
- High temperature corrosion
- Corrosion via hydrogen embrittlement



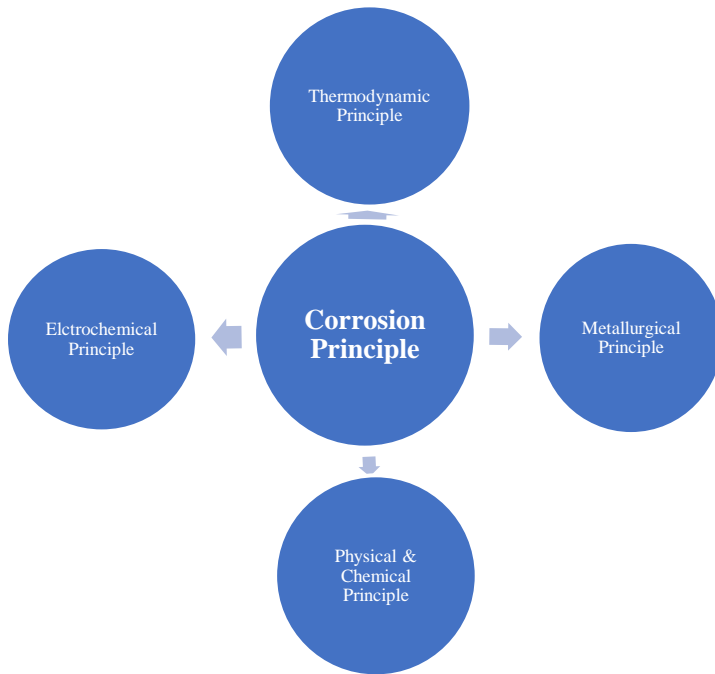
**Fig. 4.** Various forms of Corrosion



## 1.7 Principles of corrosion

### *Thermodynamic principle*

Thermodynamic principles are applicable to corrosion processes involving **free energy, electrical double layer, Nernst equation for electrode potentials** and **Pourbaix diagrams**. It is used to determine whether corrosion is theoretically possible or not. Different metals have different tendencies to corrode in a given corrosive environment. Thermodynamic approaches have been also widely used to explain and understand the fundamental corrosion problems.



**Fig. 5.** Principles of Corrosion

## 1.8 Electrochemical Principle

Electrochemical corrosion is a spontaneous process that denotes the existence of anodic and cathodic zones, where an electrolyte is also required.

**Anode reaction:**  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}$

**Cathode reaction:**  $2\text{H}^{+} + 2e^{-} \rightarrow \text{H}_2$  ;  $\text{O}_2 + 2\text{H}_2\text{O} + 4e^{-} \rightarrow 4(\text{OH}^{-})$

## 1.9 Metallurgical Principles

The corrosion behaviour of a metal is well understood by metallurgical principles. In many cases, the metallurgical structure of an alloy can be changed so as to improve its corrosion resistance.

## 1.10 Physical and Chemical Principles

The mechanism of corrosion reactions, the surface conditions of metals and other basic properties are understood by the physical and chemical principles. Physical corrosion is caused by impact, stress or exhaustion of the material. Chemical corrosion is caused by **oxygen, sulphur, fluorine, chlorine or other gases**, which act directly on the metal under environmental conditions that facilitate this phenomenon.

## 1.11 Theories of corrosion

There are two theories of corrosion, they are: 1. Homogeneous theory  
2. Heterogeneous theory.

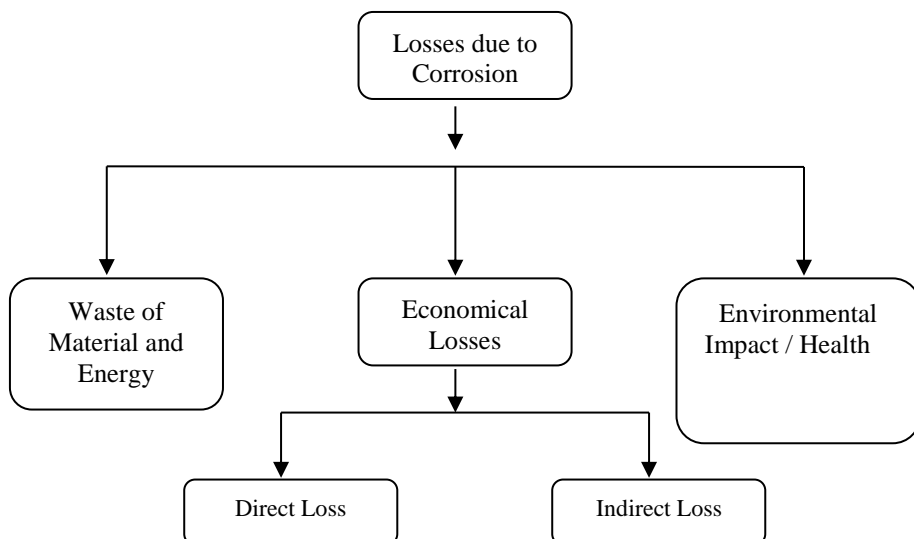
### *Homogeneous Theory*

A corroding metal irrespective of the presence or absence of any micro heterogenetics can be regarded as a single electrode on which a reaction takes place. Therefore, it is necessary that the potential difference across the interface be more negative (anodic) than the equilibrium potential for the metal dissolution or more positive (cathode) than the equilibrium potential for the electro nation.

### *Heterogeneous Theory*

According to this theory corrosion is caused when the metal is exposed towards the moist atmosphere. Here corrosion is caused by local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity.

## 1.12 Losses due to Corrosion



**Fig. 6.** Cost of Corrosion

## 1.13 Waste of Material and Energy

In India loss due to corrosion has been reported to account for more failure in terms of cost and tonnage than any other environment. Economical losses have been divided into: direct loss and indirect loss. The up-to-date study indicates that technological changes have provided a lot of new ways to prevent corrosion, and the better use of available corrosion management techniques. The cost was determined by analysing the following industrial sectors: Bridges, oil gas transmission pipelines, waterways, airports, railroads, motor vehicles, refining, agricultural and food processing, electronics & home appliances, pulp, paper, chemical, petrochemical, pharmaceutical, defence and nuclear waste disposal.

## 1.14 Economic Effects

In modern business environment, successful enterprises cannot tolerate major corrosion failure (bridges, aircraft, automobiles, gas pipelines, broken connections in pacemakers, and fracture of weight-bearing prosthetic devices, etc) especially those involving personal injuries (such as pins, screw, plates, hip joints, pacemakers, and other implants or even loss of life) fatalities, unscheduled shutdown and environmental contamination. Losses due to corrosion could be approximately Rs. 2.0 lakh crores per annum (in the year of 2015) in India [109].

### 1.15 Other effects

- Loss of time and corrosion products may contaminate dyes, chemicals, packaged goods, pharmaceuticals with direct penalties to consumers.
- Loss of metal strength leading to leaking containers storage tanks; water and oil transportation lines and fuel tanks cause (breakdown) significant loss of product and may generate severe accidents and hazards.
- International concern was aroused by the disclosure of the serious deterioration of the artistically and culturally significant gilded bronze statues in Venice, Italy.

### 1.16 Corrosion management and common methods of corrosion prevention

In most industrial situations it is virtually impossible to prevent corrosion but it can be minimised to a certain extent by corrosion resistance materials, rubber covered steel, resin bonded carbon.

- Increasing use of metals in all fields of technology. Use of rare and expensive metals whose protection require special precautions. Right metal in the right way in the right place is important (necessary).
- Use of new high strength alloys which are usually more susceptible to certain types of corrosive attack.
- Increase awareness, change policies, regulations, standards and management practices to increase corrosion savings through sound corrosion management.
- Improve education and training of staff in recognition of corrosion control.
- Advance life prediction, advance design practices for better corrosion management.
- Avoid metal-metal or metal-non-metallic contacting materials that facilitate corrosion.
- Bimetallic couple
- Designs that lead to erosion-corrosion and heterogeneity in the metal
- Use inorganic coatings e.g., (vitreous, enamel, glasses, ceramics) and organic coatings e.g., oil, enamels, white washing, paint, plastics.

### 1.17 Scope of the present investigation

Studies in a number of countries have attempted to determine the national cost of corrosion. For this reason, considerable efforts are generally employed in corrosion control at the operational phase. Actually, something can and should be done to prolong the life of metallic structure and components exposed to the corrosive environments. ***Therefore, there is a need for a plant extract that provides an excellent inhibition, low cost, and is environmentally safer.*** There is growing demand for corrosion inhibitors that are less toxic and biodegradable compared to current formulations. In this present study, the plant extracts in 1N HCl medium as a corrosion inhibitor in mild steel as a research study to investigate the inhibiting effect of aqueous



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## Chapter 2

# Inhibitor

### 2.1. Background of Corrosion Inhibitor

A studied topic in the field of corrosion inhibitor is one of the most important tools for mitigation of material. Large numbers of books and journals have been published on this subject [1-5]. Several **seminars** and **conferences** on corrosion discuss the development and application of corrosion inhibitor [6-33]. The natural products that have been used as corrosion inhibitors for metallic protection could be traced to the last half of the **19<sup>th</sup> century** [34]. The first research in corrosion inhibition was given to **Baldwin** [35] which involved the use of **molasses and vegetable oils**. Organic molecules operating as corrosion inhibitors were developed in the petroleum industry in the 1950's and concrete industry in the early 1990's. **Marangoni and Stephanelli** used extract of *glue, gelatin and bran* to inhibit the corrosion of metal in HCl acid [36-38].

### 2.2. Corrosion Inhibitor

Corrosion inhibition is reversible and a minimum concentration (**e.g.~10<sup>-4</sup>M**) of the inhibiting compound is required to maintain the inhibiting surface film. Inhibitors are usually too high to be commercially feasible for the reduction of the corrosion rate of the metal [39-41]. Good circulation and the absence of any stagnant areas are also needed to maintain inhibitor concentration. While using a corrosion inhibitor for a specific problem it is essential to make a proper selection of corrosion inhibitor, as **no universal corrosion inhibitor** exists. Inhibitor being a complicated subject may cause potential hazards also. Inhibitor efficiency (IE) is given as:

$$IE \% = \frac{I_{\text{Corr}} - I_{*\text{Corr}}}{I_{\text{Corr}}} \times 100$$

Where  $I_{\text{Corr}}$  &  $I_{*\text{Corr}}$  is the corrosion current with inhibitor & without inhibitor respectively.

## 2.3. Importance of Corrosion Inhibition

In India professional organization such as the *Central Electrochemical Research Institute (CECRI)* and other parts of the world *National Association of Corrosion Engineers (NACE)* provide **Corrosion Education and Training** which includes **research, Degree programs, Certification program and General education**. Few **National Universities** and **Colleges** offer courses in Corrosion and Corrosion Control as part of their engineering curriculum [42-44].

There are two important reasons why **Scientists and Engineers** are interested in methods to control or inhibit corrosion by the use of corrosion inhibitor. The first is the issue of **safety**. The second reason is an **Economical Impact** [45-48].

## 2.4. Classification of Inhibitors

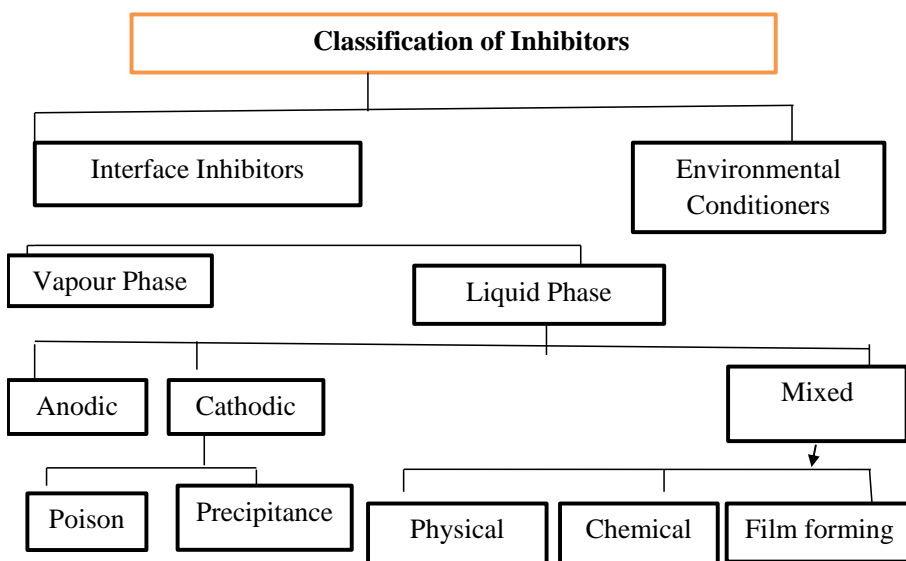
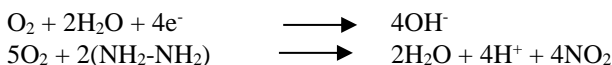


Fig. 8. Classifications of Inhibitors

## 2.5. Environmental Conditioners (Scavengers)

Corrosion can be controlled by removing the corrosive species in the medium. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called Environmental Conditioners or Scavengers



## 2.6.Interface Inhibitors

Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid and vapor-phase inhibitors.

## 2.7.Liquid-Phase Inhibitors

When adsorption occurs (or may occur) at the interface between a fluid phase and a solid, the solid is usually called the adsorbent; for gas/liquid interfaces it may be in some, but not in all cases useful to call the liquid/gas phase adsorbent as Liquid-phase inhibitors. This system is classified as anodic, cathodic or mixed inhibitors, depending on whether they inhibit the anodic, cathodic or both electrochemical reactions.

## 2.8.Vapor-Phase Inhibitors (VPI)

The process of vapor-phase inhibition involves two steps: transport of inhibitor to the metal surface and interaction of inhibitor on the surface. AVPI may first dissociate and then vaporize. Example: dicyclohexylamine.

## 2.9.Anodic Inhibitors

Anodic inhibitors are usually used in near-neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides, or salts, are formed. Anodic inhibitors are often called passivating inhibitors.

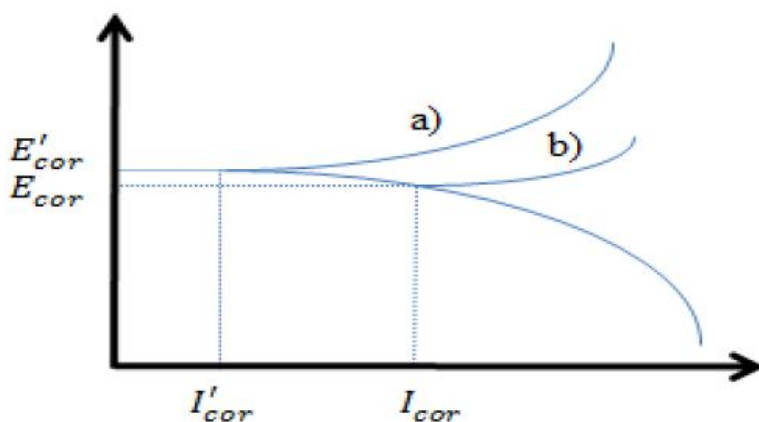
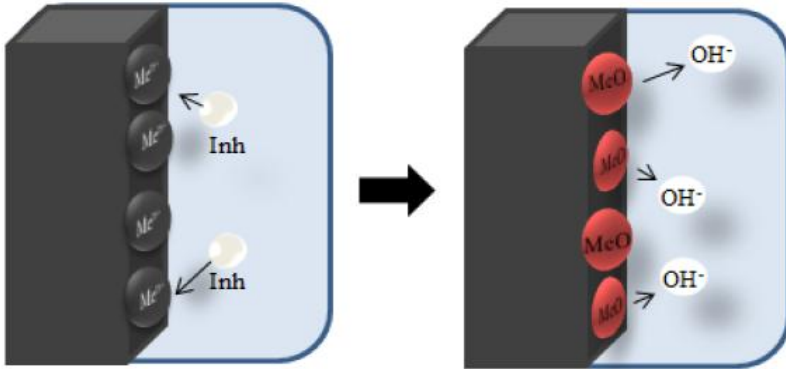


Fig. 9. Mechanism of Anodic Inhibitor

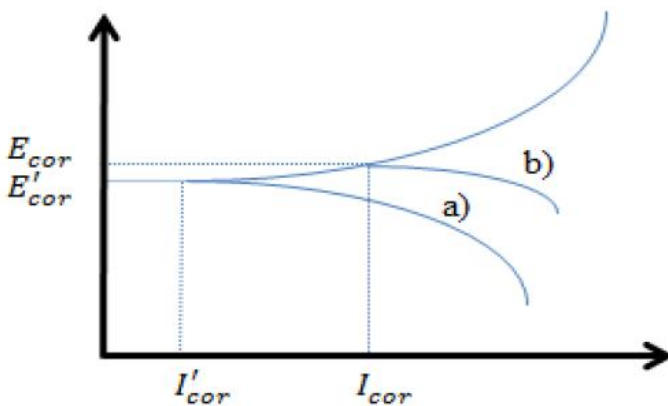
The mechanism of anodic inhibition can be explained using the polarization diagram of an active passive metal. In the absence of inhibitors, the metal corrodes in the active state at a rate corresponding to point. As the concentration of inhibitor is increased, the corrosion rate also decreases until a critical concentration and a critical corrosion rate (*Fig. 10*) are reached.



**Fig. 10.** Anodic aspects of Corrosion Inhibition

## 2.10. Cathodic Inhibitors

Cathodic inhibitors control corrosion by either decreasing the reduction rate (cathodic poisons example; sulfides and selenides) or by precipitating selectively on the cathodic areas (cathodic precipitators Examples arsenic, bismuth, and antimony).



**Fig.11.** Mechanism of Cathodic Inhibitor

The effect of a cathodic inhibitor on the polarization curves is shown in *Fig. 12*. In

this case, the slope of the anodic polarization curve is unaffected, but the slope of the cathodic polarization curve is changed [49-50].

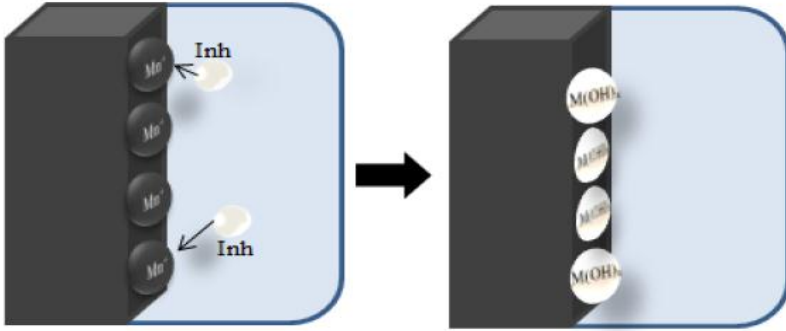


Fig. 12. Cathodic aspects of Corrosion Inhibition

## 2.11. Mixed Inhibitors

About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film formation [51-56].

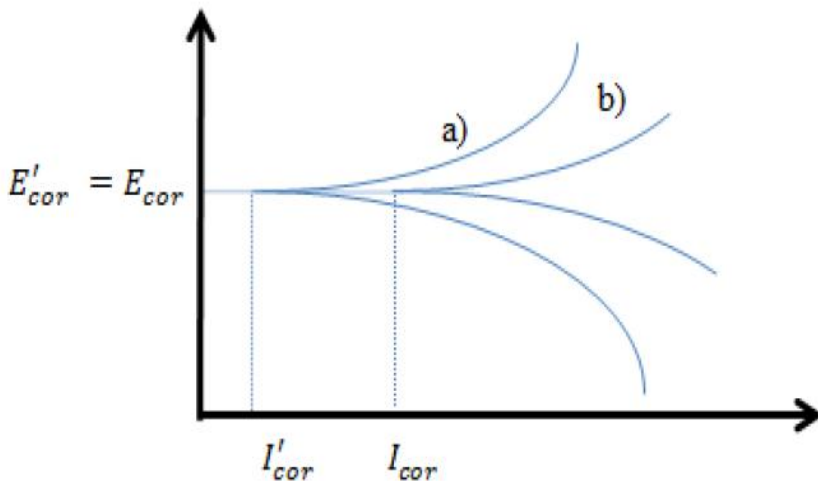
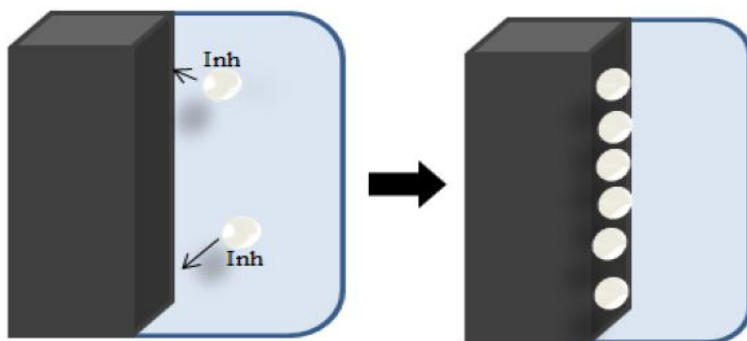


Fig. 13. Mechanism of Mixed Inhibitor



**Fig. 14.** Mixed aspects of Corrosion Inhibition

## 2.12. Adsorption Studies

The material in the adsorbed state is called the *adsorbate*. Adsorption is the enrichment (positive adsorption) or depletion (negative adsorption) of one or more components (or both of the bulk phases and capable of being adsorbed) of the phases forming the interface. It is said to form a spread layer (often spread monolayer when the layer is known to be only one molecule in thickness). The adsorption theory of protective activity has been proposed by most workers, which says that inhibitors are absorbed (the term adsorption may also be used to denote the process) on the metal surface forming a protective layer.

## 2.13. Types of Adsorption

The adsorption was considered either as Physical or Chemical adsorption.

### 2.13.1. Physisorption

Physisorption (or physical adsorption) is an adsorption in which the forces involved are intermolecular forces (Vander Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term Vander Waals adsorption is synonymous with physical adsorption, but its use is not recommended.

### 2.13.2. Chemisorptions

Chemisorptions (or chemical adsorption) is an adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. No absolutely sharp distinction can be made and intermediate cases exist. For example, adsorption involving strong hydrogen bonds or weak charge transfer.

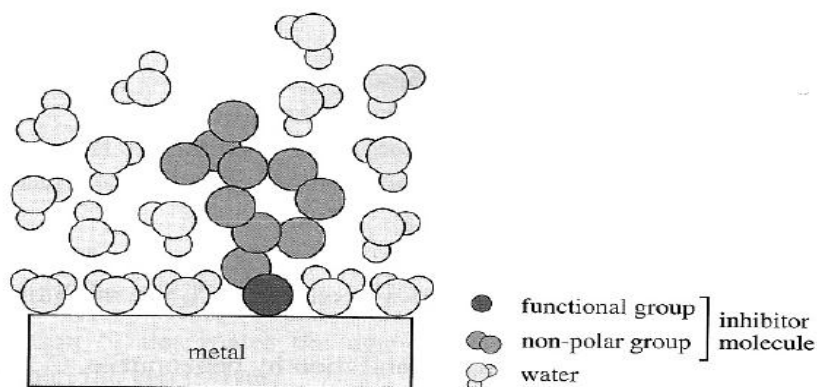


**Table 1.** Difference between Chemical and Physical Adsorption

<b>Physisorption</b>	<b>Chemisorption</b>
Forces of attraction are Vander Waals' forces	Forces of attraction are chemical bondforces
Low enthalpy of adsorption (20-40) KJ/mole	High enthalpy of adsorption (200-400) KJ/mole
This process is observed under conditions of low temperature	This process takes place at high temperatures
Not specific	Highly specific
Multi-molecular layers may be formed	Generally, monomolecular layer is formed
This process is reversible	This process is irreversible

## 2.14. Adsorption from Liquid Mixtures

Adsorption from liquid mixtures is said to have occurred only when there is a difference between the relative composition of the liquid in the interfacial layer and that in the adjoining bulk phase(s) and observable phenomena results from this difference. For liquids, accumulation (positive adsorption) of one or several components is generally accompanied by depletion of the other(s) in the interfacial layer which is smaller than the adjoining bulk liquid. Negative adsorption may occur also in the case of adsorption from highly compressed gas mixtures. For liquid/liquid interfaces an arbitrary unsymmetrical nomenclature may not be appropriate [57].

**Fig.15.** Mechanism of Adsorption

## 2.15. Adsorption isotherm

In this section, different adsorption isotherms are discussed. Isotherms describe adsorption using the relationship between the amounts of adsorbate (inhibitor molecules) which is adsorbed on the adsorbent (surface of mild steel). The adsorption isotherms explored are the **Langmuir isotherm, Hasley, Freundlich, Pearson, Bockris-swinkless, De Boer, Hills El-Awardy, Dhor-Flory-Huggins, Temkin isotherm, Flory-Huggins (FH) isotherm** and **Frumkin isotherm**. From the suitable plot, the free energy of adsorption of the organic inhibitor can be obtained [58-61].

**Table 2.** Various isotherms and the corresponding equation

S.No	Adsorption	Plots
1	Temkin Isotherm	$\theta$ versus $\log C$
2	Frumkin Isotherm	$\log C$ versus $\theta$
3	Langmuir isotherm	$C/\theta$ versus $C$
4	Flory-Huggins Isotherm	$\log (\theta/C)$ versus $\log (1 - \theta)$
5	Freundluich isotherm	$\log (\theta/C)$ versus $\theta$

## 2.16. Gibbs Free Energy

The equilibrium adsorption constant (K) is determined from the adsorption isotherm and can be used to find the standard Gibbs free energy of adsorption using

$$\Delta G_{\text{ads}} = -2.303 RT \log (55.5 K)$$

Where T is the temperature in Kelvins and R is the universal gas constant.

## 2.17. Industrial applications of corrosion inhibitors

1. Petroleum Production
2. Internal Corrosion of Steel Pipelines
3. Water
4. Automobile
5. Paint

## 2.18. Corrosion behaviour of mild steel in different selective media

1. Acidic environment included HCl, H<sub>2</sub>SO<sub>4</sub>
2. Sea Water environment
3. Base medium

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## Chapter 3

# Review of Literature

### 3.1. Background of review

This chapter focuses on **research** and **collection of data** from various sources such as **journals, books, websites, conferences, thesis, seminar and others** should be reviewed whether it is appropriate before making references [1].

The study of **organic, inorganic, polymer, oil, gum, coating, coordination complex, industry and bakery waste, amino acid, protein, hetero cyclic compounds** as inhibitor for corrosion of metal and alloys specifically, mild steel in acidic media are reviewed [2-10]. The responsibility of an inhibitor is to form a barrier of one or a number of molecular layers against acid attack. Also review is the usage of plant materials for corrosion of metals such as **carbon, aluminium, copper, zinc, and alloys namely stainless steel and mild steel**. The *reviewed* (research) work carried out is presented below.

### 3.2. Inorganic Inhibitor

A number of inorganic elements (minerals) are essential for the growth of living things present in **almost all foodstuffs**. **Chromates, phosphate, selenium, tellurium, sulphur and arsenic, antimony** is among the most common substances used as inhibitors or incorporated in anticorrosive pre-treatments of aluminium alloys. Recently it is shown that addition of heavy metal ions such as **lead, manganese, cadmium and lanthanide salts** exhibit excellent anti-corrosive properties [11].

**Arena et al** [12] also studied the inhibition of localized corrosion process in 3.56 g wt 5% NaCl for tin (Sn) after the addition of cerium solution. The optimum concentration among those which were studied was 1000 ppm  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  with 96% efficiency of protection.

### 3.3. Organic Inhibitor

**Ambrish Singh, Eno E. Ebenso and M.A Quraishi** [13] had reported *Andrographis paniculata*, *Strychnos nuxvomica* and *Moringa oleifera* extracts showed inhibition efficiency above 98 %. The extracts of *Andrographis paniculata*, *Strychnos nuxvomica* and *Moringa oleifera* were found to be mixed type of inhibitors.

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P.R. Sivakumar et. al, *Green Corrosion Inhibitors: Reviews and Applications*,  
<https://doi.org/10.34256/iorip1973>

### 3.4. Polymer compounds

Several researches have been indicated that some polymers can be used as corrosion inhibitors because, through their functional group, they form complexes with metal ions and on the metal surfaces. For example gum arabic, were reported by **Umoren et al** [14] potential corrosion inhibitors for aluminum corrosion by gum arabic was attributed to the presence of arabinogalactan, oligosaccharides, polysaccharides, and glucoproteins since these compounds contain oxygen and nitrogen atoms which are the centers of adsorption.

**Khairou and Sayed** [15] have evaluated the inhibiting action of polyacrylamide, PVA, sodium polyacrylate, poly (ethylene glycol), pectin, and carboxymethyl cellulose on the corrosion of Cd in 0.5 M HCl solution.

### 3.5. Aluminium and its Alloys

**Noor** [16] has used an aqueous extract of Hibiscus sabdariffa leaves for inhibiting the corrosion of aluminium in alkaline solutions. Electrochemical measurements revealed that AEHSL acts as mixed-type inhibitor with an inhibition category that belongs to geometric blocking.

Corrosion behaviour of aluminium in the presence of an aqueous extract of hibiscus rosa-sinensis has been evaluated by **Rajendran et al** [17]. The formulation consisting of 8ml flower extract (FE) and 50 ppm of  $Zn^{2+}$  had 98 % inhibition efficiency.

**Abdallah et al** [18] investigated that the corrosion inhibition of non - toxic plant extract of Hibiscus teterifa on the corrosion of chill cast Al-Zn-Mg alloy in 0.5 Molar solution of NaOH was studied using weight loss method.

SEM-EDS characterization of natural products on corrosion inhibition of Al-Mg-Si alloy has been studied by **R. Rosliza and S. Izman** [19]. The corrosion protections and the mechanism of corrosion inhibitions of natural products for an Al-Mg-Si alloy in seawater were investigated at room temperature.

### 3.6. Copper

As early as 1967, **Cotton et al** [20] studied corrosion inhibition of Cu by benzotriazole and analogous compounds where one or two of the N atoms of benzotriazole are substituted by C or the labile H atom is replaced by a  $CH_3$  group, i.e., indazole, benzimidazole, indole and methyl benzotriazole. Generally 5-membered heterocyclics, imidazole, 1, 2, 4-triazole, and pyrazole and their derivatives showed little inhibitive effect.

**Walker** [21] reviewed the use of BTAH as a corrosion inhibitor and the theory of its mode of protection of Cu in aqueous systems. BTAH is a good inhibitor for Cu and Brass when added to many neutral and alkaline solutions and acts as a weak buffer.

**Walker** [22] studied the corrosion of Cu in acidic, neutral and alkaline solutions containing triazole, benzotriazole and naphthotriazole. Triazole was a poor inhibitor, while benzotriazole and naphthotriazole were better. Naphthotriazole gave the best protection.

### 3.7. Zinc metal

The inhibitive action of water extract of naturally occurring **Elettaria cardamomum** [23] plant against the corrosion of zinc in 1 M HCl solution was investigated by using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. EC extract showed high inhibitory effect due to its adsorption on the metallic surface through its electron rich functional groups. The adsorption of the investigated water extract on a zinc surface follows Langmuir's adsorption isotherm.

### 3.8. Carbon steel

**Johnsirani et al** [24] studied that the inhibition efficiency of an aqueous extract of the (curcuma longa l) plant material rhizome powder has been used as a corrosion inhibitor in controlling corrosion of carbon steel in sea water by weight loss study. The result showed that 93 % IE was provided.

**A. S. Fouda et al** [25] have studied the aqueous extract of Propolis as corrosion inhibitor for carbon steel in aqueous solutions was investigated by weight loss and electrochemical measurements. Potentiodynamic polarization curves revealed that this extract acts as a mixed type inhibitor and the inhibition efficiency of up to 92 % can be obtained.

**Denni Asra Awizar et al** [26] have studied the Nano silicate extraction from rice husk ash as green corrosion inhibitor. Silica was extracted from rice husk ash (RHA) and used to produce corrosion inhibitor for carbon steel. The corrosion inhibition efficiency of nano silicate attained 99 % as measured using the potentiodynamic polarization and weight loss measurements after 6 hrs exposure.

### 3.9. Different Metals

**Saleh and his co-workers** [27] carried out an intensive study on the inhibition effect of aqueous extract of *Opuntia ficusindica*, Aloe Vera leaves and peels of orange, mango and pomegranate fruits on the corrosion of steel, aluminium, zinc and copper in both HCl and H<sub>2</sub>SO<sub>4</sub> acid solutions using gravimetric and polarization measurement techniques.

Corrosion control by water-soluble extracts from leaves of economic plants has been studied by **Rehan** [28]. Water extracts from leaves of date palm, phoenix dactylifera, henna, Lawsoniainerims and corn, Zea mays, were tested as corrosion inhibitors for steel, aluminium, copper and brass in acid chloride and sodium hydroxide solutions using weight loss, solution analysis and potential measurements. The inhibitive action of the extract of *Ficus nitida* leaves toward general and pitting



corrosion of C-steel, nickel and zinc in different aqueous media was investigated by **El-Etre and El-Tantawy** [29] using weight loss, potentiostatic and potentiodynamic polarization techniques. They found that the presence of ficus extract in the corrosive media (acidic, neutral or alkaline) decreases the corrosion rates of the three tested metals.

The aqueous extract of the leaves of henna (*lawsonia*) is tested as corrosion inhibitor of C-steel, nickel and zinc in acidic, neutral and alkaline solutions, using the polarization technique was studied by **El-Etre and El-Tantawy** [30]. The extract acts as a mixed inhibitor.

**Yee** [31] determined the inhibitive effects of organic compounds namely; honey and *rosmarinus officinalis* L on four different metals-aluminium, copper, iron, and zinc each polarized in two different solutions, that is, sodium chloride and sodium sulphate. The experimental approach employed potentiodynamic polarization method. Rosemary extracts showed some cathodic inhibition when the metal was polarized in sodium chloride solution.

### 3.10. Stainless Steel

The inhibitive effect of the extract of khillah (*Ammivisnaga*) seeds, on the corrosion of stainless steel in HCl solution was determined by **El-Etre** [32] using weight loss measurements as well as potentiostatic technique. The inhibitive effect of khillah extract was discussed on the basis of adsorption of its components on the metal surface.

**N. A. Abdel Ghanyl et al** [33] have investigated the inhibitive effect of some amino acids on the corrosion behaviour of 316 L stainless steel in sulphuric acid solution. Glycine, Leucine and Valine inhibit the corrosion process, but Arginine accelerates the corrosion phenomenon. Glycine has the highest inhibition efficiency, its efficiency increases with increasing the concentration to attain 84.2 % at 0.1 M.

### 3.11. Mild Steel

**R. Saratha and V.G. Vasudha** [34] studied the efficiency of acid extract of dry *Nyctanthes arbor-tristis* leaves as corrosion inhibitor for mild steel in 1 N H<sub>2</sub>SO<sub>4</sub> solution. The leaves extract showed good corrosion inhibition type inhibiting both cathodic as well as anodic reactions.

**Oguzie** [35] studied that the corrosion inhibition of mild steel in 1 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> by leaf extracts of *Occimum viridis* (OV) using the gasometric technique. Synergistic effects increased the inhibition efficiency in the presence of halide additives namely KCl, KBr, KI. Comparative analysis of the inhibitor adsorption behaviour in 1 M HCl and 1M H<sub>2</sub>SO<sub>4</sub> as well as the effect of halide (KCl, KBr, KI) additives were also studied.

**Gunavathy et al** [36] investigated the inhibition efficiency of acid extract of dry *musa acuminata* bract as corrosion inhibitor for mild steel in 1 N HCl. Potentiodynamic polarization curves revealed that inhibitor performed as a mixed type of inhibitor.

**C.B. Pradeepkumar et al** [37] studied the inhibition effect of *plumeriarubra* extracts on the corrosion of mild steel in industrial water medium by mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. Potentiodynamic polarization studies revealed that PR extracts act as a mixed type inhibitor.

### 3.12. Recent study

Recently, studies on the use of some researchers to drugs are heterocyclic; hence, they have great potentials of competing with plant extracts. The field of extracting eco-friendly corrosion inhibitors has been promising and effective. It has been observed that the natural inhibitors could potentially serve as effective substitute for the chemical inhibitors, since some studies showed that their inhibition efficiency is significantly better than that of synthetic inhibitors. Modern studies have tested different extracts for corrosion inhibition applications. The examples are numerous such as coffee beans and chickpeas [38], *Chenopodium Ambrosioides* [39], *Garcinia Kola* [40], *Musa Acuminata* [41], *Cannabis* [42], Mexican *Argemone* [43], *Lavandula Dentata* [44], *Aframomum Melegueta* [45], *Osmanthus Fragan* [46], *Neolamarckia Cadamba* (Bark, Leaves) [47], *Murraya Koenigii* [48], *Coptis Chinensis* [49], *Hibiscus Sabdariffa* [50], *Artemisia Oil* [51], *Musa Species* [52], *Hibiscus Rosa-Sinensis* Linn [53], *Opuntia-Ficus-Indica* (Nopal) [54], Tobacco [55], *Curcuma Longa* [56], Onion Juice [57], *Vernonia Amygdalina* [58], Mangrove Tannin [59], *Punica Granatum* [60] used as green inhibitor.

Available literature has shown that the naturally occurring plant extract such as Phoenix *Dactylifera* Fruit Juice [61], Rain Water Containing Garlic [62], Olive Mill Waste Water [63], *Morinda Tinctoria* [64], Creosote Bush (*Larrea Tridentata*) [65], *Prosopis Laevigata* [66], *Lavandula Stoeckas* [67], Caffeine [68], Purine and Adenine [69], Vitamin B1 [70], Vitamin C [71], Pteroyl L Glutamic acid (Vitamin M) [72], Citric acid [73], Benzoic Acid [74], Peptin [75], Vitamin B1, B6 and C [76], Lignin Terpolymer [77], Cassava Starches [78], Carrageenan [79], Chitosan [80], *Cassia Fistula* [81], *Bougainvillea Spectabilis* [82], *Mirabilis Jalapa* [83], *Amodiaquine* [84], *Benincasa Hispida* [85], *Dodonaea Viscosa* [86], *Cassia Alata* [87], *Cocos Nucifera* [88], *Frontiers Ofeco* [89], *Cocos Nucifera* [90], *Cocos Nucifera-Coconut Palm-Petiole* [91], Polyvinyl alcohol-Anthranilic acid composite [92], Ortho Chlophenyl 2-Imidazoline [93], 3,4,5-Trimethoxyphenyl-2-Imidazolines [94], *Cyamopsis Tetragonoloba* [95], *Borassus Flabellifer* Linn [96], Bakery Waste [97], Dicycloimine Hydrochloride [98], Poly (Vinyl Alcohol Aniline) water soluble composite [99], Polyvinyl alcohol-Sulphanilic acid water soluble composite [100], *Ervatamia Coronaria* [101], *Cocos Nucifera* [102], Poly (Vinyl Pyrrolidone-Aniline) [103], Poly Ethylene Glycol Aniline Composite [104], Carbon prepared from agro waste in the removal of dye [105], *Myristica Frangans* [106], Dyeing with a natural dye on silk-annatto seeds dye [107], *Abrus Precatorus* [108], Chloro Quine Phosphate [109], *Amodiaquine* [110], *Phaseolus Aureus* [111], Poultry waste [112], Aquatic waste- fish scales [113], *Ficus Benghalensis* [114] were used as corrosion inhibitor for the protection of metal surface.

The various plant extract exhibited excellent corrosion inhibitors which include, *Cinnamomum Zeylancium* [115], *Elettaria Cardamomum* [116], *Embllica Officinalis* [117], *Eucalyptus Globulus* [118], *Paniala* (*Flacourtia Jangomas*) [119], *Garcinia Kola* [120], *Glycine max* oil [121], *Brugmansia Suaveolens* [122], *Cassia Roxburghii* [123], *Andrographis Paniculata* [124], *Strychnous Nuxvomica* [125], *Moringa Oleifera* [126], *Nyctanthes Abortristis* [127], *Phyllanthus Amarum* [128], *Acacia* trees [129], *Aloes* extract [130], *Polyalthia Longifloia* of hydrochloric acid [131], *Polyalthia Longifloia* of sulphuric acid [132], *Honey* [133], *Cassia Acutifolia* [134], *Ziziphus Spina-Christi* [135], *Lupines Termis* [136], *Brassica Nigra* [137], *Trigonella Foenum-Graecum* [138], *Jatropha Curcas* [139], *Jatropha Curcas Oil* [140], *Allium Sativum* [141], *Juglans Regia* [142], *Pogostemon Cablin* [143], *Vitex Negundo* [144], *Tamarind* [145], *Tea Leaves* [146], *Pomegranate Juice and Peel* [147], *Terminalia Bellerica* [148], *Eucalyptus Oil* [149], *Gum Exudate* [150], *Musa Sapientum Peel* [151], *Auforpio Turkiale* [152], *Azydracta Indica* [153], *Mango/Orange Peels* [154], *Argemome Mexicana* [155] act as eco-friendly corrosion inhibitors.

Also, the extract of *Garlic* [156], *Carrot* [157], *Castor Seed* [158],  $\text{CeCl}_3$  and *Mercapto benzothiazole* [159], *Vanillin* [160], *Rosmarinus Officinalis*-*Netural Phenol* [161], *Sulphates/Molybdates* and *Dicharomates* as passivators [162], *Amino and Polyaminoacids-Aspartic Acid* [163], *Pyridine* and its selected derivatives [164], *Rutin and Quercetin* [165], *Polybutadieonic Acid* [166], *Saccharides-Mannose and Fructose* [167], *Vernonia Amygdalina* [168], *Prosopis-Cineraria* [169], *Tannin Beetroot* [170], *Saponin* [171], *Acacia Concianna* [172], *Opuntia* [173], *Metal Chelates of Citric Acid* [174], *Black Radish* [175], *Garcinia Mangostana* [176], *Ipomea Involcrata* [177], *Soya Bean* [178], *Terminalia Catappa* [179], *Caffeic Acid* [180], *Gossypium Hirsutum* [181], *Carmine and fast green dye* [182], *Aniline and its derivatives* [183], *Cyperuc Esculentus L. Oil* [184], *Dacroydes Edulis* [185] were also to be used as corrosion inhibitors.

The use of natural products as corrosion inhibitors are *Telfaria Occidentalis* [186], *Occimum Basilicum* [187], *Anacardium Occidentale* [188], *Zenthoxylum Alatum* [189], *Mimosa Tannin* [190], *Prunus Cerasus* [191], *Menthe Pulegium* [192], *Magnifera Indica* [193], *Carica Papaya* [194], *Datura Metel* [195], *Natural Artemisia Oil* [196], *Jojoba Oil* [197], *Khillah Extract* [198], *Eclipta Alba* [199], *Eggplant Peel* [200], *Tectona Grandis* [201], *Nettle Extract* [202], *Withania Somnifera* [203], *Wrightiatinctoria* [204], *Cleroden drumplomidis* [205], *Ipomoeatriloba* [206], *Alpha Amlose* [207], *Plumeria Rubra* [208], *Lavandula Stoeches* [209], *Lebbeck* [210], *Albizia Lebbeck* [211], *Raphia Hookeri* [212], *Pelto-Phorum Pterocarpum* [213], *Abutilon Indium* [214], *Amrican Marigold* [215], *Tegetes Erecta* [216], *Dimethylaminobenzylidene Acetone* [217], *Techoma Stans* [218], *Coffea Arabica* [219], *Crossandra Infundibuliformis* [220], *Vitis Vinifera* [221], *Ricinus Communis* [222], *Citrus Aurantifolia* [223], *Biodiesel-Oil Gloom* [224], *Uranyl Hydrazinesulfinates and Sulphite Hydrazinates* [225], *Solaum Verbascifolium* [226], *Michelia Champaca* [227], *Paisam Sativum* [228], *Pongamia Pinnata Biodisel-Diesel Blends* [229], *Jatropha Oil* [230], *Long Chain Amines* [231], *Tegetes Errecta* [232], *Solanum Elaegnifolium* [233], *Lycopersicon Esculentum* [234], *Sapodilla* [235],

Macrotyloma Niflorum [236], 4-Hydroxy Coumarin [237], Pisonia Grandis [238], Manihot Esculentum [239], Methylene Blue [240], Sida Rhombifolia [241], Nerium Oleander [242], Artocarpus Hetrophyllis [243], Nerium Indicum [244], Erythrina Suberosa [245], Calenduler Officinals [246], Autaborrys Odorcitissimus [247], Hexadecyl Amine and Octa Decyl Amine [248], Trichodesma Indium Linn R.Br [249], Juniperus [250], Lawsonia Extract (Henna) [251], Natural Amino Acid [252] act as excellent corrosion inhibitors.

The inhibitive action of plant extract of naturally occurring Curcumin Dye [253], Metformin [254], Ocimum Tenuiflorum Syn [255], Chromolaena Odarata L [256], Ananas Sativum [257], Hibiscus Teterifa [258], Azadirachia Plants [259], Ambrosia Maritime L [260], Ficus Religeosa [261], Rosemary [262], Ginseng [263], Nelumbo Nucifera [264], Oxystelma Esculentum [265], Policourea Guianensis [266], Nypa Fruticans Wurmb [267], Brassica-Junceae-Cruciferae [268], Prosopis Juliflora [269], Mangifera Indica [270], Piper Nigrum L [271], Ocimum Sanctum Linn [272], Parthenium Hysterophorus [273], Alfa Alfa [274], Adenanthera Pavonina [275], Phaseolus Lunatus [276], Sesbania Grandiflora [277], Eugenia Caryophyllata [278], Zea Mays [279], Cashew Nut Shell Liquid [280], Acacia Seyal VarSeyal [281], Red Onion Skin [282], Calotropis Procera and Calotropis Gigantea [283], Propolis [284], Propolis Laevigata [285], Swertia Aungustifolia [286], Pachylobus Edulis [287], Sansevieria Trifasciata [288], Psidium Guajava [289], Rice Husk Ash [290], Rosmarinus Officinalis L [291], Salvia Judica [292], Salvia Officinalis [293], Santalum Paniculatum [294], Senna Auriculata [295], Sesamum Indium [296], Solanum Nigrum [297], Solanum Torvum [298], Solanum Tuberosum [299], Chelidonium Majus [300], Lycium Shawii [301], Teucrium Oliverianum [302] have been shown to be effective corrosion inhibitor for metal in acid environment.

To prevent the corrosion of metal in acid medium, inhibitor such as Ochradenus Baccatus [303], Anvillea Garcinii [304], Cassia Italic [305], Artemisia Sieberi [306], Carthamus Tinctorius [307], Tripleurospermum Auriculatum [308], Rhizophora Racemosa [309], Fenugreek [310], Olea Europaea [311], Cotula Cinerea, Retama Retam and Artemisia Herba [312], Rauvolfia Serpentine [313], Lupinus Albus [314], Nauclea Latifolia [315], Ammi Visnaga [316], Embilica Uflicianalis, Terminalia Chebula and Terminalia Bellirica [317], Mentha Pulegium [318], Zanthoxylum Alatum [319], Thyme, Coriander, Hibiscus, Anis, Black Cumin and Garden Cress [320], Centella Asiatica [321], Combretum Bracteosum [322], Banana Peels [323], Medicago Sativa [324], Oxandra Asbeckii [325], Aegle Marmelos [326], Anna Squamosal [327], Heinsia Crinite [328], Syzygium Cumini [329], Piper Longum [330], Citrus Aurantium [331], Bacopa Monnieri [332], Terminalia Arujna [333], Delonix Regia [334], Piper Guinensis [335], Poinciana Pulcherrima [336], Cassia Occidentalis [337], Datura Stramonium [338], Acorus Calamus [339], Ajowan Seeds [340], Allium Cepa [341], Anacyclus Pyrethrum L [342], Aningeria Robusta [343], Argemone Mexicana [344], Asafoetia [345], Ficus Virens [346], Ocimum Basilicum [347], Caparis Deciduas [348], Asparagus Racemosus [349], Azadirachta Indica [350], Trachyspermum Coptium [351], Camellia Sinensis [352], Cassia Auriculata [353] and many oils extracted from different parts of plants [354]. Some researchers have used the inhibitors extracted from both plant leaves and fruits [355]. Many of

these natural substances proved their ability to serve as corrosion inhibitors for the corrosion of different types of metals.

The diverse set of research summarized and discussed indicates ongoing intensive research being carried out to tackle the problem of metal corrosion. Although it is realized that the preceding discussion are not infinitive the literature provided in this review reveal concerted efforts directed at the search for more green inhibitors as alternatives to the fossil origin toxic corrosion inhibitor. One main drawback is even with the growing interest in the search for green inhibitor the amount of research being undertaken is not significant compared to the effect of corrosion to the economy given the current consumption of mild steel. However, regardless of the drawback mentioned, this review has shown that the use of the green corrosion inhibitors is the way forward in the search for safer and environmentally secure protection against metal corrosion. The use of green inhibitors also has been the potential of being cost effective due to the renewability of its resources.

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## Chapter 4

# Materials and Methods

### 4.1. Experimental Work

This chapter mainly deals with the methodology adopted for the plant extractions (**aqueous and alcoholic**) and evaluation of corrosion inhibition of plant extracts as green inhibitor on mild steel in 1N HCl medium.

### 4.2. Objectives

The present research is undertaken to:

1. Study of efficacy of acid extract of the selected plants as corrosion inhibitor for mild steel in 1N HCl by weight loss and electrochemical methods and fit a suitable adsorption isotherm for the thermostat experimental data.
2. To compare the results obtained by various methods.
3. To determine which part of the plants, provide better inhibition.
4. To analyse the surface of substrate by FTIR and SEM techniques.

### 4.3. Mild steel specimens

Weight loss and electrochemical experiments were conducted on mild steel specimens of dimensions 4 cm X 2 cm X 0.1 cm and having the area of 1 cm<sup>2</sup> for 24 hours having the composition used throughout the present investigation.

**Table 3.** Composition of mild steel

Elements	C	Mn	Si	P	S	Cr	Mo	Ni	Cu	Fe
Wt %	0.030	0.169	0.015	0.031	0.029	0.029	0.016	0.030	0.017	Bal.

### 4.4. Preparation of inhibitor

#### *Aqueous extract preparation*

The plants are organic in nature and are much used as a **medicinal plant in ayurvedic medicine, mainly; it helps against disease of the digestive tract and fever**. The leaves, flower, (roots), stem, tubers, fruits, (seeds) of the medicinal plants **AL, SS, HI, ML, GSL and PD** were taken and cut into small pieces, and dried in

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<https://doi.org/10.34256/ioriip1974>

room temperature and ground well into powder. 150 g of the powder from each was refluxed in 500 ml distilled water and kept overnight. The refluxed solution was then filtered carefully; the filtrate volume was made up to 1000 ml using double distilled water which was the stock solution. Various concentrations of the plant extracts were prepared by dissolving the known quantity of the resultant powder in acid media. The concentrations of all additives were expressed in v/v. Thus the concentration (5, 10, 15, 20 v/v) was prepared by diluting 5 ml, 10 ml, 15 ml 20 ml of plant extract with 95 ml, 90 ml, 85 ml, 80 ml of HCl acid solution [1-6].

### ***Alcoholic extract preparation***

The **leaves, flower, (roots), stem, tubers, fruits, (seeds, seeds peels)** of the medicinal plants ***AL, SS, HI, ML, GSL***, and ***PD*** were taken and cut into small pieces, and dried in room temperature and ground well into powder. 150 g of the powder from each was refluxed with alcohol in soxlet apparatus for 24 hours kept overnight. The refluxed solution was filtered carefully and the filtrates were heated on water bath to evaporate fully the moisture or impurities content and the excess of alcohol was removed by distillation method. The resulting residue was dark green in colour and had a pleasant smell. The crude was boiled with little quantity of activated charcoal to remove impurities; the pure plant extract after drying completely was collected and stored in a desiccator. The residue was used in preparing different concentration of the extract in HCl acid.

## **4.5. Reason for selection of acid medium**

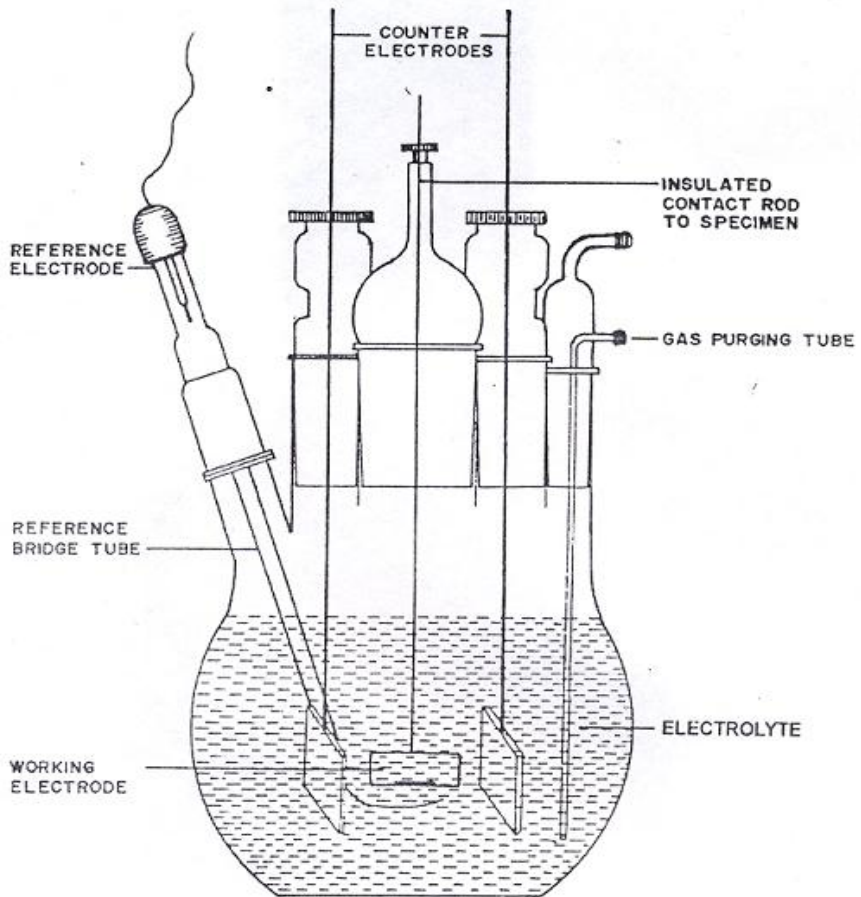
- Corrosion in acidic medium is more commonly encountered in industry than neutral or alkaline medium.
- Due to tremendous increase in industrial activities, HCl are increasingly used in acidic pickling and descaling. So, our experiments are performed in 1N HCl.

## **4.6. Reagents used**

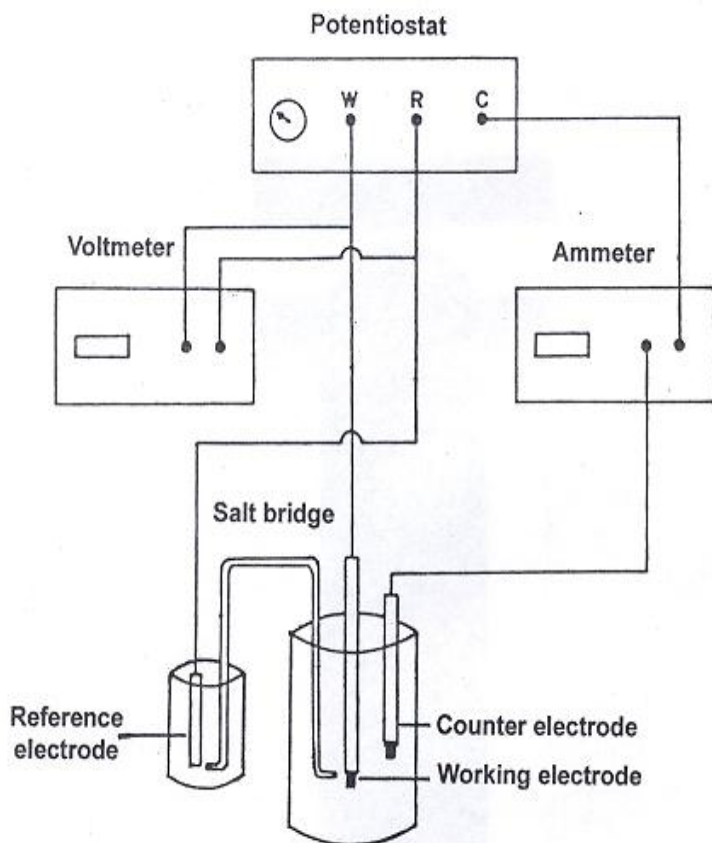
**Acids:** For this study Analar grade Hydrochloric acid was used and for the preparation of 1N HCl double distilled water was used.

## **4.7. Equipment**

- ❖ Electronic balance-SHIMADZU BY-220 S
- ❖ Bruker alpha 8400 S FT-IR spectrophotometer
- ❖ Electrochemical work station CHI model 660 E Amp Booster & CHI 608 D
- ❖ JEOL computer-SEM



**Fig. 16** Electrochemical cell assembly



**Fig. 17** Schematic representation of the circuit



## 4.8. Working plan

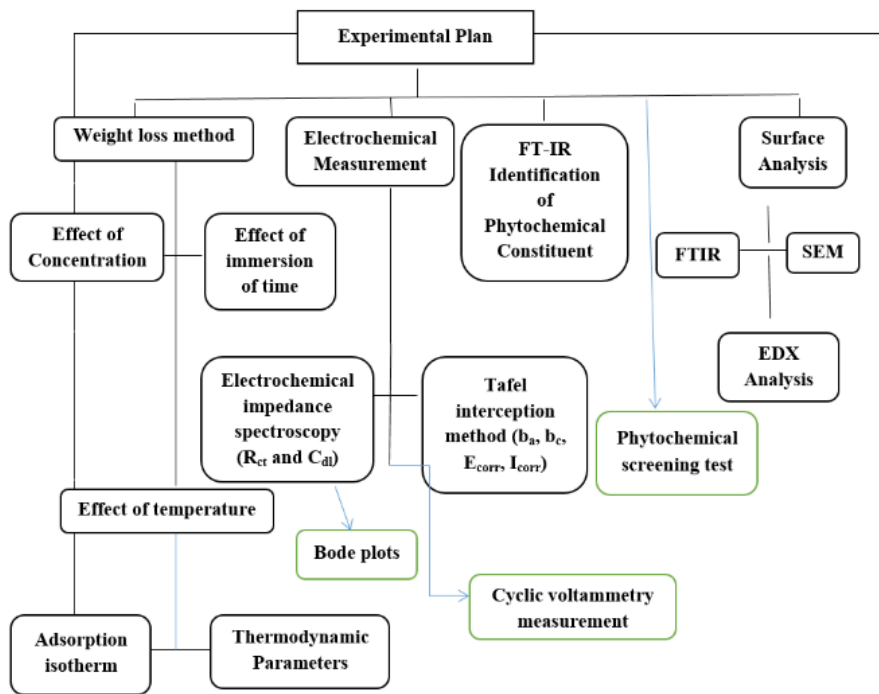


Fig. 18 Work plan for various methods

## METHODS

### 4.9. Weight loss method

Weight loss analysis is one of the basic, easiest and frequently used methods and classical way to determining corrosion inhibition and corrosion rate of mild steel. Coupons were completely immersed vertically in 250 ml of the test solution with and without inhibitor for 24 hours. The experiment was carried out at various immersion period (1, 3, 5, 7, 12 hrs and 3 days) and corrosion inhibition studies were also carried out at various temperature ranges at 303-323 K. From the mass loss measurements, the corrosion rate was calculated by using the following relationship:

$$CR \text{ (mmpy)} = \frac{K \times \text{Weight loss}}{D \times A \times t \text{ (in hours)}} \quad (1)$$

Where,  $K = 8.76 \times 10^4$  (constant),  $D$  is density in  $\text{gm/cm}^3$  (7.86),  $W$  is weight loss in grams and  $A$  is area in  $\text{cm}^2$ .

$$IE \% = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

Where,  $W_0$  and  $W_i$  are the weight loss with and without of the inhibitor.

#### 4.10. FT-IR spectra

FT-IR spectroscopy allows us to examine the molecular structure and confirmation of biological macro molecules because it measures the absorption energy, which produces an increase in the vibrational or rotational energy of atoms or groups of atoms within the molecules. FT-IR spectrum (KBr pellets) of the surface film was recorded using Bruker alpha 8400 S spectrophotometer in the wave number range of 4000- 400  $\text{cm}^{-1}$ .

#### 4.11. Electrochemical studies

Electrochemical (Polarization and impedance) measurements were obtained using CHI 660 E Electrochemical workstation. An electrochemical cell with a three electrode cell set up was used. Mild steel ( $1\text{cm}^2$ ) was used as a working electrode; Pt electrode was used as counter electrode, and a saturated calomel electrode was used as reference electrode. The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers and washed with distilled water before usage. Prior to experiment the working electrode was immersed in the test solution for 20 minutes to reach open circuit potential (OCP). The anodic and cathodic polarization curves were obtained from -800 to -200 mV at a scan rate of 1  $\text{mVs}^{-1}$ . The percentage inhibition efficiency was calculated by using this equation:

$$IE \% = \frac{I_{\text{Corr}} - I_{*\text{Corr}}}{I_{\text{Corr}}} \times 100 \quad (3)$$

Where,  $I_{\text{corr}}$  and  $I_{*\text{corr}}$  are corrosion current without and with inhibitors.

Impedance spectroscopy is one of the most simple and consistent techniques and also used to study the characterization of electrode (surface) behavior in 1N HCl solution. AC signal with amplitude of 10 mV at OCP in the frequency range from 100 KHz to 10 MHz. The impedance parameters were obtained from Nyquist plots. The double layer capacitance ( $C_{dl}$ ) was determined using formula:

$$C_{dl} = \frac{1}{2\pi} f_{\text{max}} R_{ct} \quad (4)$$

Where,  $R_{ct}$  is charge transfer resistance, and  $C_{dl}$  is double layer capacitance.

The percentage inhibition efficiency (IE%) was calculated by using the following formula:

$$IE\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (5)$$

Where,  $R_{ct}$  and  $R_{ct}^0$  are the charge resistance values for inhibited and uninhibited solution.

#### 4.12. Surface Analysis

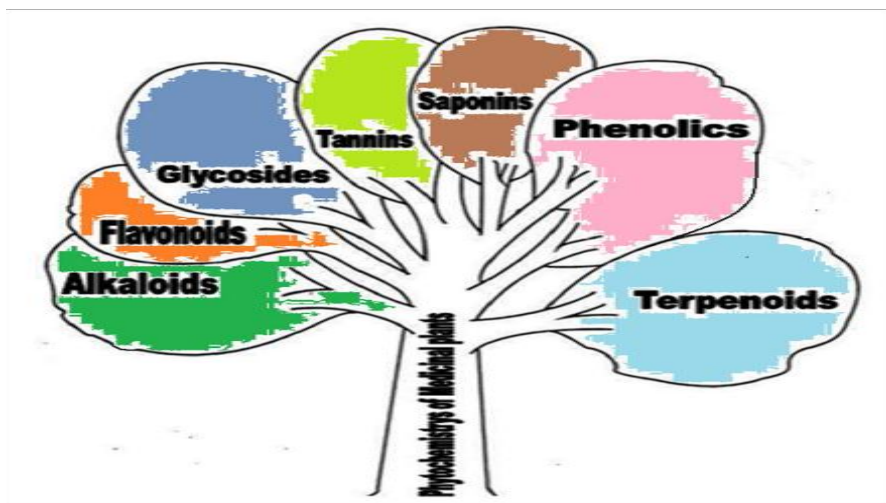
The mild steel specimens used for surface morphology examination were immersed in 100 ml of 1N HCl acid (blank solution) containing (optimum) various concentrations of green inhibitor for a period of one day. Then, they were removed, rinsed quickly with double distilled water, dried and examined for their surface morphology using scanning electron microscope.

#### 4.13. Cyclic Voltammetry Measurement

Cyclic voltammetry method was carried out with CHI-660 E Electrochemical analyzer. The experiments were carried out in conventional three electrode cell assembly as that for cyclic voltammetry. The plants extract was performed in acidic medium. The cyclic voltammograms (CVs) corresponding to 10 cycles of plant extract in 1 N HCl acid, during the sequential potential range between  $-0.4$  v to  $1.5$  v at a scan rate of  $10 \text{ mVs}^{-1}$ .

#### 4.14. Phytochemical Screening

Phytochemical screening was carried out on the aqueous and alcoholic extract freshly prepared according to the common Phytochemical method described earlier by **Harborne** [7]. The different chemical constituents were tested which included Alkaloids, Terpinoids, Sterols, Triterpenes, Anthraquinones and Flavonoids etc.



**Fig. 19** Various test for phytochemical screening test.

#### 4.15. Description of plants

In view of the advantages of green corrosion inhibitors we had explored the plant species belonging to various families. Our research on these families had resulted in the report of alkaloids and terpinoids as anti-corrosive agents. In continuation of our study on green corrosion inhibitors, few plants have been chosen in view of the reports of presence of heterocyclic constituents particularly alkaloids. Thus, the study is aimed at screening the chosen species of plants belonging to these few families for their anti-corrosion effects and the mechanism of action of these plant extracts by standard methods.

Literature survey of various plant sources belonging to *Gloriosa Superba* Linn, *Madhuca longifolia*, *Alangium lamarckii*, *Holoptelea integrifolia*, *Pithecellobium dulce* and *Schreabera swietenoids* were chosen for the study.

- i) *Madhuca longifolia* (ML)
- ii) *Gloriosa Superba* Linn (GSL)
- iii) *Alangium lamarckii* (AL)
- iv) *Holoptelea integrifolia* (HI)
- v) *Pithecellobium dulce* (PD)
- vi) *Schreabera swietenoids* (SS)

#### 4.16. *Madhuca Longifolia* (ML)

***Madhuca Longifolia*** (ML) is a tree found largely in the central and north Indian plains and forest. **Tamil name: *iluppai***. It is fast growing up to 20 m height. The seeds, flowers and wood are used for the care of the skin, to manufacture of soap or detergents, and as a vegetable butter. The saying “*aalai illaa oorukku iluppai poo charkkarai*” indicates when there is no cane sugar available; the flowers of this plants can be used as it is very sweet. Several part of the tree is used for various purposes including the bark, flowers for their medicinal properties.



#### 4.17. *Glorisa Superba* Linn (GSL)

The *Gloriosa Superba* Linn (GSL) is the state flower of Tamil Nadu. This species is the national flower of Zimbabwe. **Tamil name: *Chengkanthal***. In general this plant is common worldwide and used both as medicinal and poison. It is a fast growing plant up to 6 m long. It has been used in the treatment of snake bites, kidney problems, cancer, sexually transmitted diseases and many types of internal parasites. The plant can be



propagated sexually by seeds or vegetative by dividing the rhizomes. Both the fruit and the rhizome are harvested. Other uses of this plant include arrow poison in Nigeria and snake repellent in India.

#### 4.18. Pithecellobium Dulce (PD)

Pithecellobium Dulce (PD) is a species of flowering plants in the Fabaceae family. **Tamil name: Kodukkapuli.** That tree reaches a height of about 10 to 15 m. In Mexico it is eaten raw as an accompaniment to various meat dishes and used as a base for drink with sugar and water. The seeds are also refined to extract oil, which amount to 10 % of their weight. Barks extract also used against dysentery, chronic diarrhoea and tuberculosis. The ground seed is used to clean ulcers.



#### 4.19. Alangium Lamarckii (AL)

Alangium Lamarckii (AL) commonly known as sage leaved alangium is a flowering plant in the alangiaceae family. **Tamil name: Alinsol.** In Ayurveda the roots and fruits are used for the treatment of rheumatism and haemorrhoid. The bark is also used in traditional medicine for skin problems and as an antidote for snake bite. It's used as an emetic and purgative and toothbrush. It's considered to be good for making musical instruments and for making furniture.



#### 4.20. Holoptelea Intergrifolia (HI)

Holoptelea Intergrifolia (HI) has been found to be large deciduous tree to 25 m height. **Tamil name: Aaya.** Leaves simple alternate stipules lateral, scarious petiole 5-10 mm. flowers, bark, seeds are used as medicine. Children eat seeds.



#### 4.21. Schreabera Swietenioids (SS)

Schreabera Swietenioids (SS) is a species of plant in the oleaceae family in the Himalayas, India. **Tamil name: Mahalingam maram.** It has many seeds, flats, winged. Fruting March onwards, almost persistent. Bark, roots, leaves and fruits are used as medicine. These are also used as a remedy for cancer.





**Fig. 20** Phytochemicals screening in plant extract

**4.22. The standard procedure for phytochemical tests shows the following results.**

**1. TEST FOR ALKALOIDS:**

**Wagner's test:** The plant extract was dissolved in chloroform. The chloroform layer was evaporated, and the residue was acidified to which was added few drops of Wagner's reagent (iodine in potassium iodide). Orange red precipitate was observed.

**2. TEST FOR SAPONINS:**

**Foam test:** 1 ml of the plant extract was shaken with 2 ml of water. The foam was produced within 10 minutes, which indicates the presence of saponin.

**3. TEST FOR FLAVONIODS:**

**Neutral  $FeCl_3$  test:** To a small quantity of the alcoholic solution of the extract, a few drops of neutral  $FeCl_3$  solution were added. A green colour was formed which shows the presence of flavonoids.

**4. TEST FOR COUMARINS:**

To 1 ml of the plant extract, 1 ml of 10 % NaOH was added. The presence of coumarins was indicated by the formation of yellow colour.

**5. TEST FOR TANNINS:**

**Lead acetate test:** To 5 ml of the extract a few drops of 1 % solution of lead acetate was added. Formation of yellow precipitate indicates the presence of tannins.

**6. TEST FOR PROTEINS:**

**Bireut test:** To 1 ml of the extract a few drops of  $CuSO_4$  and 1 ml of NaOH were added. Formation of violet colour shows the presence of protein.

## 7. TEST FOR ANTHROCYANINS:

To the extract 10 % NaOH was added. No characteristic change was noticed. This shows the absence of anthrocyanins.

## 8. TEST FOR QUINONES:

To 1 ml of the extract, 1 ml of conc.  $\text{H}_2\text{SO}_4$  was added, no characteristic change took place. This proves the absence of quinones.

## 9. TEST FOR ANTHRAQUINONES:

To 1 ml of plant extract, 2 ml of  $\text{NH}_4\text{OH}$  was added, no characteristic change. Absence of anthroquinones.

## 10. TEST FOR CARBOHYDRATES:

**Molisch test:** To the extract molisch reagent conc.  $\text{H}_2\text{SO}_4$  was added. Formation of violet colour shows the presence of carbohydrates.

### 4.23. Properties and application

Plants have long been used as food and a source of lamp oil, but now, it serves as a raw material of biological and paramedical products. The plant contain high concentration of glycosides, alkaloid, phenols, amine, flavonoids, saponins, carbohydrates, steroids, proteins and amino acids and tannings which have fused benzene ring and heteroatom in the ring. Medicinal plant considered an antipyretic, tonic, antidiabetic, immunomodulatory, anti-inflammatory, diuretic, vermifuge, antimicrobial, antihyperlipidemic, anticarcinogenic, antioxidant, anthelmintic, cytotoxic activities etc. due to presence of a variety of active phytochemicals have been reported in the literature [8-16]. In fact, the *first patented corrosion inhibitors used were either natural product such as flour, yeast* etc. Later, interest in using natural products as corrosion inhibitors increased substantially and scientists around the world reported several plant extracts as promising green anticorrosive agents.

### 4.24. Phytochemical screening test

In view of its phytochemical investigation, it was very clear that the presence of phytochemicals is responsible for the anticorrosion action. The screening test was carried out on a freshly prepared extract and various chemical constituents are presented in **Tables 4-9**. The result indicates that the natural product (alkaloids, tannis, steroids, terpinoids) absolutely inhibited the corrosion product on the metal surface. The possible reason for the absence or presence of these compounds in our test could be a very little amount and/or non-extraction of these compounds using aqueous and alcoholic solution of HCl, because they are below the analytical detection limit [17-26].

Inspection of the chemical structure of these phytochemical constituent revealed that these compounds are easily hydrolysable and the compounds can be adsorbed on the metal surface via the lone pair of electron present in their nitrogen and oxygen atoms (i.e they contain multifunctional group such as OH, NH, CO, COOH as well as O heterocyclic atom) which are barriers for charge and mass transfer leading to decrease the interaction of the metal with the corrosive environment. As a



result, the corrosion rate of the metal was decreased. The formation of film layer essentially blocks the discharge of  $H^+$  and dissolution of the metal ion. Due to electrostatic interaction, the protonated constituent's molecules are adsorbed (physisorption) and high inhibition is expected.

**Table 4** Phytochemical screening test of extract of *Madhuca Longifolia* (ML) plant

Aqueous extract					Alcoholic extract			
Phytochemical test	Leaves	Fruits	Barks	Seed peel	Leaves	Barks	Fruits	Seed peel
Alkaloids	+	+	+	+	+	+	-	-
Carbohydrates	+	+	-	-	+	+	+	+
Proteins	+	+	+	-	-	+	+	+
Saponins	-	-	+	+	+	-	-	-
Thiols	+	-	-	-	-	+	-	-
Tannins	-	-	+	-	+	-	+	-
Flavanoids	+	+	-	+	-	+	-	+
Phenol	+	+	+	-	+	+	+	-
Glycosides	-	+	+	+	-	-	-	-

(+).. Presence (-)... Absence

**Table 5** Phytochemical screening test of extract of *Gloriosa Superba* Linn (GSL) plant.

Aqueous extract					Alcoholic extract			
Phytochemical test	Leaves	Flowers	Tubers	Stem	Leaves	Stem	Flowers	Tubers
Alkaloids	+	+	+	+	+	+	+	+
Carbohydrates	+	+	+	-	-	-	-	+
Proteins	+	+	+	-	+	+	+	+
Saponins	-	-	+	+	-	+	+	-
Thiols	-	-	-	-	-	-	-	-
Tannins	-	-	+	-	+	-	+	+
Flavanoids	-	+	+	+	+	+	+	+
Phenol	+	+	+	-	+	-	-	+
Glycosides	-	+	+	+	-	-	-	-

(+).. Presence (-)... Absence



**Table 6** Phytochemical screening test of extract of *Pithecellobium Dulce* (PD) plant.

Aqueous extract					Alcoholic extract			
Phytochemical test	Leaves	Fruits	Barks	Seeds	Leaves	Fruits	Barks	Seeds
Alkaloids	+	+	+	+	+	+	+	+
Carbohydrates	+	+	-	-	+	-	-	-
Proteins	+	+	+	+	-	-	-	+
Saponins	-	-	+	+	-	+	-	+
Thiols	+	-	-	-	+	-	-	-
Tannins	-	-	-	-	-	-	-	-
Flavanoids	-	+	-	-	-	+	-	-
Phenol	+	+	+	-	+	-	+	+
Glycosides	-	+	+	+	-	+	-	+

(+).. Presence (-)... Absence

**Table 7** Phytochemical screening test of extract of *Alangium Lamarckii* plant.

Aqueous extract					Alcoholic extract			
Phytochemical test	leaves	Barks	Fruits	Seeds	Leaves	Barks	Fruits	Seeds
Alkaloids	+	+	+	+	+	+	+	+
Carbohydrates	+	-	-	-	+	-	+	+
Proteins	+	-	+	+	+	+	-	+
Saponins	-	-	-	+	-	+	+	-
Thiols	-	-	-	+	+	-	-	+
Tannins	-	-	+	-	-	+	-	-
Flavanoids	-	-	-	+	-	-	+	+
Phenol	+	+	+	-	+	+	+	-
Glycosides	-	-	+	+	+	-	-	+

(+).. Presence (-)... Absence

**Table 8** Phytochemical screening test of extract of *Holoptelea Integrifolia* (HI) plant.

Aqueous extract					Alcoholic extract			
Phytochemical test	Leaves	Seeds	Flowers	Barks	Leaves	Seeds	Flowers	Barks
Alkaloids	+	+	+	+	+	+	+	+
Carbohydrates	+	+	-	-	+	-	+	+
Proteins	+	+	+	-	+	+	+	-
Saponins	-	-	+	+	-	-	+	-
Thiols	+	-	-	-	-	-	-	+
Tannins	-	-	-	-	-	-	-	-
Flavanoids	-	-	+	+	-	+	+	-
Phenol	+	+	+	-	+	+	-	+
Glycosides	+	-	-	+	-	-	+	-

(+).. Presence (-)... Absence

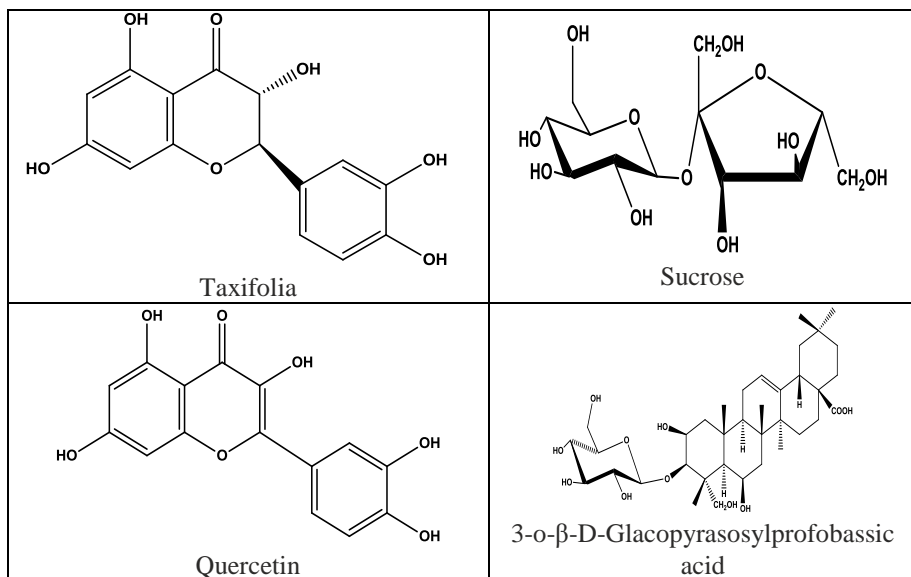
**Table 9** Phytochemical screening test of extract of Schreabera Swietenioids (SS) plant.

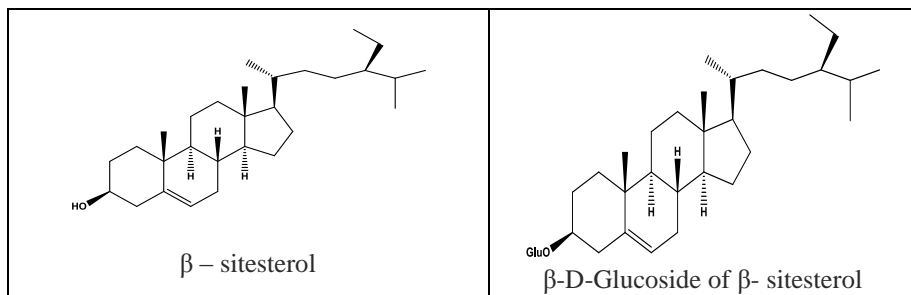
Phytochemical test	Aqueous extract				Alcoholic extract			
	leaves	fruits	seeds	barks	leaves	fruits	Seeds	barks
Alkaloids	+	+	-	+	+	-	+	+
Carbohydrates	+	-	-	-	+	-	-	-
Proteins	+	-	+	-	+	+	+	-
Saponins	-	-	+	+	-	-	-	-
Thiols	-	-	-	-	-	-	-	-
Tannins	-	-	-	-	-	-	-	-
Flavanoids	-	-	+	-	-	-	-	+
Phenol	+	+	+	+	+	+	+	+
Glycosides	-	-	-	+	-	-	+	-

(+).. Presence (-)... Absence

Gas chromatography – mass spectroscopy examination identified all organic species quantitatively, and can be detected that all species consists of possible major compounds [27-31]. Since holding time of majority of composites is close to each other and it is very difficult to separate them, the plant extract as such was used for corrosion inhibition studies. The following component with structure contains electron rich oxygen and nitrogen that can be served as good active ingredients which are responsible for corrosion inhibition in plants.

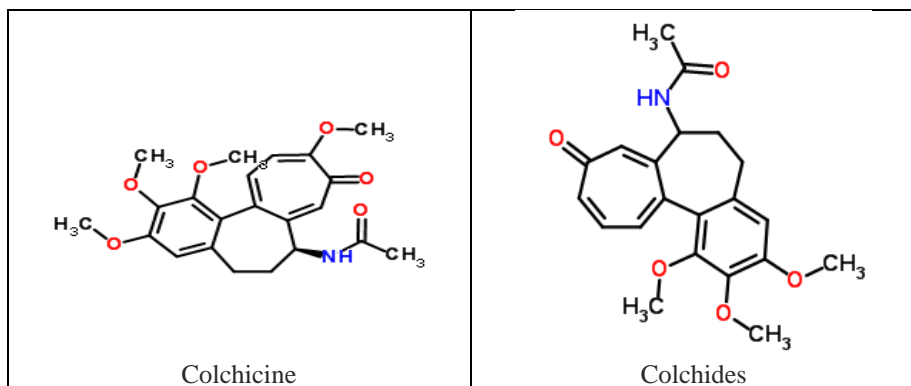
### *Madhuca Longifolia (ML)*





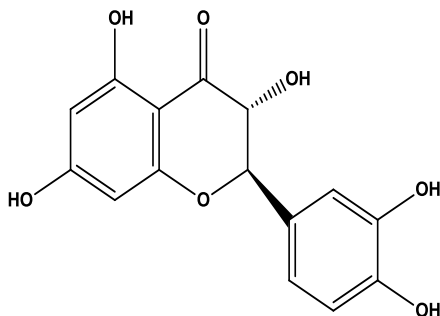
**Fig. 21** The chemical molecular structure of major constituents of ML plants extract

***Gloriosa Superba L (GSL)***

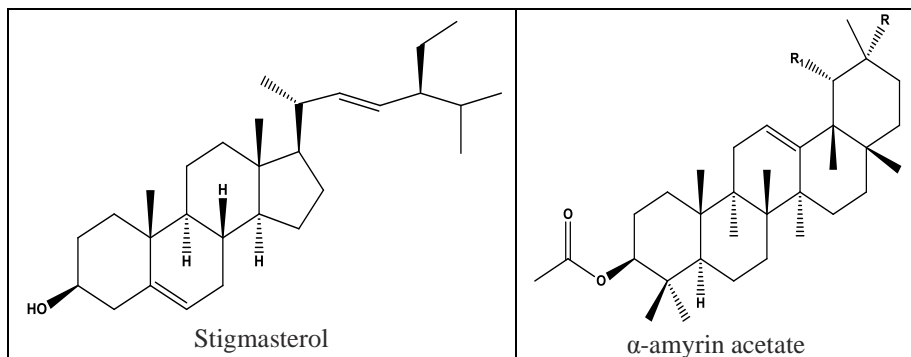


**Fig. 22** The chemical molecular structure of major constituents of GSL plants extract

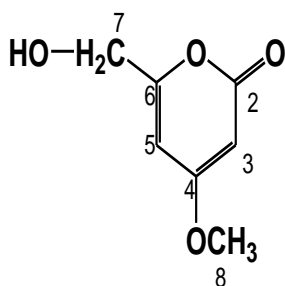
***Pithecellobium Dulce (PD)***



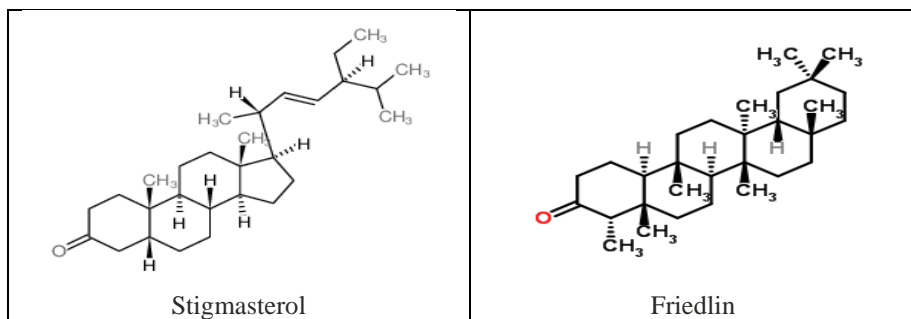
**Fig. 23** The chemical molecular structure of major constituents of (Quercetin) PD plants extracts.

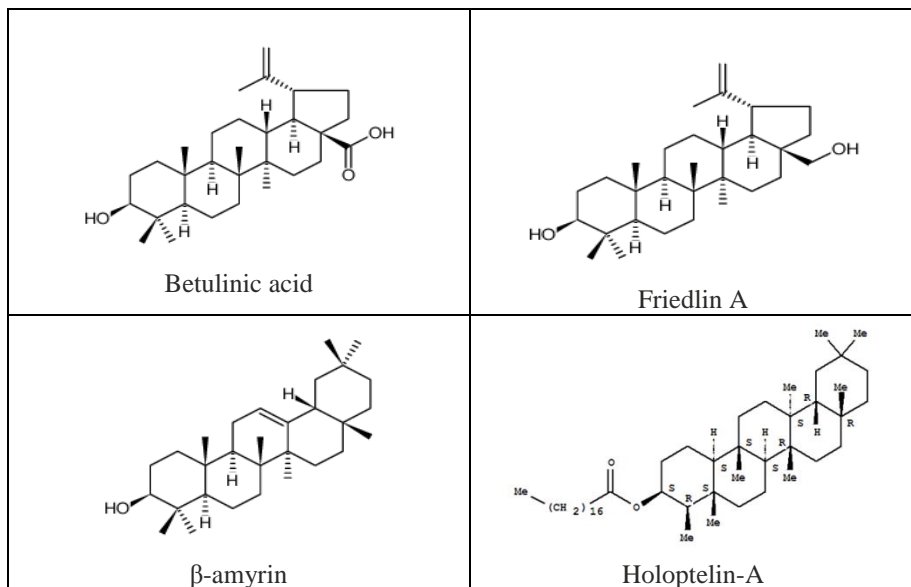
*Alangium Lamarckii (AL)*

**Fig. 24** The chemical molecular structure of major constituents of AL plants extract

*Schreabera Swietenioids (SS)*

**Fig. 25** The chemical molecular structure of major constituents (opuntiol) of SS plants extract

*Holoptelea Integrifolia (HI)*



**Fig. 26** The chemical molecular structure of major constituents of HI plant extracts

From the figure of constituent, it is clear that these constituents are having pi bonds and heteroatom (oxygen). Therefore, the adsorption process occurs either by the electrostatic interaction in charged molecules and constituents of inhibitors or by the interaction of unshared electrons of inhibitor molecules. The adsorption of the protonated molecules in the plants extract also occurs on the mild steel surface by direct interaction of the lone pairs of electrons on O and N with the vacant d- orbitals of Fe. These lone pair of electrons could also form metal inhibitor complex with  $\text{Fe}^{2+}$  ions formed from the anodic dissolution of steel. These complexes may adsorb onto the steel surface through Vander Waals force, providing more protection against corrosion [32-36]. In this present study, our result shows that due to lack of isolating these compounds, it is not possible to determine what components presents in plant extract created their relatively high ability to inhibit corrosion.

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## Chapter 5

# Results and Discussion

### 5.1. Weight loss method

In recent year, the natural products have been used as the best inhibitor in the field of corrosion. The weight loss process is ***undoubtedly the most commonly used method of primary calculation***. For the purpose of present study, mild steel samples were used in 1N HCl solution containing acid in the absence and presence of plant extract for 24 hours with various concentrations. Weight loss experiments were performed in triplicate and the results showed good reproducibility, the average values were taken and used in subsequent calculation.

The corrosion parameters obtained in the weight loss method (both in aqueous and alcoholic extract) were listed in ***Tables 10 - 15***. From the table, it was cleared that the corrosion rate was decreased with increasing concentration of the inhibitor and the inhibition efficiency increased with increasing the concentration of both extracts.

The observation of maximum surface coverage clearly suggests that the heteroatoms such as nitrogen and oxygen present in the inhibitor molecules can be able to bind with the metal ions by ***very strong adsorption and protect the metal ions*** from corrosive environment.

The corrosion process in acid medium can be attributed to the presence of OH<sup>-</sup>, O<sub>2</sub>, H<sub>2</sub> and Cl<sup>-</sup>. Generally, the inhibitor molecules suppress the metal dissolution by forming a protecting film adsorbed on the metal surface and separate it from the corrosion medium. In such solution the surface film is insoluble but may be locally attacked by aggressive anions, particularly chlorides. Accordingly, chloride ions are first adsorbed on the metal surface in 1N HCl medium and consequently the metal surface becomes negatively charged. The corrosion suppressing ability of the inhibitor molecules (adsorption of inhibitor liked to presence of heteroatom and long carbon chain as well as pi bond or aromatic ring) originates from the tendency to form either strong or weak chemical bond with Fe atom using the lone pair of electron in the oxygen and pi electron or aromatic ring in their molecules structure.

Very good inhibition efficiency (IE %) was obtained at 20 v/v and this concentration was chosen to be the optimum concentration of the inhibitor. No significant increase in inhibition efficiency was to be above 20 v/v. The comparative inhibition effect was investigated at the optimum concentration (20 v/v) of the both extract. From the ***Table 10***, it is evident that the aqueous extract of optimum



concentration for *Madhuca Longifolia leaves* was found to be 20 v/v with maximum inhibition efficiency of **97.14 %**, *barks* at 20 v/v with maximum inhibition efficiency of **82.98 %**, *fruits* at 20 v/v with maximum inhibition efficiency of **92.25 %**, *seeds peels* at 20 v/v with maximum inhibition efficiency of **91.04 %**. Also, for the alcoholic extract the highest inhibition efficiency was found to be **92.95 %** for *leaves*, *barks* at **85.16 %**, *fruits* at **91.02 %**, and *seed peels* at **90.34 %** for a period of one day of immersion time.

From the *Table 11*, it is noted that the aqueous extract of optimum concentration for *Gloriosa Superba Linn leaves* was found to be 20 v/v with maximum inhibition efficiency of **94.49 %**, **92.83 %** for *stems*, **88.90 %** for *flowers*, and **92.92 %** for *tubers* respectively. For alcoholic extract of the same plants, the highest inhibition efficiency of **94.12 %** was achieved for *leaves*, **92.13 %** for *stems*, **90.18 %** for *flowers* and at **90.35 %** for *tubers* respectively.

As can be seen from the *Table 12* that the IE values increased for mild steel immersed in the aqueous extract of *Pithecellobium dulce plants*. The maximum IE values at optimum concentration (20 v/v) was found to be **90.92 %** for *seeds*, **89.07 %** for *leaves*, **88.41 %** for *fruits* and **84.70 %** for *barks* extracts respectively. On the other hand, for the alcoholic extract the obtained IE values are (**90.13**, **84.46**, **86.93** and **89.32 %**) for *seeds*, *leaves*, *fruits* and *barks* respectively.

From the *Table 13*, it is evident that the highest inhibition efficiency was obtained for aqueous extract of *Alangium lamarckii leaves* at **99.79 %**, *barks* at **99.00 %**, *fruits* at **99.42 %** and *seeds* at **99.64 %**. On the other hand, for the alcoholic extract the obtained IE values are (**98.50**, **97.34**, **97.13** and **99.22 %**) for *leaves*, *barks* *fruits* and *seeds* respectively.

From the *Table 14*, it is evident that the maximum inhibition efficiencies that were obtained for the aqueous extract of *Holoptelea integrifolia* **84.39 %** for *leaves*, **89.34 %** for *bark*, **88.97 %** for *flowers* and **88.04 %** for *seeds* respectively. For alcoholic extract of the same plants, the highest inhibition efficiency of **87.63 %** was achieved for *leaves*, **86.36 %** for *barks*, **88.23 %** for *flowers*, and **89.21 %** for *seeds* respectively.

*Table 15* showed that the aqueous extract of *Schrebera swietenioides plants* was found to be optimum IE for *leaves* at **88.80 %**, *barks* at **91.93 %**, *fruits* at **90.74 %** and *seeds* at **92.84 %**. On the other hand, for the alcoholic extract, the IE obtained were for *seeds* at **80.77 %**, *leaves* at **89.25 %**, *fruits* at **89.17 %** and *barks* at **87.28 %**. This result indicated that the plant extract could act as effective corrosion inhibitor for mild steel in 1N HCl. On comparison, optimum inhibition efficiency was found in *Alangium lamarckii leaves* extracts with **99.79 %** at **15 v/v** concentration. All the *aqueous and alcoholic extract shows excellent* inhibitory character.

**Table 10** Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium

Aqueous extracts of ML plants					Alcoholic extracts of ML plants			
Parts of (ML) plant	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	IE (%)	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	IE (%)
Madhuca Longifolia leaves	Blank	0.1203	37.218	-	Blank	0.1147	44.008	-
	5	0.1018	4.188	40.23	5	0.0111	6.628	55.45
	10	0.0204	2.486	57.55	10	0.0717	3.326	62.05
	15	0.0093	1.454	73.20	15	0.213	1.234	75.22
	20	0.0048	0.070	97.14	20	0.0115	0.070	92.95
Madhuca Longifolia barks	Blank	0.1445	20.830	-	Blank	0.0395	19.030	-
	5	0.0842	5.117	42.07	5	0.0246	4.077	57.91
	10	0.0549	2.018	58.18	10	0.0140	2.918	64.48
	15	0.0093	1.106	79.76	15	0.0099	1.303	78.29
	20	0.0061	0.981	82.98	20	0.0085	1.031	85.16
Madhuca Longifolia fruits	Blank	0.0850	19.110	-	Blank	0.0350	10.610	-
	5	0.0587	8.181	48.18	5	0.0274	3.817	60.12
	10	0.0354	4.136	63.13	10	0.0212	2.716	75.82
	15	0.0109	2.119	71.39	15	0.0105	1.216	82.17
	20	0.0047	1.045	92.25	20	0.0090	0.042	91.02
Madhuca Longifolia seeds peel	Blank	0.0849	10.281	-	Blank	0.0594	14.071	-
	5	0.0380	6.063	49.41	5	0.0189	4.206	65.19
	10	0.0223	2.970	62.04	10	0.0103	2.140	72.04
	15	0.0144	1.450	78.76	15	0.0070	1.185	86.39
	20	0.0116	0.978	91.04	20	0.0055	0.980	90.34

**Table 11** Percentage of corrosion rate (CR) and inhibition efficiency (IE %) at different concentration of inhibitor in 1N HCl medium

Aqueous extract of GSL plants					Alcoholic extract of GSL plants			
Parts of plant	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	IE (%)	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	IE (%)
<i>Gloriosa Superba</i> Linn leaves	Blank	0.2104	16.258	-	Blank	0.1101	34.258	-
	5	0.0211	2.938	72.60	5	0.0104	16.638	64.12
	10	0.0117	1.786	82.12	10	0.0097	10.986	79.64
	15	0.0103	1.354	89.31	15	0.0053	8.754	84.02
	20	0.0045	0.570	94.49	20	0.0037	1.870	94.12
<i>Gloriosa Superba</i> Linn Stems	Blank	0.0947	25.830	-	Blank	0.0622	25.830	-
	5	0.0238	4.801	70.18	5	0.0446	14.817	61.54
	10	0.0193	2.310	78.79	10	0.0241	8.318	69.02
	15	0.0096	1.017	82.14	15	0.0198	2.116	84.52
	20	0.0078	2.031	92.83	20	0.0103	1.031	92.13
<i>Gloriosa Superba</i> Linn flowers	Blank	0.0350	20.310	-	Blank	0.0480	20.310	-
	5	0.0283	9.817	59.13	5	0.0303	10.817	66.66
	10	0.0102	6.912	72.73	10	0.0202	8.116	69.45
	15	0.0099	3.108	80.18	15	0.0105	6.290	72.22
	20	0.0094	1.321	88.90	20	0.0080	4.321	90.18

(continued)

**Table 11 (continued)**

<i>Gloriosa Superba</i> <i>Linn</i> <b>tubers</b>	Blank	0.0641	29.281	-	Blank	0.0845	17.281	-
	5	0.0384	5.166	51.02	5	0.0680	14.166	31.15
	10	0.0303	3.170	71.70	10	0.0389	10.170	52.17
	15	0.0182	2.965	78.19	15	0.0236	6.965	73.48
	20	0.0100	1.385	92.92	20	0.120	4.900	90.35

**Table 12** Data from Weight Loss Method for MS corroding in 1 N HCl solutions at various concentrations of PD leaves extract

Aqueous extract of PD plants					Alcoholic extract of PD plants		
Parts of (PD) plant	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Pithecellobium Dulce leaves	Blank	0.3362	38.345	-	0.2409	26.258	-
	5	0.3041	25.030	16.06	0.2024	14.634	55.04
	10	0.2413	10.986	39.84	0.1837	10.206	61.69
	15	0.1243	7.754	71.35	0.0914	4.561	81.08
	20	0.0910	4.870	89.07	0.0880	3.708	84.46
Pithecellobium Dulce barks	Blank	0.2440	25.083	-	0.0632	12.830	-
	5	0.1064	14.817	40.86	0.0442	9.874	38.73
	10	0.0940	9.842	58.31	0.0361	6.318	69.37
	15	0.0824	6.137	69.02	0.0204	4.116	79.49
	20	0.0335	3.031	84.70	0.0135	3.030	89.32
Pithecellobium Dulce fruits	Blank	0.0650	20.310	-	0.0750	18.310	-
	5	0.0303	9.818	60.83	0.0512	5.817	70.78
	10	0.0202	4.210	78.94	0.0301	4.116	79.37
	15	0.0150	2.416	84.58	0.0245	3.290	84.75
	20	0.0111	2.221	88.41	0.0140	2.321	86.93
Pithecellobium Dulce seeds	Blank	0.0532	17.428	-	0.0446	22.312	-
	5	0.0402	11.106	48.58	0.0280	12.166	52.49
	10	0.0310	9.070	58.53	0.0169	9.170	79.66
	15	0.0120	6.113	78.97	0.0133	6.965	88.14
	20	0.090	2.583	90.92	0.0110	3.385	90.13

**Table 13** Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium

Aqueous extract of AL plants					Alcoholic extracts of AL plants			
Parts of plant	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)
<i>Alangium Lamarckii</i> leaves	Blank	0.1107	14.258	-	Blank	0.4328	13.104	-
	5	0.0011	0.638	79.00	5	0.0102	4.986	80.58
	10	0.0017	0.986	84.58	10	0.0087	3.875	86.80
	15	0.0013	0.754	99.79	15	0.0067	2.754	89.04
	20	0.0015	0.870	87.80	20	0.0020	0.638	98.50
<i>Alangium Lamarckii</i> barks	Blank	0.0445	25.830	-	Blank	0.0966	16.817	-
	5	0.0046	4.817	86.21	5	0.0047	2.358	88.18
	10	0.0040	2.318	89.88	10	0.0035	2.011	93.72
	15	0.0001	0.116	99.00	15	0.0022	0.106	97.34
	20	0.0035	2.031	92.13	20	0.0883	7.817	65.20
<i>Alangium Lamarckii</i> fruits	Blank	0.0350	20.310	-	Blank	0.0140	22.321	-
	5	0.0083	4.817	76.28	5	0.0025	5.290	86.37
	10	0.0002	0.116	99.42	10	0.0012	0.934	97.13
	15	0.0005	0.290	98.57	15	0.0070	6.965	81.01
	20	0.0040	2.321	88.99	20	0.0020	3.385	90.24

**Table 13 (continued)**

<i>Alangium Lamarckii</i> seeds	Blank	0.0849	19.281	-	Blank	0.0196	11.992	-
	5	0.0089	5.166	89.51	5	0.0010	0.170	98.31
	10	0.0003	0.170	99.64	10	0.0003	0.120	99.22
	15	0.0120	6.965	88.86	15	0.0134	3.203	87.65
	20	0.0110	6.385	87.04	20	0.0109	3.480	87.04

**Table 14** Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium

Aqueous extract of HI plants					Alcoholic extract of HI plants		
Parts of (HI) plant	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)
<i>Holoptelea Integrifolia</i> leaves	Blank	0.1003	34.105	-	0.3734	30.100	-
	5	0.0401	15.938	54.10	0.1100	10.389	70.15
	10	0.0297	10.546	77.58	0.0820	9.654	79.03
	15	0.0143	6.354	84.39	0.0643	8.525	87.63
	20	0.0195	8.470	80.13	0.0464	8.848	84.28
<i>Holoptelea Integrifolia</i> barks	Blank	0.5450	46.823	-	0.1050	18.830	-
	5	0.4689	19.417	46.21	0.600	9.417	43.22
	10	0.0408	12.318	69.88	0.0408	2.318	70.83
	15	0.0019	4.116	89.34	0.0219	1.116	86.36
	20	0.0035	5.009	82.67	0.0395	2.009	83.84
<i>Holoptelea Integrifolia</i> flowers	Blank	0.6510	20.310	-	0.0510	20.310	-
	5	0.0283	11.317	66.28	0.0390	2.317	86.61
	10	0.0192	10.026	69.12	0.0284	1.026	88.23
	15	0.0115	5.970	80.37	0.0421	0.970	82.70
	20	0.0102	4.321	88.97	0.0435	0.321	82.90
<i>Holoptelea Integrifolia</i> seeds	Blank	0.0492	19.281	-	0.0403	13.014	-
	5	0.0189	13.166	59.51	0.0289	7.103	55.73
	10	0.0033	12.070	62.73	0.0182	1.170	64.33
	15	0.0020	8.865	78.16	0.0108	0.865	76.92
	20	0.0010	6.385	88.04	0.0039	0.385	89.21

**Table 15** Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium

Aqueous extract of SS plants					Alcoholic extract of SS plants		
Parts of (SS) plant	Conc. of the extract (v/v)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)
<i>Schreabera swietenoides</i> leaves	Blank	0.0347	24.902	-	0.2090	30.113	-
	5	0.0294	10.600	39.66	0.1314	10.638	58.39
	10	0.0157	6.986	64.09	0.0982	7.652	73.11
	15	0.0110	4.334	83.32	0.0630	4.286	84.57
	20	0.0015	3.100	88.80	0.0115	3.070	89.25
<i>Schreabera swietenoides</i> barks	Blank	0.0782	21.670	-	0.0445	23.137	-
	5	0.0546	14.908	40.01	0.0352	14.817	56.34
	10	0.0347	9.128	69.88	0.0223	5.318	78.56
	15	0.0091	2.116	89.60	0.0131	3.116	87.28
	20	0.0035	2.011	91.93	0.0195	4.030	82.55

(continued)

Table 15 (continued)

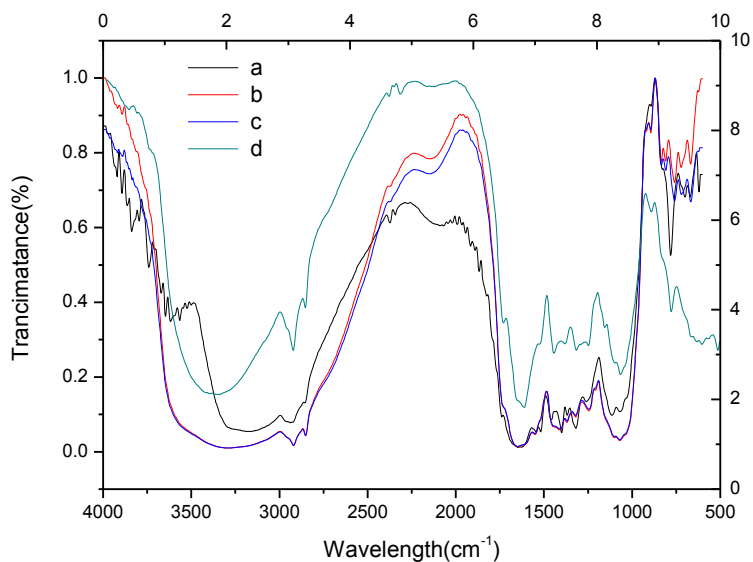
Schreabera swietenioids fruits	Blank	0.0370	18.560	-	0.0460	17.043	-
	5	0.0280	7.817	66.02	0.0383	8.189	52.67
	10	0.0182	5.116	79.11	0.0222	5.780	76.40
	15	0.0108	3.290	88.07	0.0135	2.236	86.76
	20	0.0099	2.301	90.74	0.0100	2.000	89.17
Schreabera swietenioids seeds	Blank	0.0641	29.021	-	0.0249	14.762	-
	5	0.0480	15.166	49.78	0.0189	8.112	50.40
	10	0.0203	9.170	63.46	0.0109	6.100	69.89
	15	0.0101	6.078	85.19	0.0087	4.965	78.86
	20	0.0082	3.385	92.84	0.0066	3.005	80.77

## 5.2. FT-IR Measurement

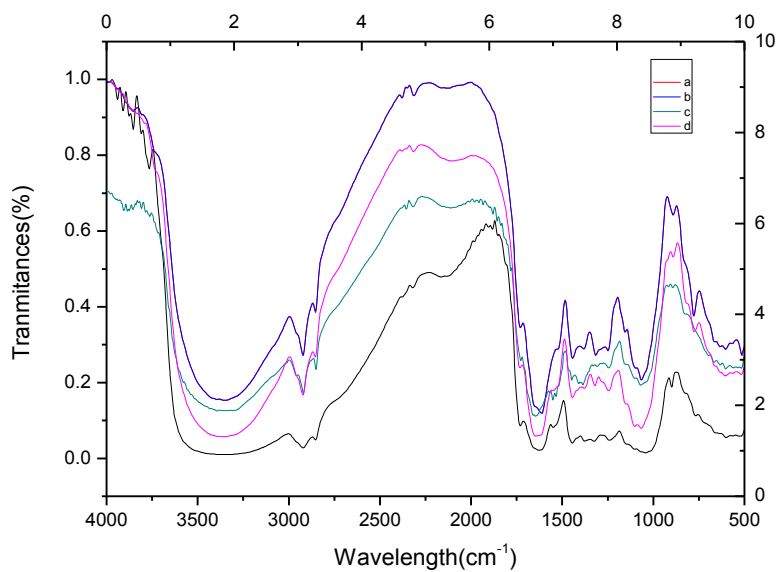
Among molecular vibrational spectroscopic techniques, FT-IR is most frequently used for the identification of organic functional groups. The surface film formed on the metal specimen examined by FT-IR spectra of the both (aqueous and alcoholic) extract of water - soluble and alcoholic - soluble fraction were recorded within the wavelength ranging between  $4000 - 400 \text{ cm}^{-1}$  using a Bruker alpha 8400 S models.

The FT-IR spectroscopy is *not capable to firm exactly the main structure* of the extract, but the evident shows that (what it) the more abundant chemical composites, it is *very difficult to identify each compound separately* to know the functional group present in the plants extracts, which contributed in effective working in the inhibitor.

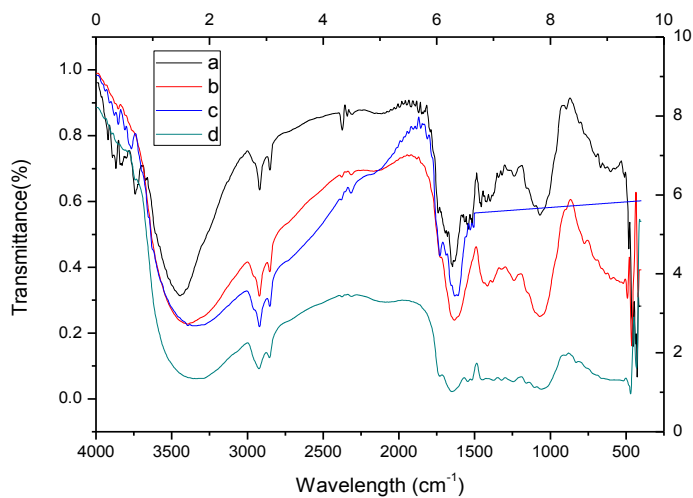
FT-IR spectra of all the selected *plants* of various parts like leaves, barks, fruits, seed peels or roots and tubers of both extracts were shown in **Figures 27 - 38**. For (*leaves, flowers, barks, fruits, tuber or stems and seed (or) seeds peels*) which contain bands corresponding  $3301, 3272, 3396, 3170, 3308 \text{ cm}^{-1}$  can be assigned to (*hydroxyl group*) and a strong band around  $1738 \text{ cm}^{-1}$  which reveals the presence of (*carbonyl*) stretching vibration respectively. Peak at  $2130, 2191 \text{ cm}^{-1}$  indicates the presence of *CN group* respectively. The peak at  $1096.64 \text{ cm}^{-1}$  is due to the *oxygen atom* present in the aromatic ring. For GSL, PD, AL, HI and SS plants of both extract, the similar kinds of functional groups are presented in there molecule. The band due to the protect film formed on the metal surface by aqueous and alcoholic extract clearly indicated that the mild steel has co-ordinated (*coordination between  $\text{Fe}^{2+}$  - organic constituent*) with the O - atom of the OH group, C = O group and the ring oxygen atom.



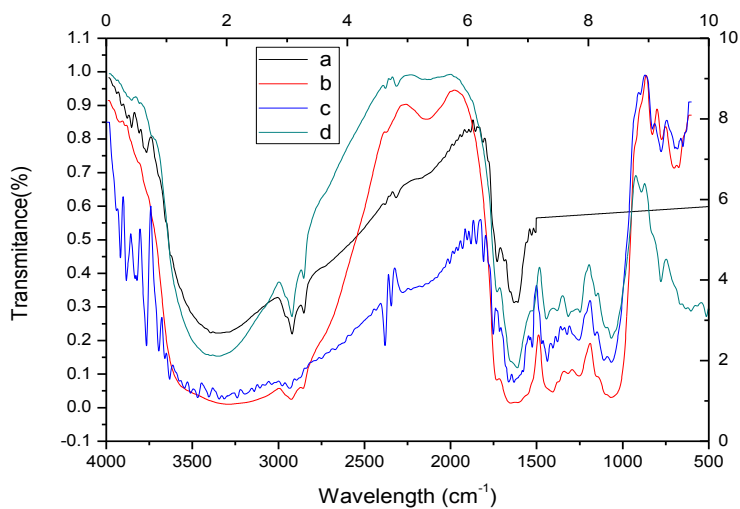
**Fig. 27** FTIR spectra of ML plants (aqueous extract)



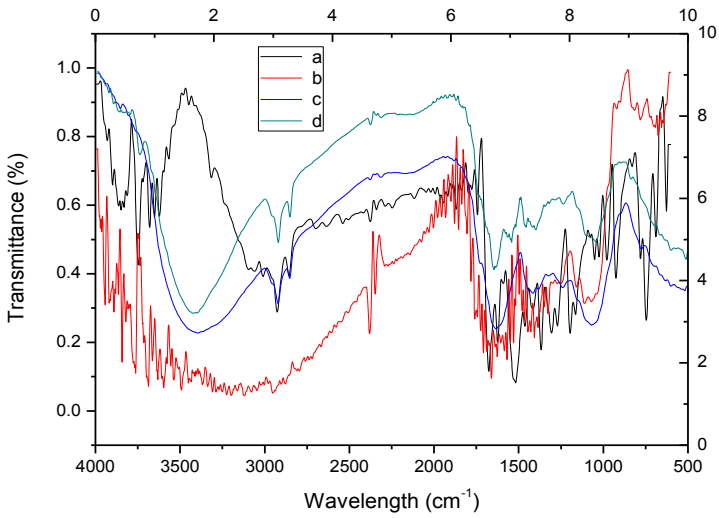
**Fig. 28** FTIR spectra of ML plants (alcoholic extract)



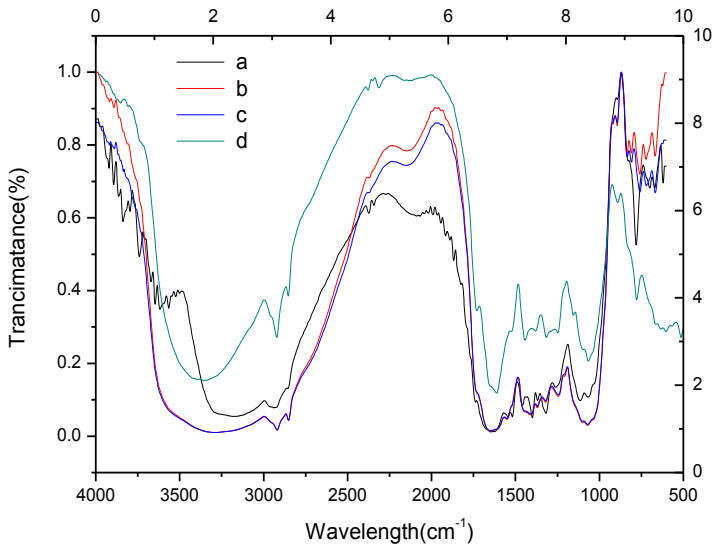
**Fig. 29** FTIR spectra of GSL plants (aqueous extract)



**Fig. 30** FTIR spectra of GSL plants (alcoholic extract)

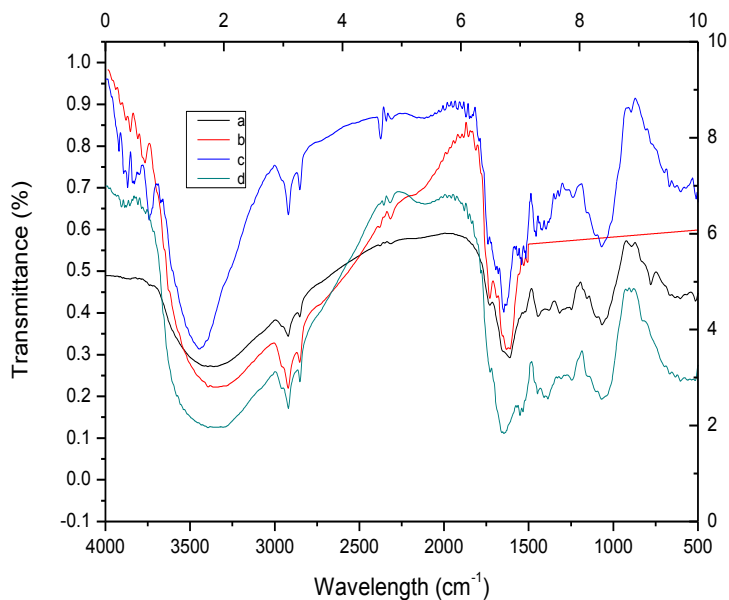


**Fig. 31** FTIR spectra of PD plants (aqueous extract)

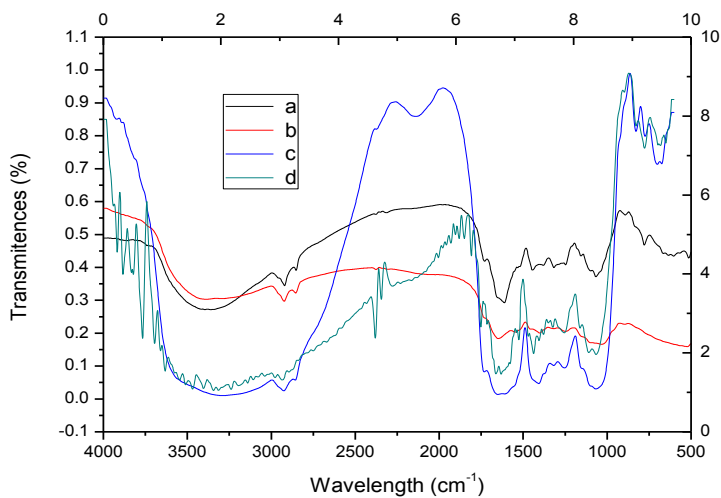


**Fig. 32** FTIR spectra of PD plants (alcoholic extract)

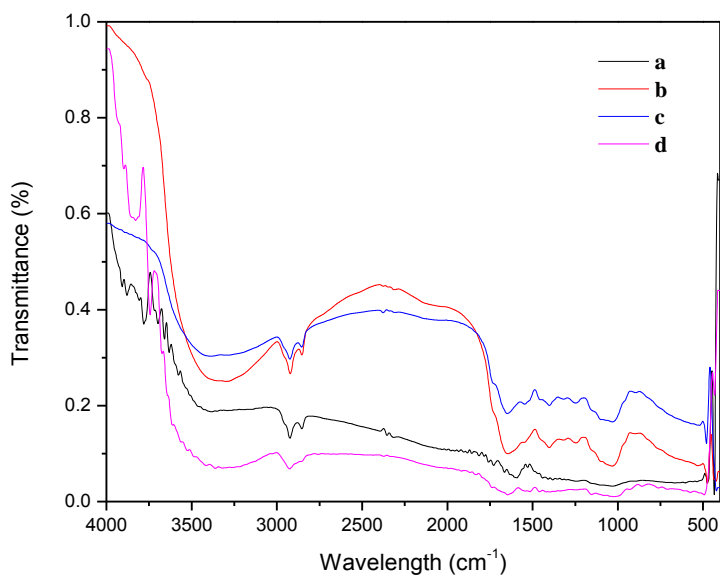




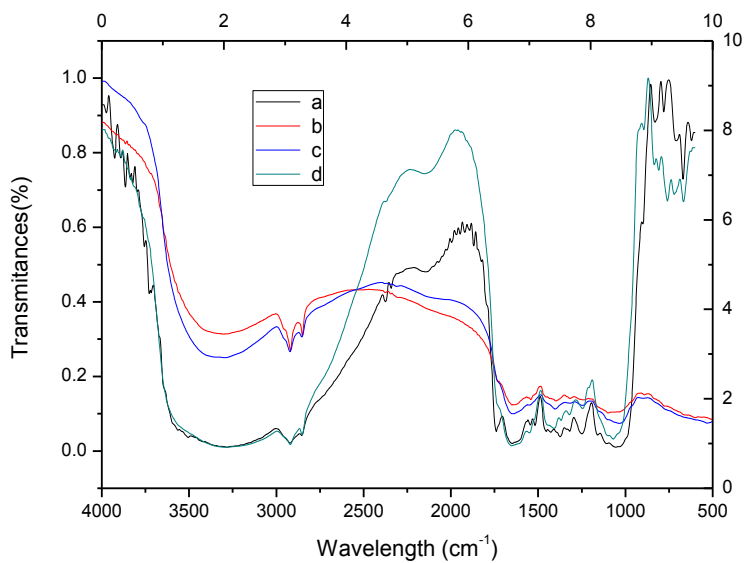
**Fig. 33** FTIR spectra of AL plants (aqueous extract)



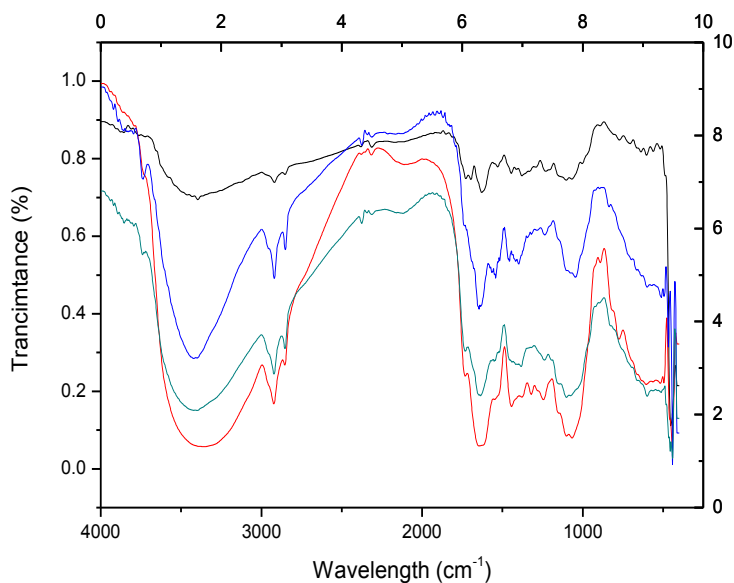
**Fig. 34** FTIR spectra of AL plants (alcoholic extract)



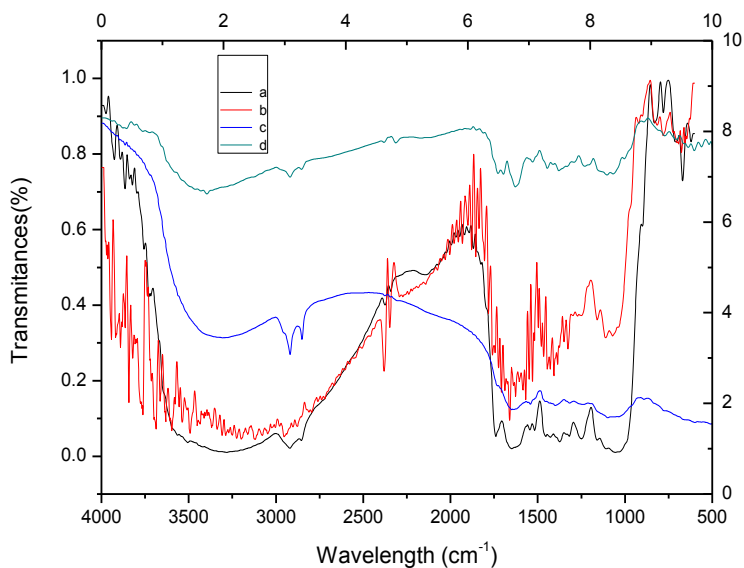
**Fig. 35** FTIR spectra of HI plants (aqueous extract)



**Fig. 36** FTIR spectra of HI plants (alcoholic extract)



**Fig. 37** FTIR spectra of SS plants (aqueous extract)



**Fig. 38** FTIR spectra of SS plants (alcoholic extract)

### 5.3. Potentiodynamic polarization methods

The effect of aqueous and alcoholic extracts of various concentration on the anodic and cathodic polarization behaviour of mild steel in 1N HCl solution has been studied by polarization measurements and the recorded Tafel slopes data are given in **Tables 16 – 21** and their polarization curves are shown in **Figures 39 - 50**. The displayed data clearly showed that the corrosion current density ( $I_{\text{corr}}$ ) value has been decreased in the presence of plant extract indicates that the corrosion process of steel has supported in 1N HCl acid media.

It is noted that the lowest ( $I_{\text{corr}}$ ) values are observed in the presence of extract possess strongest inhibitive properties and suggesting that natural plant extract could serve as effective green corrosion inhibitor. From the **Tables 16 – 21**, it is observed that there is not much variation in the  $E_{\text{corr}}$  values among the studied system. However, the shift in the values of corrosion potential ( $E_{\text{corr}}$ ) for both plant extract is not significant.

The corrosion kinetic parameters such as corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $I_{\text{corr}}$ ), anodic Tafel slope ( $b_a$ ) and cathodic Tafel slopes ( $b_c$ ) obtained from Tafel values are given in **Table 16** for ML plant extracts. From the table, it is observed that the  $I_{\text{corr}}$  values are found to decrease with increase in the inhibitor concentrations (both extract), ranging from 5 to 20 v/v. The maximum inhibition efficiency of **90.63 %** was observed for *Madhuca Longifolia leaves* at 20 v/v, for *barks* with **67.30 %** at 20 v/v, *fruits* with **94.25 %** at 15 v/v, and for *seeds peels* with **90.66 %** at 20 v/v of the extract. For the alcoholic extract, the maximum IE of **96.87 %** was obtained for leaves at 15 v/v, *barks* with **78.90 %** at 20 v/v, *fruits* with **96.80 %** at 20 v/v and for *seeds peels* with **97.00 %** at 20 v/v of the extract. This observation from **Fig. 39** and **Fig. 45** clearly showed that the inhibition of mild steel in the presence of the **ML** extracts control both cathodic and anodic reaction and thus the inhibitor acts like mixed type inhibitors.

The extrapolation method for the polarization curve was applied for *Gloriosa Superba linn* plant extracts and the corrosion parameters viz.,  $I_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_a$ ,  $b_c$  are shown in **Table 17**. From the results, it is found that increase in the concentration of the plant extract alters the values of corrosion potential ( $E_{\text{corr}}$ ) with respect to the mode of action of the inhibitor. **Fig. 40** and **Fig. 46** showed that the addition of GSL inhibitor did not affect the values of  $E_{\text{corr}}$  large extent but both anodic dissolution of mild steel and cathodic reduction reaction was observed, indicating that the inhibitor could be classified as mixed type inhibitor. From the **Table 17**, it is noted that the maximum inhibition efficiency of **96.38 %** was observed for *Gloriosa Superba linn tubers* at 15 v/v, for *flower* with **92.34 %** at 10 v/v, *stems* with **87.65 %** at 20 v/v, and for leaves with **93.19 %** at 15 v/v of the extract and the alcoholic extract showed a maximum inhibition efficiency of **75.98 %** for *tubers* at 10 v/v, for *flower* with **90.67 %** at 20 v/v, *stems* with **73.33 %** at 20 v/v, and for *leaves* with **80.97 %** at 20 v/v of the extract. From the tables it is found that for the both extracts,  $E_{\text{corr}}$  values are shifted in both positive and negative sides and are not shifted much remain closer to the OCP (open circuit potential) value, acting as a mixed type of inhibitor.

It is observed from the **Table 18** that the addition of the aqueous extract of

*Pithecellobium dulce* plants decreases the corrosion dissolution process and the maximum inhibition efficiency that was obtained for **fruits at 99.80 %, barks at 99.63 %, seeds at 99.21 % and leaves at 76.19 %**. On the other hand, for the alcoholic extract, IE obtained for **seeds at 94.89 %, leaves at 88.67 %, fruits at 84.90 % and barks at 89.33 % respectively**. It can be observed from the figure (**Fig. 41** and **Fig. 47**) that the addition of **PD** extracts at all the studied concentration decreased the anodic and cathodic current densities and resulted in significant decline in the  $I_{\text{corr}}$ . This indicates that **PD** extracts shifted to smaller  $I_{\text{corr}}$  values in both anodic and cathodic branches of the curve, thus, acting as a mixed type inhibitor and the decrease is more pronounced with the increase in the inhibitor concentration. By comparing polarization curves in the absence and in the presence of various concentrations of **PD** extracts, it was observed that, increase in concentration of the inhibitor shift the corrosion potential ( $E_{\text{corr}}$ ) in the positive direction and reduces both anodic and cathodic process.

It is noted from the **Table 19** that the addition of *Alangium lamarckii* plant extract decreases the dissolution rate of mild steel in 1N HCl acid media. It is evident that the optimum IE of the aqueous extract of *Alangium lamarckii* **leaves was at 95.74 %, barks at 95.57 %, fruits at 91.45 %, and seeds at 98.23 %**. Also, for the alcoholic extract the highest IE was obtained for **leaves at 90.30 %, barks at 80.22 %, fruits at 87.65 %, and seeds at 90.42 % respectively**. This observation from **Fig. 42** and **Fig. 48** clearly showed that the inhibition of mild steel in the presence of the **AL** extracts control both cathodic and anodic reaction and thus the inhibitor acts like mixed type inhibitors.

The examination of **Fig. 43** and **Fig. 49** showed that the addition of **HI** inhibitor did not affect the values of  $E_{\text{corr}}$  large extent but both anodic dissolution of mild steel and cathodic reduction reaction was observed, indicating that the inhibitor could be classified as mixed type inhibitor. It should be noted from the **Table 20** that the optimum inhibition efficiencies that were obtained for the aqueous extract of *Holoptelea integrifolia* **leaves at 97.45 %, barks at 99.89 %, flowers at 99.56 %, seeds at 98.97 %**. Also, for the alcoholic extract, the highest IE was obtained for the **leaves at 66.66 %, barks at 86.78 %, flowers at 88.00 %, and seeds at 88.90 % respectively**. The maximum inhibition efficiency detected at higher inhibitor concentration shows that more inhibitor molecules are adsorbed on the metal surface, which provides more surface coverage for the active sites of MS where direct attack occurs and migrates the corrosion attack.

As can be seen from the **Table 21** that the optimum inhibition efficiencies were that obtained for the aqueous extract of *Schrebera swietenoides* **leaves at 95.21 %, barks at 96.34 %, fruits at 96.36 %, seeds at 97.86 %**. Also, for the alcoholic extract, the highest IE was achieved for **leaves at 92.76 %, barks at 96.01 %, fruits at 93.33 %, and seeds at 96.89 % respectively**. This observation clearly showed that the (**Fig. 44** and **Fig. 50**) inhibition of mild steel in the presence of the **SS** extracts control both cathodic and anodic reaction and thus the inhibitor acts like mixed type inhibitors. The corrosion current density values decreased considerably for green inhibitor in the acid medium. This results shows that the both extract inhibits the corrosion mechanism by controlling predominantly the anodic and cathodic reaction sites in the metal

surface.

Generally, inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential in the presence of the inhibitor was more than 85 mV, with respect to that in the absence of the inhibitor. From these results, the charges of  $E_{\text{corr}}$  values are less than 85 mV for studied plants extract, which indicates that the selected plant extracts act as a ***mixed type inhibitor*** and more anodic in nature and does not alter the reaction mechanism for the corrosion of mild steel in 1N HCl medium. The corrosion prevention and protection has supported the mixed type of inhibitors is generally represented by organic compounds with donor atom Se, N, O, S, P instead of having reactive functional group which latch onto the metal, may have an important role on the corrosion inhibition of mild steel.

**Table 16** Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency

Aqueous extract of ML plants							Alcoholic extract of ML plants				
Parts of plant	Conc. (v/v)	E <sub>corr</sub> / mV/ SCE	I <sub>corr</sub> / mA/cm <sup>2</sup>	b <sub>c</sub> mV/de	b <sub>a</sub> mV/de	IE (%)	E <sub>corr</sub> / mV/ SCE	I <sub>corr</sub> / mA/cm <sup>2</sup>	b <sub>c</sub> mV/de	b <sub>a</sub> mV/de	IE (%)
ML Leaves	Blank	-0.471	4.7x10 <sup>-3</sup>	208	153	*	-0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	-0.468	3.3x10 <sup>-3</sup>	184	133	29.78	-0.468	1.2x10 <sup>-5</sup>	64	66	92.0
	10	-0.469	1.3x10 <sup>-3</sup>	166	101	72.34	-0.453	4.7x10 <sup>-5</sup>	147	68	96.87
	15	-0.483	8.5x10 <sup>-4</sup>	162	115	81.91	-0.455	2.4x10 <sup>-5</sup>	134	68	90.68
	20	-0.476	4.4x10 <sup>-4</sup>	132	093	90.63	-0.458	2.0x10 <sup>-5</sup>	129	69	90.70
ML Barks	Blank	-0.471	5.2x10 <sup>-3</sup>	199	140	*	-0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	0.469	3.2x10 <sup>-3</sup>	180	127	36.46	-0.444	1.5x10 <sup>-5</sup>	265	90	23.90
	10	-0.466	3.3x10 <sup>-3</sup>	203	136	38.57	-0.456	2.7x10 <sup>-5</sup>	135	67	57.89
	15	-0.469	1.7x10 <sup>-3</sup>	174	104	67.30	-0.459	2.1x10 <sup>-5</sup>	130	69	65.16
	20	-0.474	1.8x10 <sup>-3</sup>	172	125	67.30	-0.460	1.8x10 <sup>-5</sup>	127	71	78.90
ML Fruits	Blank	-0.471	4.0x10 <sup>-3</sup>	208	153	*	-0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	-0.469	1.5x10 <sup>-3</sup>	171	118	62.50	-0.462	2.4x10 <sup>-5</sup>	120	70	90.45
	10	-0.486	2.6x10 <sup>-4</sup>	141	088	93.58	-0.460	1.8x10 <sup>-5</sup>	115	70	93.58
	15	-0.475	2.4x10 <sup>-4</sup>	152	098	94.25	-0.460	1.4x10 <sup>-5</sup>	114	72	94.89
	20	-0.491	5.3x10 <sup>-4</sup>	137	098	86.70	-0.461	1.2x10 <sup>-5</sup>	112	75	96.80
ML Seed peels	Blank	-0.471	4.0 x10 <sup>-3</sup>	208	153	*	-0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	-0.479	1.5x10 <sup>-3</sup>	167	122	74.87	-0.460	1.3x10 <sup>-5</sup>	115	74	95.88
	10	-0.479	6.7x10 <sup>-4</sup>	146	097	83.79	-0.462	1.2x10 <sup>-5</sup>	115	76	96.99
	15	-0.482	1.1x10 <sup>-3</sup>	157	118	90.56	-0.463	1.1x10 <sup>-5</sup>	116	77	96.99
	20	-0.485	9.7x10 <sup>-7</sup>	148	110	90.57	-0.464	1.0x10 <sup>-5</sup>	116	80	97.00

**Table 17** Polarization measurement and calculated values of IE (%) at different concentration of GSL extract

Aqueous extract of GSL plant							Alcoholic extract of GSL plant				
Parts of <i>GSL</i> plant	Conc. v/v	$E_{corr}/\text{mV/SCE}$	$I_{corr}/\text{mA/cm}^2$	$b_c/\text{mV/dec.}$	$b_a/\text{mV/dec.}$	IE (%)	$E_{corr}/\text{mV/SCE}$	$I_{corr}/\text{mA/cm}^2$	$b_c/\text{mV/dec.}$	$b_a/\text{mV/dec.}$	IE (%)
<i>GS Linn leaves</i>	Blank	- 0.471	$4.7 \times 10^{-3}$	208	153	*	- 0.477	$1.5 \times 10^{-3}$	128	87	*
	5	- 0.468	$1.0 \times 10^{-3}$	160	115	78.72	- 0.463	$0.9 \times 10^{-4}$	138	72	40.0
	10	- 0.475	$7.2 \times 10^{-4}$	165	90	84.68	- 0.471	$0.7 \times 10^{-5}$	138	72	53.33
	15	- 0.476	$3.2 \times 10^{-4}$	131	100	93.19	- 0.475	$0.4 \times 10^{-5}$	135	66	73.49
	20	- 0.465	$6.0 \times 10^{-4}$	146	90	87.23	- 0.469	$0.7 \times 10^{-6}$	147	65	80.97
<i>GS Linn flowers</i>	Blank	- 0.471	$4.7 \times 10^{-3}$	208	153	*	- 0.477	$1.5 \times 10^{-3}$	128	87	*
	5	- 0.455	$8.8 \times 10^{-4}$	155	93	81.27	- 0.445	$0.9 \times 10^{-5}$	134	67	76.95
	10	- 0.444	$1.3 \times 10^{-3}$	191	104	92.34	- 0.467	$0.3 \times 10^{-4}$	142	67	84.65
	15	- 0.451	$1.5 \times 10^{-3}$	174	116	89.08	- 0.489	$0.6 \times 10^{-4}$	139	66	90.67
	20	- 0.448	$5.5 \times 10^{-4}$	188	87	88.29	- 0.478	$0.6 \times 10^{-4}$	139	66	90.67
<i>GS Linn stems</i>	Blank	- 0.471	$4.7 \times 10^{-3}$	208	153	*	- 0.477	$1.5 \times 10^{-3}$	128	87	*
	5	- 0.477	$8.9 \times 10^{-4}$	166	86	51.08	- 0.477	$0.9 \times 10^{-6}$	150	90	74.32
	10	- 0.461	$1.6 \times 10^{-3}$	179	129	65.95	- 0.486	$0.6 \times 10^{-6}$	143	100	60.00
	15	- 0.482	$1.2 \times 10^{-3}$	160	138	74.46	- 0.472	$0.7 \times 10^{-6}$	154	90	73.33
	20	- 0.475	$5.8 \times 10^{-4}$	143	94	87.65	- 0.472	$0.8 \times 10^{-6}$	154	89	73.33
<i>GS Linn tubers</i>	Blank	- 0.471	$4.7 \times 10^{-3}$	208	153	*	- 0.477	$1.5 \times 10^{-3}$	128	87	*
	5	- 0.479	$4.5 \times 10^{-4}$	153	84	33.90	- 0.483	$1.6 \times 10^{-6}$	87	125	60.89
	10	- 0.462	$3.6 \times 10^{-3}$	178	128	56.67	- 0.474	$1.2 \times 10^{-6}$	137	96	75.98
	15	- 0.474	$7.3 \times 10^{-4}$	156	87	89.54	- 0.462	$2.6 \times 10^{-6}$	146	88	53.78
	20	- 0.477	$1.0 \times 10^{-3}$	163	122	96.38	- 0.469	$2.6 \times 10^{-6}$	133	89	53.78

**Table 18** Electrochemical parameters from polarization measurement, calculated values of inhibition efficiency

Aqueous extract of PD plants							Alcoholic extract of PD plants				
Parts of PD plant	Conc. (v/v)	E <sub>corr</sub> / mV/ SCE	I <sub>corr</sub> / mA/cm <sup>2</sup>	b <sub>c</sub> mV/ dec	b <sub>a</sub> mV/dec	IE (%)	E <sub>corr</sub> / mV/ SCE	I <sub>corr</sub> / mA/cm <sup>2</sup>	b <sub>c</sub> mV/dec.	b <sub>a</sub> mV/dec.	IE (%)
PD leaves	Blank	- 0.471	5.2 x10 <sup>-3</sup>	199	140	*	- 0.504	1.5 x10 <sup>-4</sup>	128	87	*
	5	- 0.477	2.0x10 <sup>-4</sup>	127	093	33.97	- 0.240	1.7x10 <sup>-9</sup>	126	54	88.67
	10	- 0.493	1.8x10 <sup>-4</sup>	121	095	41.72	- 0.315	0.7x10 <sup>-7</sup>	112	112	53.34
	15	- 0.502	1.2x10 <sup>-4</sup>	116	090	61.65	- 0.313	1.0x10 <sup>-7</sup>	113	112	53.34
	20	- 0.510	7.5x10 <sup>-5</sup>	112	092	76.19	- 0.375	1.4x10 <sup>-7</sup>	101	115	50.56

(continued)

**Table 18 (Continued)**

PD barks	Blank	- 0.471	5.2x10 <sup>-3</sup>	199	140	*	- 0.504	1.5 x10 <sup>-4</sup>	128	87	*
	5	- 0.473	5.9x10 <sup>-4</sup>	174	86	76.00	- 0.345	2.0 x10 <sup>-7</sup>	87	127	86.86
	10	- 0.461	7.2x10 <sup>-4</sup>	165	82	99.63	- 0.367	1.6x10 <sup>-7</sup>	97	116	89.33
	15	- 0.465	4.0x10 <sup>-4</sup>	167	68	99.59	- 0.365	2.2x10 <sup>-7</sup>	89	126	85.33
	20	- 0.474	2.5x10 <sup>-4</sup>	152	73	85.29	- 0.378	2.1x10 <sup>-7</sup>	95	120	85.34
PD fruits	Blank	- 0.446	3.7x10 <sup>-3</sup>	203	132	*	- 0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	- 0.449	2.8x10 <sup>-3</sup>	194	124	86.00	- 0.455	2.3x10 <sup>-5</sup>	139	66	84.90
	10	- 0.458	1.9x10 <sup>-3</sup>	173	119	99.79	- 0.463	2.3x10 <sup>-4</sup>	79	83	84.89
	15	- 0.459	1.5x10 <sup>-3</sup>	171	117	99.80	- 0.392	2.6x10 <sup>-7</sup>	74	118	83.67
	20	- 0.461	1.1x10 <sup>-3</sup>	167	107	91.01	- 0.477	3.3x10 <sup>-5</sup>	134	34	80.90
PD seeds	Blank	- 0.471	4.7x10 <sup>-3</sup>	208	153	*	- 0.540	1.5x10 <sup>-4</sup>	128	87	*
	5	- 0.462	6.5x10 <sup>-4</sup>	171	080	90.44	- 0.335	1.4x10 <sup>-7</sup>	154	91	89.58
	10	- 0.476	4.0x10 <sup>-4</sup>	142	097	99.21	- 0.337	1.7x10 <sup>-7</sup>	105	130	88.89
	15	- 0.469	1.4x10 <sup>-4</sup>	159	063	84.50	- 0.330	1.2x10 <sup>-7</sup>	105	63	92.00
	20	- 0.476	3.9x10 <sup>-4</sup>	131	101	99.00	- 0.439	1.1x10 <sup>-5</sup>	148	36	94.89

**Table 19** Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency

Aqueous extract of AL plants						Alcoholic extract of AL plants					
Parts of AL Plant	Conc. (v/v)	E <sub>corr</sub> /mV/SCE	I <sub>corr</sub> /mA/cm <sup>2</sup>	b <sub>c</sub> mV/dec.	b <sub>a</sub> mV/dec	IE (%)	E <sub>corr</sub> /Mv/SCE	I <sub>corr</sub> /mA/cm <sup>2</sup>	b <sub>c</sub> mV/dec	b <sub>a</sub> mV/dec	IE (%)
AL Leaves	Blank	- 0.446	3.7x10 <sup>-3</sup>	203	132	*	- 0.471	4.7x10 <sup>-3</sup>	208	153	*
	5	- 0.445	1.4x10 <sup>-3</sup>	197	104	61.14	- 0.468	1.0x10 <sup>-3</sup>	160	115	73.70
	10	- 0.445	1.2x10 <sup>-3</sup>	192	101	66.80	- 0.475	7.2x10 <sup>-4</sup>	165	90	80.45
	15	- 0.454	1.6x10 <sup>-3</sup>	184	124	95.74	- 0.476	3.2x10 <sup>-4</sup>	131	100	90.39
	20	- 0.452	6.9x10 <sup>-4</sup>	159	097	81.71	- 0.465	6.0x10 <sup>-4</sup>	146	90	82.33
AL Barks	Blank	- 0.471	5.2x10 <sup>-3</sup>	199	140	*	- 0.471	4.7x10 <sup>-3</sup>	208	153	*
	5	- 0.460	4.5x10 <sup>-4</sup>	174	070	91.33	- 0.455	8.8x10 <sup>-4</sup>	155	93	80.22
	10	- 0.479	6.1x10 <sup>-4</sup>	146	094	88.21	- 0.444	1.3x10 <sup>-3</sup>	191	104	72.34
	15	- 0.474	4.6x10 <sup>-4</sup>	145	091	91.10	- 0.451	1.5x10 <sup>-3</sup>	174	116	68.08
	20	- 0.477	2.3x10 <sup>-4</sup>	136	074	95.57	- 0.448	5.5x10 <sup>-4</sup>	188	87	58.29
AL Fruits	Blank	- 0.466	3.7x10 <sup>-3</sup>	203	132	*	- 0.471	4.7x10 <sup>-3</sup>	208	153	*
	5	- 0.450	1.0x10 <sup>-3</sup>	147	073	71.96	- 0.477	8.9x10 <sup>-4</sup>	166	86	81.06
	10	- 0.466	7.2x10 <sup>-4</sup>	133	091	80.83	- 0.461	1.6x10 <sup>-3</sup>	179	129	65.95
	15	- 0.464	3.2x10 <sup>-4</sup>	137	075	91.45	- 0.482	1.2x10 <sup>-3</sup>	160	138	74.46
	20	- 0.492	6.0x10 <sup>-4</sup>	133	102	83.96	- 0.475	5.8x10 <sup>-4</sup>	143	94	87.65

(Continued)



**Table 19 (Continued)**

AL Seeds	Blank	- 0.472	6.4x10 <sup>-3</sup>	208	168	*	- 0.471	4.7x10 <sup>-3</sup>	208	153	*
	5	- 0.464	4.0x10 <sup>-3</sup>	205	132	38.01	- 0.479	4.5x10 <sup>-4</sup>	153	84	90.42
	10	- 0.464	2.8x10 <sup>-3</sup>	199	126	56.58	- 0.462	3.6x10 <sup>-3</sup>	178	128	72.34
	15	- 0.472	1.1x10 <sup>-5</sup>	168	111	98.23	- 0.474	7.3x10 <sup>-4</sup>	156	87	84.47
	20	- 0.470	1.7x10 <sup>-3</sup>	166	111	97.32	- 0.477	1.0x10 <sup>-3</sup>	163	122	78.72

**Table 20** Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency

Aqueous extract of HI plants							Alcoholic extract of HI plants				
Parts of plant	Con. c. (v/v)	E <sub>corr</sub> / (mV / SCE)	I <sub>corr</sub> / (mA/cm <sup>2</sup> )	b <sub>c</sub> (mV/de c.)	b <sub>a</sub> (mV/de c.)	IE (%)	E <sub>corr</sub> / (mV / SCE)	I <sub>corr</sub> / (mA/cm <sup>2</sup> )	b <sub>c</sub> (mV/de c.)	b <sub>a</sub> (mV/de c.)	IE (%)
HI leaves	Blank	- 0.471	4.7 x10 <sup>-3</sup>	208	153	*	-0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	- 0.468	1.0 x10 <sup>-4</sup>	160	115	77.32	-0.472	1.3x10 <sup>-4</sup>	138	72	13.33
	10	- 0.475	7.2 x10 <sup>-4</sup>	165	090	97.45	-0.472	1.3x10 <sup>-4</sup>	138	72	13.33
	15	- 0.476	3.2 x10 <sup>-3</sup>	131	100	93.05	-0.474	0.5x10 <sup>-4</sup>	135	66	66.66
	20	- 0.465	6.0 x10 <sup>-4</sup>	146	096	87.08	-0.455	0.6x10 <sup>-4</sup>	147	65	60.00
HI barks	Blank	- 0.471	4.0 x10 <sup>-3</sup>	208	153	*	-0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	- 0.479	4.5 x10 <sup>-4</sup>	153	084	66.01	-0.462	2.2x10 <sup>-5</sup>	134	67	85.33
	10	- 0.462	3.6 x10 <sup>-3</sup>	178	128	98.90	-0.455	3.0x10 <sup>-5</sup>	142	64	80.00
	15	- 0.474	7.3 x10 <sup>-4</sup>	156	087	99.89	-0.455	2.3x10 <sup>-5</sup>	139	66	84.67
	20	- 0.477	1.0 x10 <sup>-3</sup>	163	122	84.30	-0.456	2.0x10 <sup>-5</sup>	136	66	86.78
HI flowers	Blank	- 0.471	4.0 x10 <sup>-3</sup>	208	153	*	-0.504	1.5x10 <sup>-4</sup>	128	87	*
	5	- 0.471	7.6x10 <sup>-4</sup>	159	100	82.77	-0.445	3.9x10 <sup>-5</sup>	150	61	74.90
	10	- 0.479	7.6 x10 <sup>-4</sup>	146	101	98.01	-0.446	2.8x10 <sup>-5</sup>	143	64	81.34
	15	- 0.479	3.4 x10 <sup>-4</sup>	138	085	99.56	-0.447	3.8x10 <sup>-5</sup>	154	62	76.67
	20	- 0.476	1.4 x10 <sup>-3</sup>	167	128	90.99	-0.452	1.8x10 <sup>-5</sup>	134	64	88.00

(Continued)

Table 20 (Continued)

HI seeds	Blank	- 0.472	$6.4 \times 10^{-3}$	208	168	*	-0.504	$1.5 \times 10^{-4}$	128	87	*
	5	- 0.464	$4.0 \times 10^{-3}$	205	132	88.41	-0.403	$1.8 \times 10^{-7}$	87	125	88.90
	10	- 0.464	$2.8 \times 10^{-3}$	199	126	98.67	-0.454	$2.5 \times 10^{-5}$	137	86	83.33
	15	- 0.472	$1.1 \times 10^{-3}$	168	111	85.59	-0.451	$4.2 \times 10^{-5}$	146	75	72.53
	20	- 0.470	$1.7 \times 10^{-3}$	166	111	95.22	-0.457	$2.2 \times 10^{-5}$	133	74	70.78

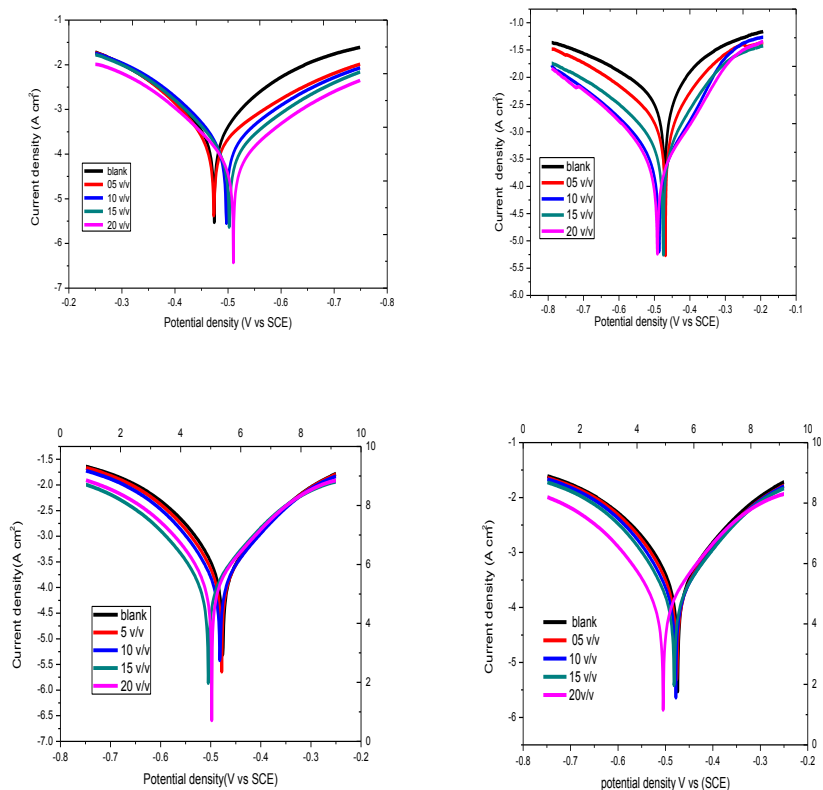
Table 21 Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency

Aqueous extract of SS plants							Alcoholic extract of SS plants				
Parts of SS plant	Conc. (v/v)	$E_{corr}$ (mV / SCE)	$I_{corr}$ (mA/cm <sup>2</sup> )	$b_c$ (mV/dec)	$b_a$ (mV/dec)	IE (%)	$E_{corr}$ (mV / SCE)	$I_{corr}$ (mA/cm <sup>2</sup> )	$b_c$ (mV/dec)	$b_a$ (mV/dec)	IE (%)
SS leaves	Blank	- 0.474	$3.1 \times 10^{-4}$	108	101	*	- 0.504	$1.5 \times 10^{-4}$	128	87	*
	5	- 0.476	$2.4 \times 10^{-5}$	103	098	92.07	- 0.111	$0.6 \times 10^{-6}$	202	386	60.00
	10	- 0.478	$2.0 \times 10^{-5}$	097	095	93.57	- 0.103	$0.7 \times 10^{-6}$	281	420	83.33
	15	- 0.482	$1.7 \times 10^{-5}$	095	093	94.53	- 0.098	$1.1 \times 10^{-6}$	252	386	92.66
	20	- 0.505	$1.5 \times 10^{-5}$	098	094	95.21	- 0.113	$1.2 \times 10^{-6}$	261	416	92.67
SS bark	Blank	- 0.472	$6.4 \times 10^{-3}$	208	168	*	- 0.504	$1.5 \times 10^{-4}$	128	87	*
	5	- 0.482	$1.8 \times 10^{-3}$	168	124	72.17	- 0.354	$0.3 \times 10^{-6}$	78	123	80.00
	10	- 0.474	$8.0 \times 10^{-4}$	155	091	94.98	- 0.298	$0.6 \times 10^{-6}$	151	78	96.01
	15	- 0.470	$5.8 \times 10^{-4}$	167	081	96.34	- 0.378	$1.3 \times 10^{-6}$	61	182	91.33
	20	- 0.475	$5.4 \times 10^{-4}$	141	090	82.00	- 0.362	$1.7 \times 10^{-6}$	57	171	88.96
SS fruits	Blank	- 0.446	$3.7 \times 10^{-3}$	203	132	*	- 0.504	$1.5 \times 10^{-4}$	128	87	*
	5	- 0.445	$1.4 \times 10^{-3}$	197	104	84.64	- 0.370	$0.9 \times 10^{-6}$	80	165	40.09
	10	- 0.445	$1.2 \times 10^{-3}$	192	101	96.36	- 0.348	$1.0 \times 10^{-6}$	82	152	93.33
	15	- 0.454	$1.6 \times 10^{-3}$	184	124	95.22	- 0.374	$1.0 \times 10^{-6}$	79	152	93.33
	20	- 0.452	$6.9 \times 10^{-4}$	159	097	93.99	- 0.376	$1.1 \times 10^{-6}$	80	150	92.87

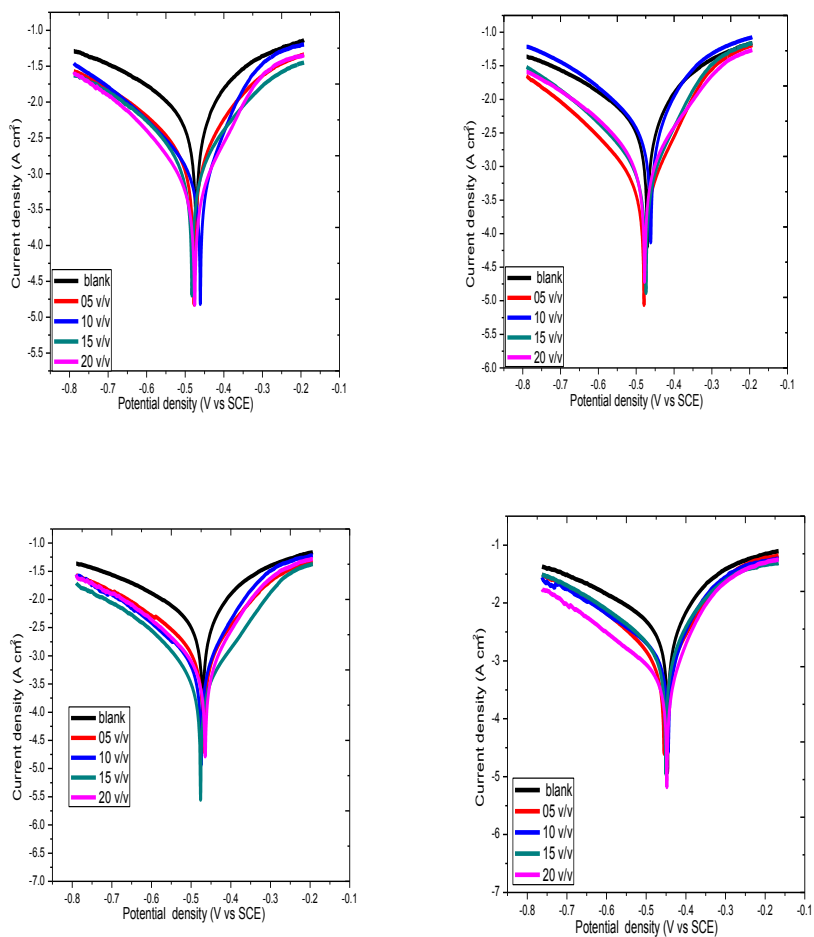
(Continued)

Table 21(Continued)

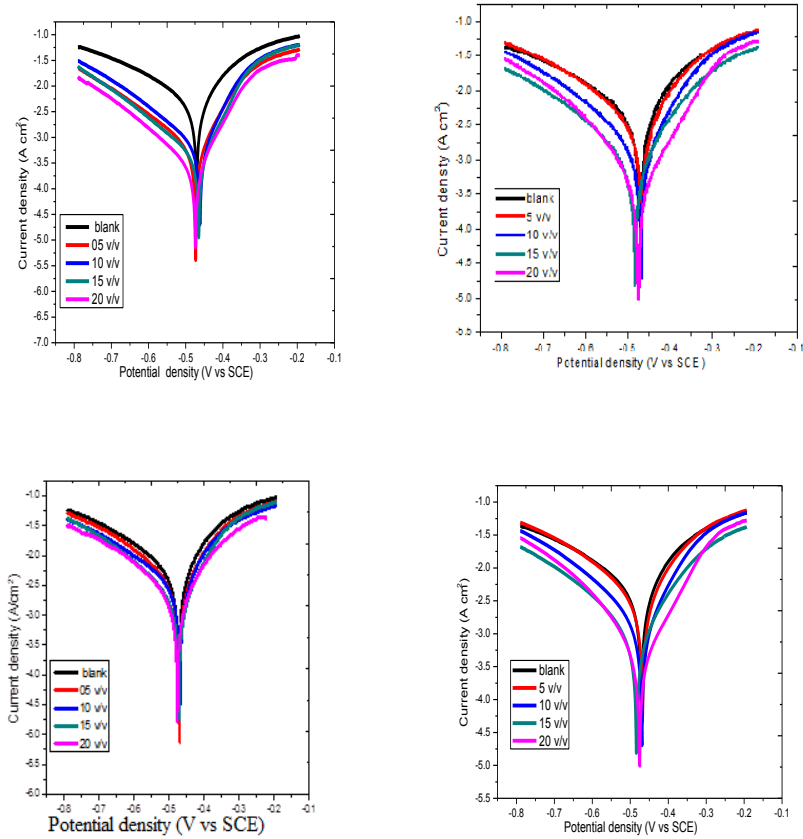
SS seeds	Blank	-	$5.2 \times 10^{-3}$	199	140	*	-	$1.5 \times 10^{-4}$	128	87	*
	5	-	$4.5 \times 10^{-4}$	174	70	86.40	-	$2.0 \times 10^{-8}$	85	123	86.66
	10	-	$6.1 \times 10^{-4}$	146	94	94.67	-	$1.5 \times 10^{-7}$	89	126	90.00
	15	-	$4.6 \times 10^{-4}$	145	91	80.55	-	$1.3 \times 10^{-7}$	88	114	91.34
	20	-	$2.3 \times 10^{-4}$	136	74	97.86	-	$0.6 \times 10^{-7}$	120	86	96.89



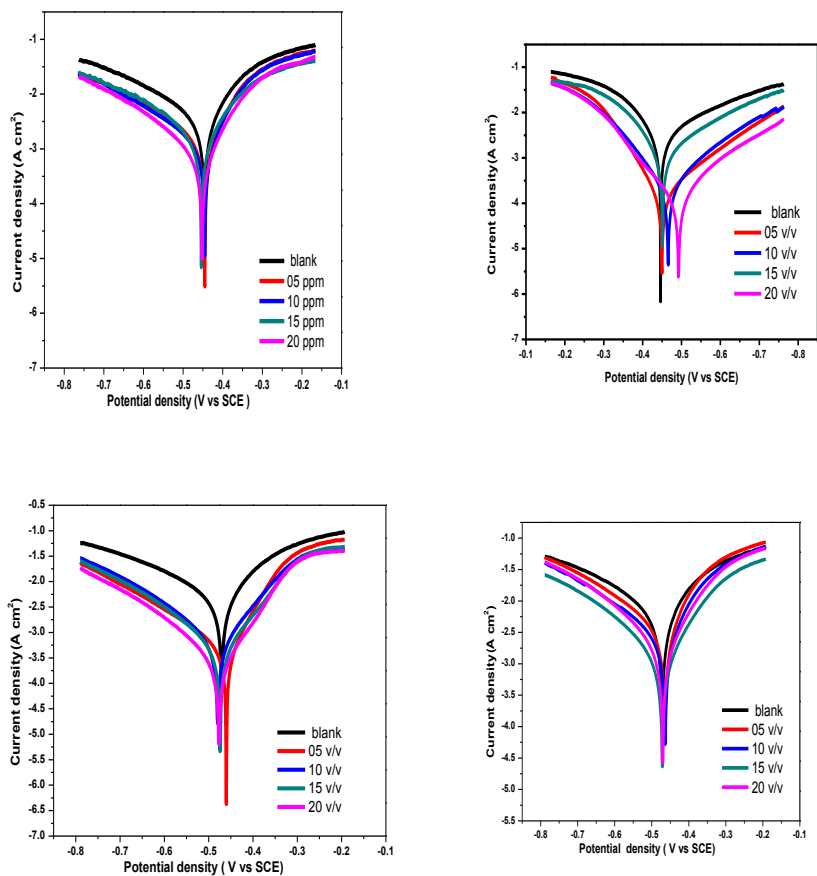
**Fig. 39** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of *Madhuca Longifolia* (aqueous) extracts of (a) leaves (b) barks (c) fruits (d) seeds peel



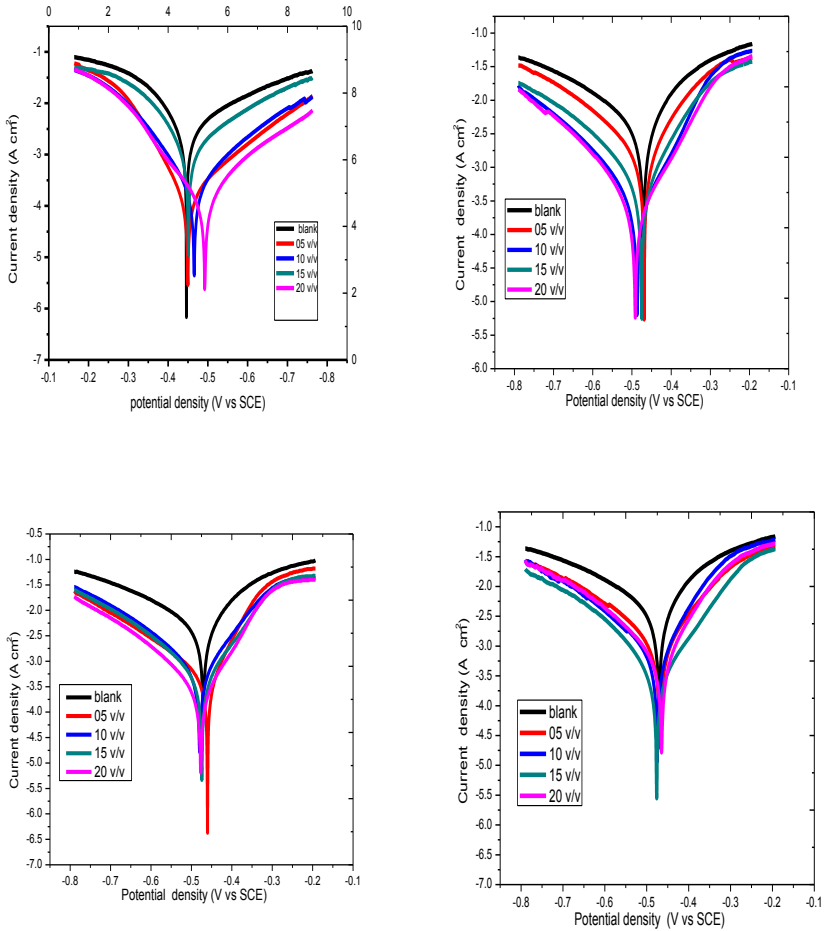
**Fig. 40** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of *Gloriosa Superba* Linn (aqueous) extracts of (a) leaves (b) stems (c) flowers (d) tubers



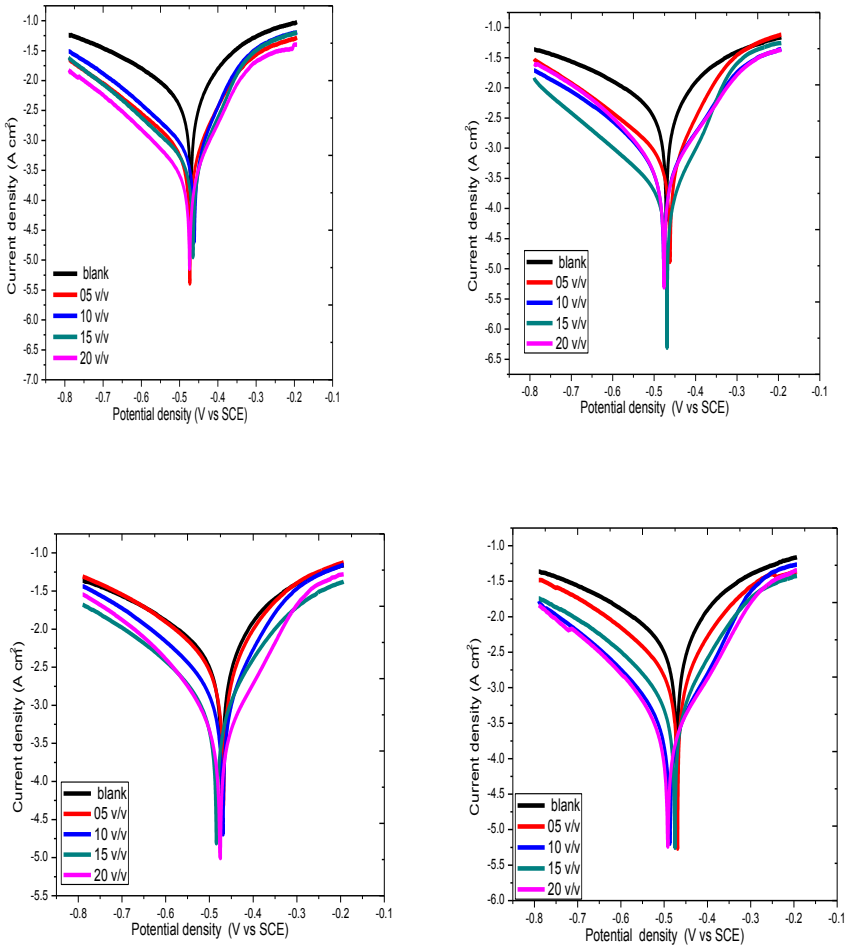
**Fig.41** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of PD (aqueous) extracts of (a) leaves (b) barks (c) fruits (d) seeds



**Fig. 42** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of Alangium lamarckii (aqueous) extracts of (a) leaves (b) barks (c) fruits (d) seeds

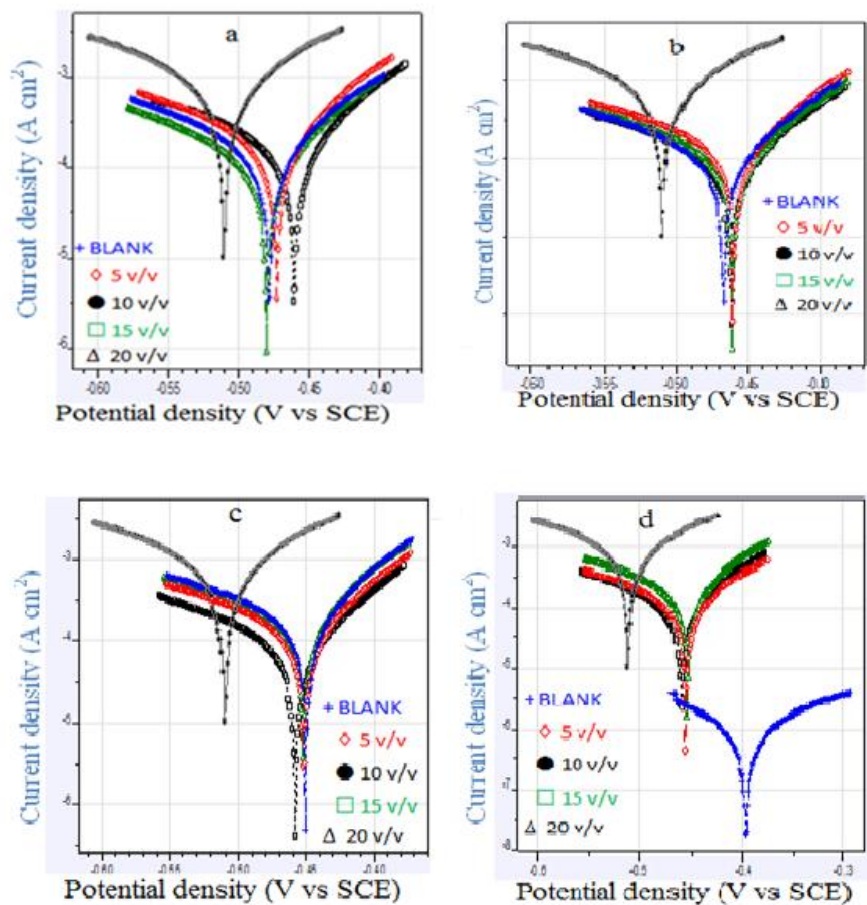


**Fig. 43** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of *Holoptelea Integrifolia* (aqueous) extracts of (a) leaves (b) barks (c) flowers (d) seeds

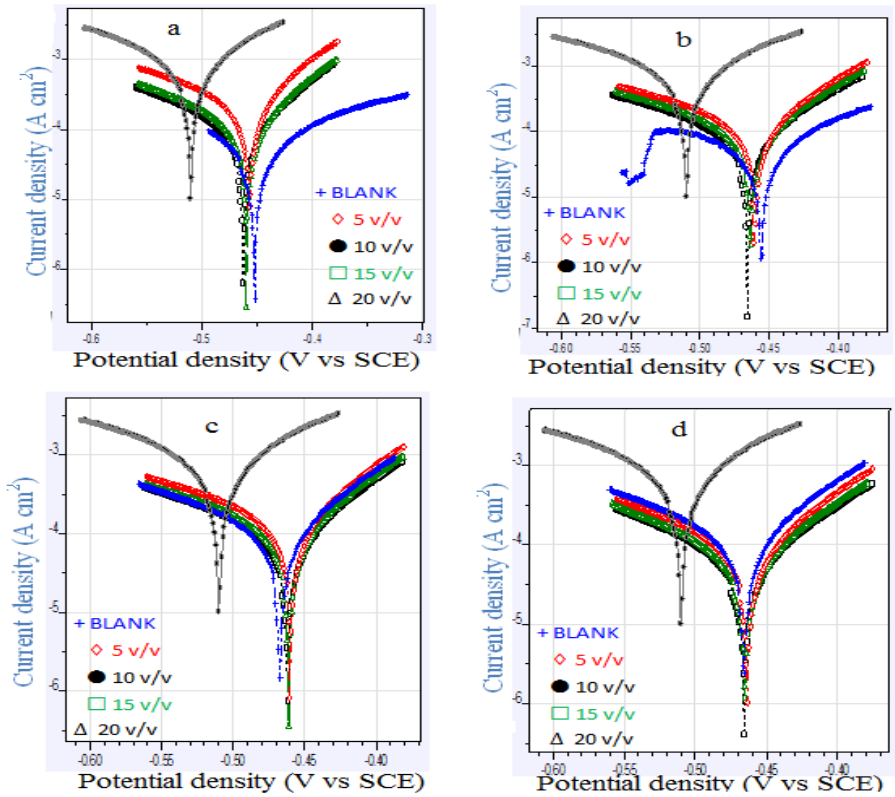


**Fig. 44** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of SS (aqueous) extracts of (a) leaves (b) barks (c) fruits (d) seeds

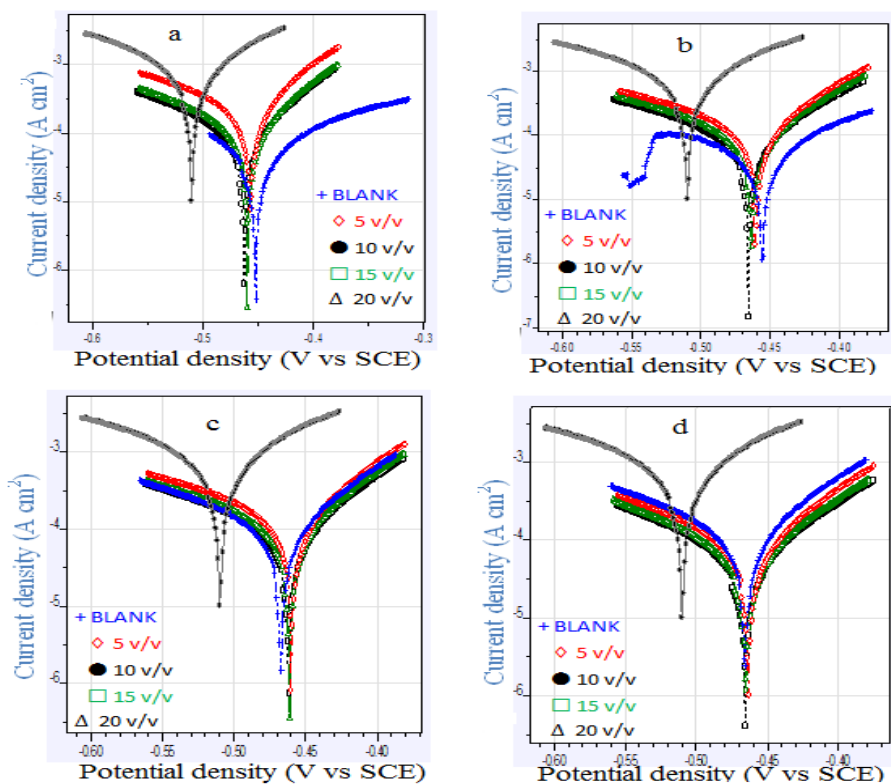




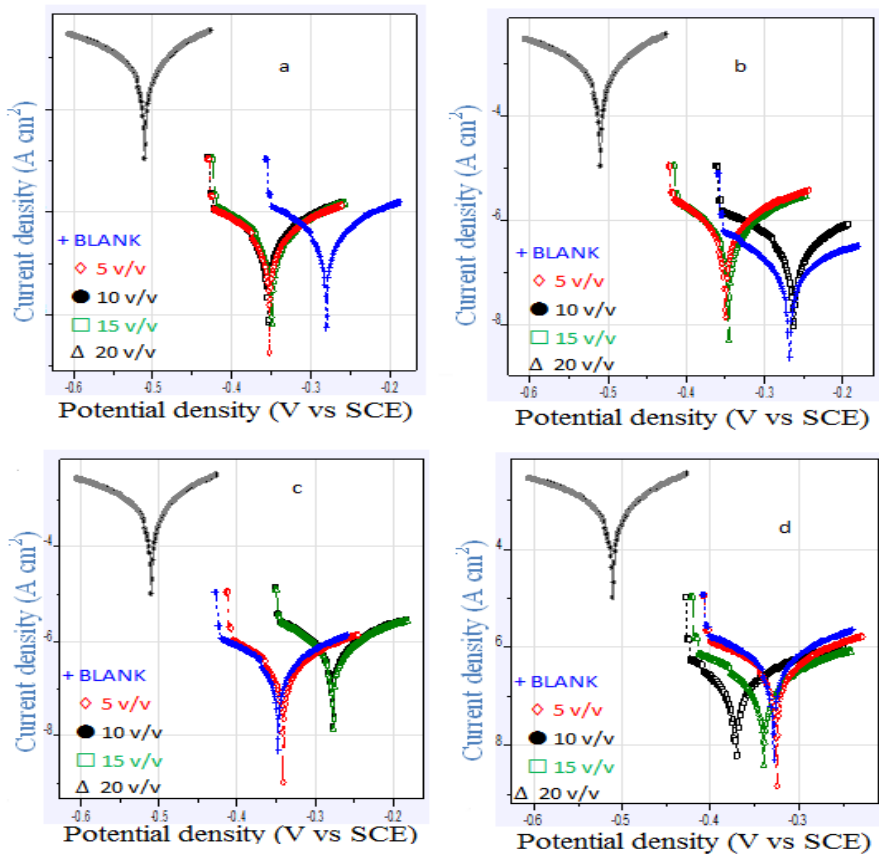
**Fig. 45** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of Madhuca Longifolia (alcoholic) extracts of (a) leaves (b) barks (c) fruits (d) seed peels



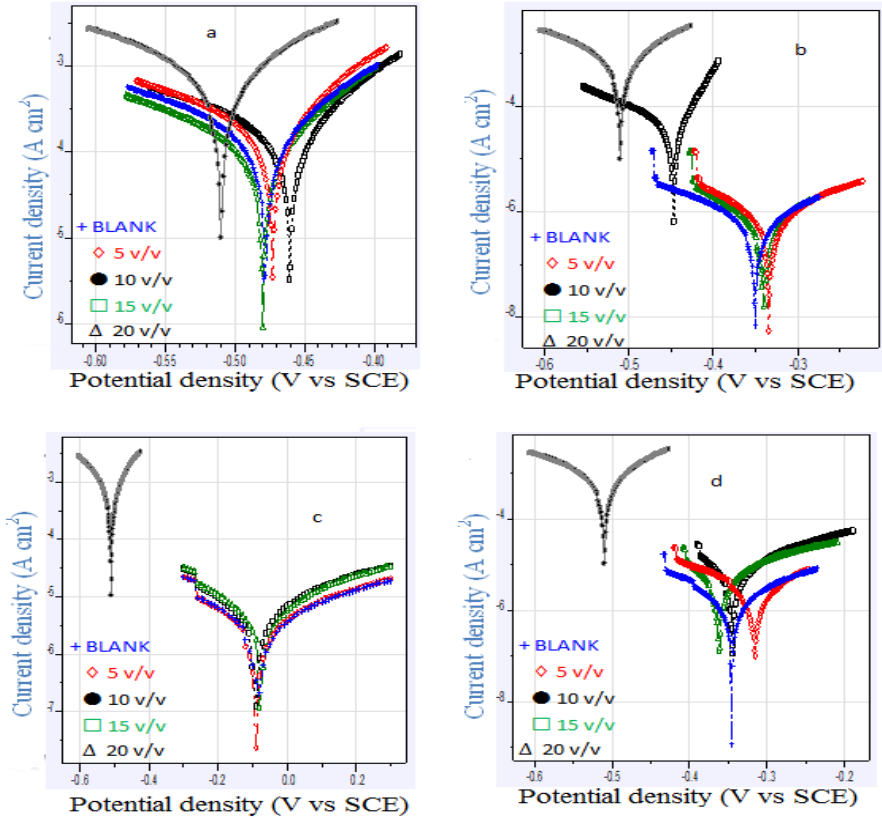
**Fig. 46** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of Gloriosa Superba Linn (alcoholic) extracts of (a) leaves (b) stems (c) flowers (d) tubers



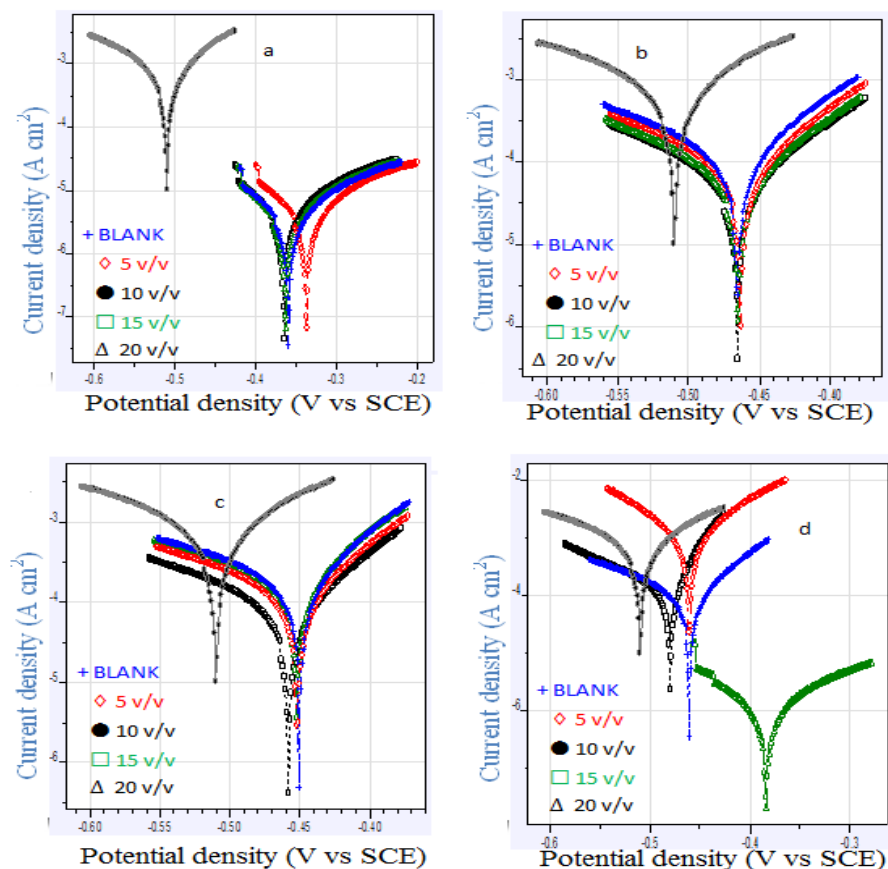
**Fig. 47** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of Pithecellobium Dulce (alcoholic) extracts of (a) leaves (b) barks (c) fruits (d) seeds



**Fig.48** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of *Alangium lamarckii* (alcoholic) extracts of (a) leaves (b) barks (c) fruits (d) seeds



**Fig. 49** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of *Holoptelea Integrifolia* (alcoholic) extracts of (a) leaves (b) barks (c) flowers (d) seeds



**Fig. 50** Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of SS (alcoholic) extracts of (a) leaves (b) barks (c) fruits (d) seeds

## 5.4. Electrochemical impedance studies

Impedance spectroscopy is one of the most simple and consistent techniques and also used to study the characterization of electrode (surface) behaviour in 1N HCl solution in the absence and presence of the plants (aqueous and alcoholic) extracts at room temperature are shown in **Figures 51 - 62**. Nyquist plot over a wide range of frequency was obtained after 20 min. Figures 51 – 62 showed the Nyquist plots of various parts of plants extracts like leaves, flowers, fruits, barks (tubers) and seed peels or stems at various concentrations. The different corrosion parameters derived from EIS measurement are presented in **Tables 22 - 27**. It is worth noting that the presence of extract did not alter the profiles of the impedance spectra show a single semicircle. It is evident from the data shown in Tables that the values of  $R_{ct}$  are increased

(formation of protective film) and  $C_{dl}$  values are decreased in the presence of plant extract could be attributed to the adsorption of the phytoconstituents or presence of plant extract over the mild steel surface as organic compounds. This indicates that the adsorption mainly controls the corrosion of mild steel surface retards the electron transfer reaction and form strong protective film. *Yan li et al [226]* studied that the irregular value of  $C_{dl}$  at the inhibitor concentration was not defined.

Nyquist plots with no loops suggest that the mild steel – inhibition system under  $R_{ct}$  control and the inhibitor is selectively adsorbed on the surface of the mild steel. It can be expected that the  $R_{ct}$  value enhanced with both extract inhibitor concentration and consequently the IE increases. Alcoholic extract of Nyquist plots [see Fig. 57-62] are not perfect (depressed) semi circles. *Jutter et al [566]* studied that this type of behaviour was attributed to metal surface roughness. The result obtained from the polarization region in acid - alcoholic solution was in *good agreement with those obtained from the EIS, with slight variation*. However, deviation from slightly depressed nature of semicircles (due to the presence of pores on the inhibitor on the electrode surface) indicated that the *extracts inhomogeneity of roughness* on the mild steel surface. This increase in size of semicircle as the inhibitor concentration increase demonstrates the corrosion inhibition properties of these alcoholic extract. Thus, the inhibitors do not alter the electrochemical reaction responsible for corrosion; but inhibit corrosion primarily through adsorption of inhibitor molecules on the metal surface.

As seen from the *Table 22*, the maximum  $R_{ct}$  value of (51.008, 15.452, 103.26, 32.093)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $1.19 \times 10^{-4}$ ,  $2.08 \times 10^{-3}$ ,  $4.25 \times 10^{-5}$ ,  $4.44 \times 10^{-4}$ )  $\mu \text{ F/cm}^2$  were obtained at the optimum concentration of *ML* plant of (leaves, barks, fruits, seeds peels) aqueous extract, which gave the maximum inhibition efficiency of (83.88, 57.41, 90.86 and 70.28 %) respectively. The same experiment was repeated in the presence of alcoholic extract (same plant, same parts) and was found to be the  $R_{ct}$  value of (60.00, 70.60, 124.60, 98.81)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $1.01 \times 10^{-6}$ ,  $1.4 \times 10^{-4}$ ,  $5.4 \times 10^{-5}$ ,  $5.1 \times 10^{-6}$ )  $\mu \text{ F/cm}^2$ , which gave the maximum inhibition efficiency of (65.55, 70.67, 83.38 and 79.05 %) respectively. These observations suggest that *ML* plant extract functioned by adsorption at the metal surface thereby causing decrease in  $C_{dl}$  values and increase in  $R_{ct}$  values. The higher  $R_{ct}$  value obtained for higher inhibitor concentration suggests that a protective film is formed on the surface of the metal.

From the inspection of data listed in *Table 23*, it was observed that the maximum values of  $R_{ct}$  (66.849, 38.800, 40.866 and 49.722)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $9.82 \times 10^{-5}$ ,  $2.78 \times 10^{-4}$ ,  $2.85 \times 10^{-4}$ ,  $5.67 \times 10^{-4}$ )  $\mu \text{ F/cm}^2$  was obtained at the optimum concentration of aqueous extract of *GSL* plant for leaves, flowers, stems and tubers, which gave the maximum inhibition efficiency of (84.78, 77.75, 84.01 and 78.63 %) respectively. The same experiment was repeated in the presence of alcoholic extract (same plant, same parts) and was found to be the  $R_{ct}$  value of (53.38, 49.80, 82.40 and 72.12)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $3.3 \times 10^{-6}$ ,  $1.8 \times 10^{-7}$ ,  $6.1 \times 10^{-6}$ ,  $6.8 \times 10^{-7}$ )  $\mu \text{ F/cm}^2$ , which gave the maximum inhibition efficiency of (61.22, 57.83, 74.87 and 71.29 %) respectively.

It should be noted from the *Table 24* that the highest  $R_{ct}$  values of (510.09,

57.915, 18.471 and 92.053)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $1.978 \times 10^{-2}$ ,  $1.287 \times 10^{-4}$ ,  $1.149 \times 10^{-3}$ ,  $5.408 \times 10^{-5}$ )  $\mu \text{ F/cm}^2$  was obtained at the optimum concentration of aqueous extract of *PD* plants (*leaves, barks, fruits and seeds*), which gave the maximum inhibition efficiency of (89.26, 78.92, 83.11 and 71.20 %) respectively. The same experiment was repeated in the presence of alcoholic extract (*same plant, same parts*) and was found to be the  $R_{ct}$  value of (108.60, 80.80, 116.12, 95.90)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $5.9 \times 10^{-5}$ ,  $6.0 \times 10^{-5}$ ,  $9.6 \times 10^{-6}$ ,  $1.0 \times 10^{-5}$ )  $\mu \text{ F/cm}^2$ , which gave the maximum inhibition efficiency of (80.93, 74.38, 82.17 and 78.41 %) respectively.

**Table 25** shows that the maximum  $R_{ct}$  values (31.03, 72.73, 203.40, 28.95)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $4.487 \times 10^{-4}$ ,  $8.604 \times 10^{-5}$ ,  $1.026 \times 10^{-5}$ ,  $6.961 \times 10^{-4}$ )  $\mu \text{ F/cm}^2$  were obtained at the optimum concentration of aqueous extracts of *AL* plant (*leaves, barks, fruits and seeds*), which gave the maximum inhibition efficiency of (75.53, 91.22, 96.32 and 83.87 %) respectively. The same experiment was repeated in the presence of alcoholic extract (*same plant, same parts*) was found to be the  $R_{ct}$  value of (66.849, 38.800, 40.866 and 49.722)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $9.82 \times 10^{-5}$ ,  $2.78 \times 10^{-4}$ ,  $2.85 \times 10^{-4}$ ,  $1.81 \times 10^{-4}$ )  $\mu \text{ F/cm}^2$ , which gave the maximum inhibition efficiency of (84.78, 73.62, 81.77 and 73.64 %) respectively.

From the **Table 26**, it is clear that the maximum values of  $R_{ct}$  (65.453, 49.123, 62.663 and 28.959)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $9.830 \times 10^{-5}$ ,  $8.438 \times 10^{-4}$ ,  $1.67 \times 10^{-3}$  and  $2.1 \times 10^{-4}$ )  $\mu \text{ F/cm}^2$  were obtained at the optimum concentration of aqueous extract of *HI* plants (*leaves, barks, flowers and seeds*), which gave the maximum inhibition efficiency of (86.42, 73.90, 87.62 and 69.54 %) respectively. The same experiment was repeated in the presence of alcoholic extract (*same plant, same parts*) and was found to be the  $R_{ct}$  value of (57.60, 83.97, 94.27 and 64.33)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $1.19 \times 10^{-4}$ ,  $8.65 \times 10^{-5}$ ,  $7.40 \times 10^{-5}$  and  $4.55 \times 10^{-5}$ )  $\mu \text{ F/cm}^2$ , which gave the maximum inhibition efficiency of (64.07, 75.34, 79.10 and 67.82%) respectively.

As can be seen from the **Table 27**, the impedance data indicated that the maximum  $R_{ct}$  value of (145.091, 38.276, 22.006 and 72.372)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $7.185 \times 10^{-3}$ ,  $2.917 \times 10^{-4}$ ,  $4.487 \times 10^{-4}$  and  $2.385 \times 10^{-4}$ )  $\mu \text{ F/cm}^2$  was obtained at the optimum concentration of aqueous extract of *SS* plant (*leaves, barks, fruits and seeds*), which gave the maximum inhibition efficiency of (71.43, 69.85, 86.78, 70.58 %) respectively. The same experiment was repeated in the presence of alcoholic extract (*same plant, same parts*) and was found to be the  $R_{ct}$  value of (72.46, 95.96, 121.10 and 87.90)  $\Omega \text{ cm}^2$  and the minimum  $C_{dl}$  values ( $3.01 \times 10^{-5}$ ,  $5.3 \times 10^{-5}$ ,  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-7}$ )  $\mu \text{ F/cm}^2$  was obtained, which gave the maximum inhibition efficiency of (71.43, 78.42, 82.90 and 76.45 %) respectively. The results showed that the  $R_{ct}$  significantly increases with increase in concentration of the inhibitor and  $C_{dl}$  tends decrease. In fact, in the presence of the plant extracts, the charge transfer resistance ( $R_{ct}$ ) values have enhanced and the values of double layer capacitance ( $C_{dl}$ ) were brought down to the maximum extent. The decrease in  $C_{dl}$  showed that the adsorption of the inhibitor takes place on the metal surface in acidic solution. The increase in  $R_{ct}$  values is attributed to the formation of protective film at the metal solution interface.



**Table 22** Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of ML inhibitor

Aqueous extract of ML plants					Alcoholic extract of ML plants		
Parts of Madhuca Longifolia plant	Conc (v/v)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE (%)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE (%)
Madhuca Longifolia leaves	Blank	8.221	$6.79 \times 10^{-4}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	9.182	$6.66 \times 10^{-4}$	11.68	52.30	$9.1 \times 10^{-5}$	60.42
	10	19.202	$1.20 \times 10^{-4}$	57.18	49.63	$2.1 \times 10^{-5}$	58.29
	15	31.031	$4.49 \times 10^{-4}$	73.50	59.32	$5.3 \times 10^{-1}$	65.10
	20	51.008	$1.74 \times 10^{-4}$	83.88	60.00	$1.0 \times 10^{-6}$	65.55
Madhuca Longifolia barks	Blank	6.581	$1.19 \times 10^{-2}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	10.236	$5.10 \times 10^{-3}$	39.82	21.95	$4.6 \times 10^{-5}$	05.69
	10	10.966	$4.29 \times 10^{-3}$	40.45	60.18	$8.1 \times 10^{-5}$	65.60
	15	13.969	$2.29 \times 10^{-3}$	52.88	70.60	$1.2 \times 10^{-4}$	70.67
	20	15.452	$2.08 \times 10^{-3}$	57.41	68.40	$1.4 \times 10^{-4}$	69.73
Madhuca Longifolia fruits	Blank	9.436	$6.89 \times 10^{-3}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	18.225	$1.65 \times 10^{-3}$	48.22	73.20	$6.6 \times 10^{-5}$	71.72
	10	83.448	$7.28 \times 10^{-5}$	88.69	99.30	$6.2 \times 10^{-5}$	79.15
	15	42.037	$2.90 \times 10^{-4}$	77.55	113.7	$5.9 \times 10^{-5}$	81.79
	20	103.26	$4.25 \times 10^{-5}$	90.86	124.6	$5.4 \times 10^{-5}$	83.38
Madhuca Longifolia seed peels	Blank	9.633	$6.43 \times 10^{-3}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	16.560	$1.66 \times 10^{-3}$	41.82	31.10	$5.9 \times 10^{-5}$	33.44
	10	32.420	$4.44 \times 10^{-4}$	70.28	67.60	$1.0 \times 10^{-5}$	69.37
	15	24.093	$8.60 \times 10^{-4}$	60.01	74.67	$8.2 \times 10^{-5}$	72.27
	20	22.126	$8.47 \times 10^{-4}$	56.46	98.81	$5.1 \times 10^{-6}$	79.05

**Table 23** EIS parameter for MS in 1N HCl acid solution without and with the varied concentration of GSL plant extract

Aqueous extract of GSL plants					Alcoholic extract of GSL plants		
Parts of GSL plant	Concentration (v/v)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE(%)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE (%)
Gloriosa Superba Linn leaves	Blank	10.622	6.2385	*	20.70	$1.0 \times 10^{-5}$	*
	5	23.091	$9.72 \times 10^{-4}$	55.96	33.09	$8.2 \times 10^{-5}$	37.44
	10	25.416	$6.57 \times 10^{-4}$	59.99	35.42	$6.4 \times 10^{-5}$	41.55
	15	66.849	$9.82 \times 10^{-5}$	84.78	46.85	$7.2 \times 10^{-5}$	55.81
	20	32.213	$4.43 \times 10^{-4}$	68.43	53.38	$3.3 \times 10^{-6}$	61.22
Gloriosa Superba Linn flowers	Blank	10.622	6.2385	*	20.70	$1.0 \times 10^{-5}$	*
	5	29.125	$5.29 \times 10^{-4}$	70.36	29.14	$5.9 \times 10^{-7}$	28.96
	10	22.899	$9.35 \times 10^{-4}$	62.30	42.90	$6.5 \times 10^{-7}$	52.91
	15	14.960	1.8530	42.29	48.67	$1.3 \times 10^{-7}$	57.46
	20	38.800	$2.78 \times 10^{-4}$	77.75	49.80	$1.8 \times 10^{-7}$	57.83

(Continued)

**Table 23 (Continued)**

<i>Gloriosa Superba Linn Stems</i>	Blank	10.622	6.2385	*	20.70	$1.0 \times 10^{-5}$	*
	5	18.093	1.6131	63.88	28.91	$1.1 \times 10^{-7}$	28.39
	10	25.926	$7.29 \times 10^{-4}$	74.79	52.93	$4.3 \times 10^{-6}$	60.89
	15	28.411	$7.51 \times 10^{-4}$	77.00	82.40	$6.1 \times 10^{-6}$	74.87
	20	40.866	$2.85 \times 10^{-4}$	84.01	60.87	$4.9 \times 10^{-8}$	65.99
<i>Gloriosa Superba Linn tubers</i>	Blank	10.622	6.2385	*	20.70	$1.0 \times 10^{-5}$	*
	5	49.722	$1.81 \times 10^{-4}$	78.63	38.27	$1.9 \times 10^{-5}$	45.91
	10	17.856	3.5388	40.51	47.57	$3.4 \times 10^{-7}$	56.48
	15	28.342	$5.67 \times 10^{-4}$	62.52	58.89	$5.8 \times 10^{-7}$	64.84
	20	25.597	$7.51 \times 10^{-4}$	58.50	72.12	$6.8 \times 10^{-7}$	71.29

**Table 24** Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of PD inhibitor

Aqueous extract of PD plants					Alcoholic extract of PD plants		
Parts of PD plant	Conc. (v/v)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE(%)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE (%)
Pithecellobium Dulce leaves	Blank	115.40	$8.312 \times 10^{-2}$	*	20.70	$1.0 \times 10^{-5}$	*
	5	150.40	$3.667 \times 10^{-2}$	62.08	52.30	$9.1 \times 10^{-5}$	60.42
	10	249.80	$2.424 \times 10^{-2}$	70.84	94.74	$1.0 \times 10^{-4}$	78.15
	15	407.30	$2.200 \times 10^{-2}$	82.48	67.30	$5.6 \times 10^{-5}$	69.24
	20	510.09	$1.978 \times 10^{-2}$	89.26	108.6	$5.9 \times 10^{-5}$	80.93
Pithecellobium Dulce barks	Blank	6.742	$1.110 \times 10^{-2}$	*	20.70	$1.0 \times 10^{-5}$	*
	5	38.712	$2.892 \times 10^{-4}$	69.34	56.40	$6.8 \times 10^{-6}$	63.29
	10	27.075	$5.910 \times 10^{-4}$	60.29	73.60	$9.4 \times 10^{-6}$	71.87
	15	41.087	$2.556 \times 10^{-4}$	40.03	65.57	$5.2 \times 10^{-5}$	68.43
	20	57.915	$1.287 \times 10^{-4}$	78.92	80.80	$6.0 \times 10^{-5}$	74.38
Pithecellobium Dulce fruits	Blank	7.129	$7.203 \times 10^{-3}$	*	20.70	$1.0 \times 10^{-5}$	*
	5	9.827	$4.30 \times 10^{-3}$	61.04	22.95	$5.5 \times 10^{-5}$	09.80
	10	12.802	$2.70 \times 10^{-3}$	75.00	62.20	$3.1 \times 10^{-5}$	66.72
	15	14.328	$1.865 \times 10^{-3}$	76.98	103.10	$6.8 \times 10^{-6}$	79.92
	20	18.471	$1.149 \times 10^{-3}$	83.11	116.12	$9.6 \times 10^{-6}$	82.17
Pithecellobium Dulce seeds	Blank	8.739	$7.239 \times 10^{-3}$	*	20.70	$1.0 \times 10^{-5}$	*
	5	26.30	$6.232 \times 10^{-4}$	71.20	29.60	$1.9 \times 10^{-5}$	30.06
	10	56.351	$1.563 \times 10^{-4}$	39.09	69.10	$8.0 \times 10^{-6}$	70.04
	15	92.053	$5.408 \times 10^{-5}$	64.44	95.90	$1.0 \times 10^{-5}$	78.41
	20	55.698	$1.286 \times 10^{-4}$	57.59	82.40	$6.7 \times 10^{-6}$	74.87

**Table 25** Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of AL inhibitor

Aqueous extract of AL plants					Alcoholic extract of AL plants		
Parts of Alangium lamarckii plant	Conc. (v/v)	R <sub>ct</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	IE (%)	R <sub>ct</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	IE (%)
Alangium lamarckii leaves	Blank	7.64	6.763x10 <sup>-3</sup>	*	10.622	6.2385	*
	5	21.23	9.549x10 <sup>-4</sup>	64.06	23.091	9.72x10 <sup>-4</sup>	55.96
	10	22.06	8.723x10 <sup>-4</sup>	65.27	25.416	6.57x10 <sup>-4</sup>	59.99
	15	15.46	1.241x10 <sup>-3</sup>	50.58	66.849	9.82x10 <sup>-5</sup>	84.78
	20	31.03	4.487x10 <sup>-4</sup>	75.53	32.213	4.43x10 <sup>-4</sup>	68.43
Alangium lamarckii barks	Blank	6.38	1.162x10 <sup>-3</sup>	*	10.622	6.2385	*
	5	36.67	3.183x10 <sup>-4</sup>	82.59	29.125	5.29x10 <sup>-4</sup>	65.08
	10	31.75	4.246x10 <sup>-4</sup>	79.89	22.899	9.35x10 <sup>-4</sup>	52.80
	15	42.88	2.358x10 <sup>-4</sup>	85.11	14.960	1.8530	40.99
	20	72.73	8.604x10 <sup>-5</sup>	91.22	38.800	2.78x10 <sup>-4</sup>	73.62
Alangium lamarckii fruits	Blank	7.46	6.835x10 <sup>-3</sup>	*	10.622	6.2385	*
	5	111.2	3.481x10 <sup>-5</sup>	93.28	18.093	1.6131	60.25
	10	82.98	6.332x10 <sup>-5</sup>	90.99	25.926	7.29x10 <sup>-4</sup>	72.65
	15	203.4	1.026x10 <sup>-5</sup>	96.32	28.411	7.51x10 <sup>-4</sup>	75.33
	20	166.3	1.621x10 <sup>-5</sup>	95.51	40.866	2.85x10 <sup>-4</sup>	81.77
Alangium lamarckii seeds	Blank	4.670	2.148x10 <sup>-2</sup>	*	10.622	6.2385	*
	5	8.557	6.276x10 <sup>-3</sup>	45.43	49.722	1.81x10 <sup>-4</sup>	73.64
	10	10.06	4.140x10 <sup>-3</sup>	53.57	17.856	3.5388	37.00
	15	28.95	6.961x10 <sup>-4</sup>	83.87	28.342	5.67x10 <sup>-4</sup>	59.42
	20	14.37	2.194x10 <sup>-3</sup>	67.54	25.597	7.51x10 <sup>-4</sup>	56.51

**Table 26** Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of HI inhibitor

Aqueous extract of HI plants					Alcoholic extract of HI plants		
Parts of plant	Conc. (v/v)	R <sub>ct</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	IE (%)	R <sub>ct</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	IE (%)
<i>Holoptelea Integrifolia</i> leaves	Blank	8.935	7.047 x10 <sup>-3</sup>	*	20.70	1.57x10 <sup>-5</sup>	*
	5	22.734	1.007 x10 <sup>-3</sup>	60.66	42.90	4.09x10 <sup>-5</sup>	51.74
	10	34.009	6.870 x10 <sup>-4</sup>	64.99	52.40	1.66x10 <sup>-4</sup>	60.49
	15	65.453	9.830 x10 <sup>-5</sup>	86.42	54.50	2.97x10 <sup>-5</sup>	62.01
	20	31.098	4.417 x10 <sup>-4</sup>	71.03	57.60	1.19x10 <sup>-4</sup>	64.07
<i>Holoptelea Integrifolia</i> barks	Blank	9.295	7.047 x10 <sup>-3</sup>	*	20.70	1.57x10 <sup>-5</sup>	*
	5	49.123	1.826 x10 <sup>-4</sup>	59.11	49.71	7.24x10 <sup>-5</sup>	56.95
	10	7.803	8.046 x10 <sup>-3</sup>	60.36	62.62	8.51x10 <sup>-5</sup>	66.94
	15	27.188	5.810 x10 <sup>-3</sup>	50.99	75.34	8.44x10 <sup>-5</sup>	72.52
	20	22.421	8.438 x10 <sup>-4</sup>	73.90	83.97	8.65x10 <sup>-5</sup>	75.34
<i>Holoptelea Integrifolia</i> flowers	Blank	8.418	7.315 x10 <sup>-3</sup>	*	20.70	1.57x10 <sup>-5</sup>	*
	5	32.14	4.231 x10 <sup>-4</sup>	33.89	56.46	2.50x10 <sup>-4</sup>	63.33
	10	31.609	4.56 x10 <sup>-4</sup>	57.90	61.68	1.26x10 <sup>-4</sup>	66.43
	15	62.663	1.170 x10 <sup>-4</sup>	80.08	50.73	7.41x10 <sup>-5</sup>	59.19
	20	17.089	1.670 x10 <sup>-3</sup>	87.62	94.27	7.40x10 <sup>-5</sup>	79.10

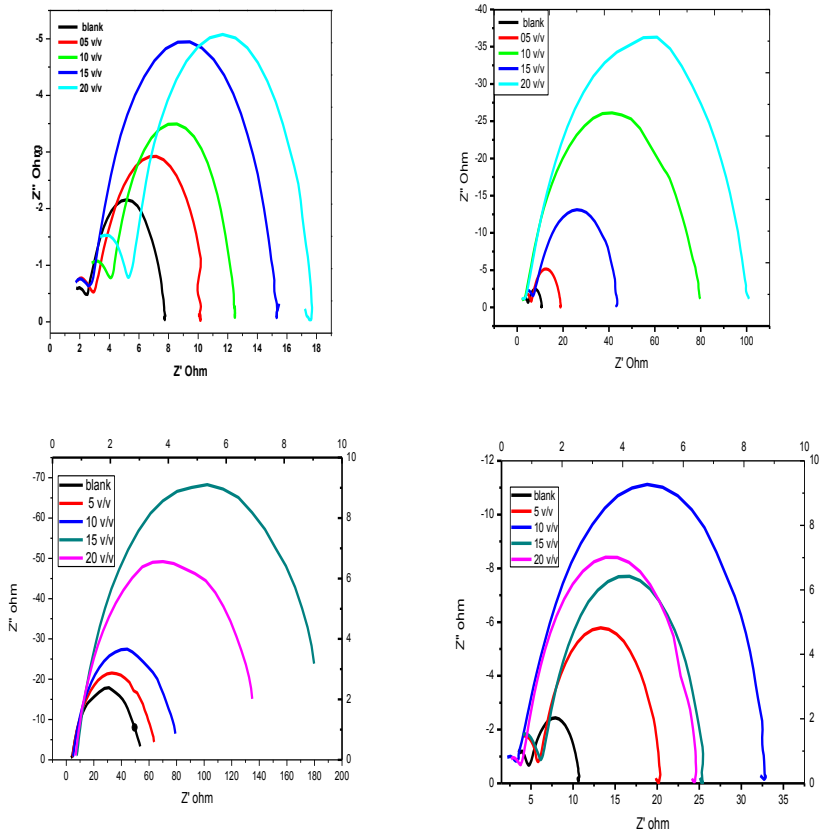
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Table 26 (Continued)

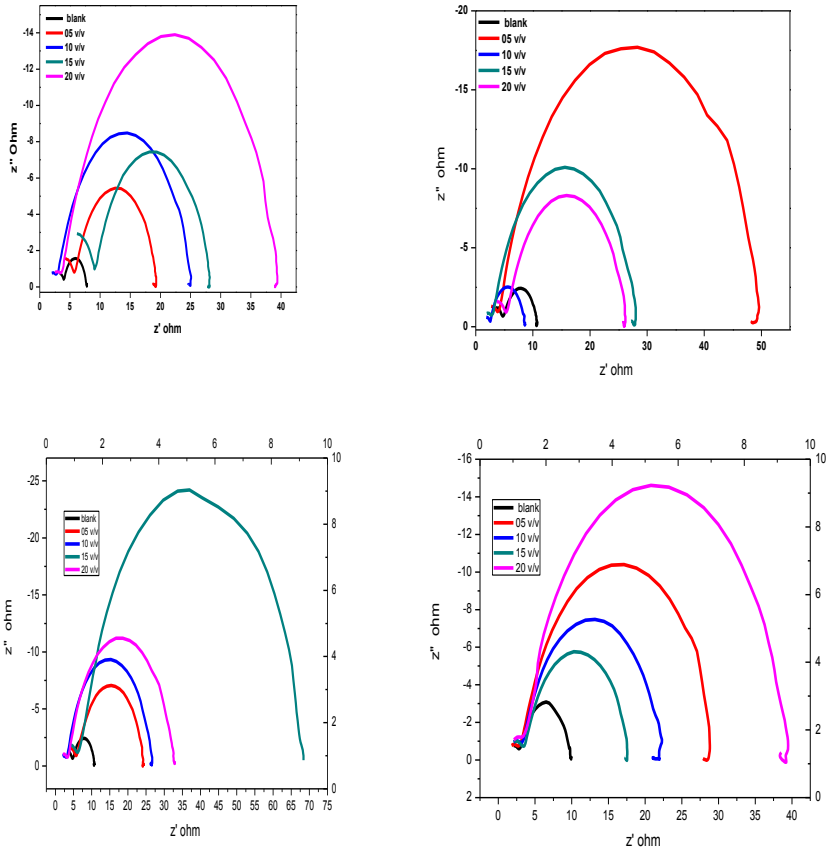
<i>Holoptelea Integrifolia</i> seeds	Blank	4.670	$2.148 \times 10^{-2}$	*	20.27	$1.57 \times 10^{-5}$	*
	5	8.557	$6.276 \times 10^{-3}$	64.09	64.33	$4.55 \times 10^{-5}$	67.82
	10	10.060	$4.140 \times 10^{-3}$	50.21	57.53	$2.47 \times 10^{-5}$	64.76
	15	28.959	$6.961 \times 10^{-4}$	65.89	57.23	$2.29 \times 10^{-5}$	64.58
	20	14.375	$2.194 \times 10^{-4}$	69.54	57.11	$4.95 \times 10^{-1}$	64.57

Table 27 Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of SS inhibitor

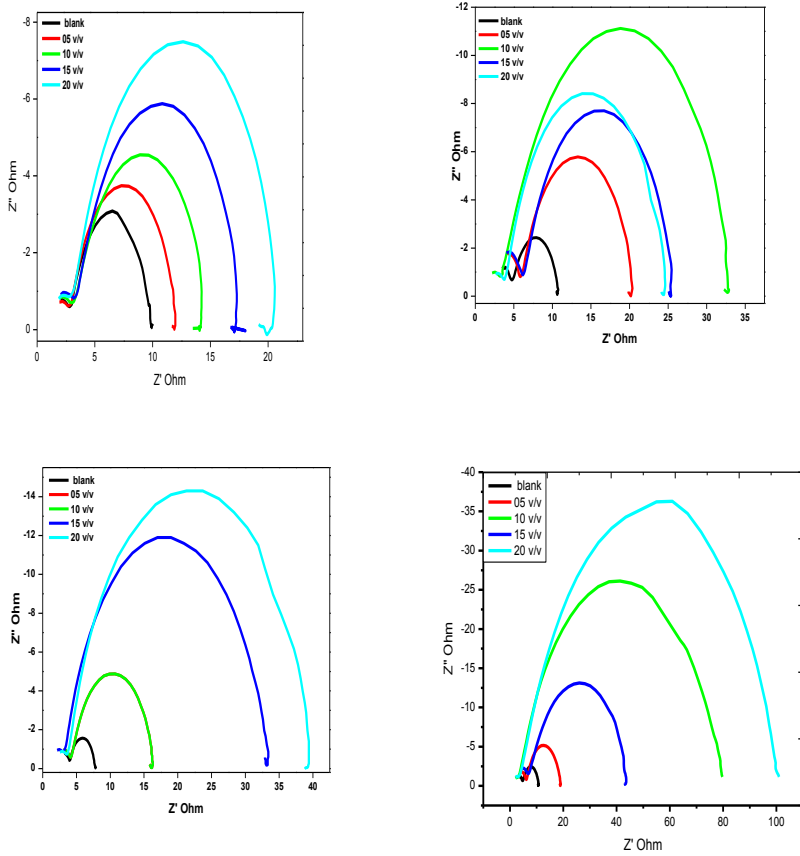
Aqueous extract of SS plants					Alcoholic extract of SS plants		
Parts of SS plant	Concentration (v/v)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE (%)	$R_{ct}$ (ohm $cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )	IE (%)
SS leaves	Blank	41.763	$8.312 \times 10^{-3}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	69.669	$8.094 \times 10^{-3}$	15.85	35.60	$4.6 \times 10^{-5}$	41.85
	10	78.871	$8.714 \times 10^{-3}$	32.27	45.23	$6.1 \times 10^{-1}$	54.23
	15	97.652	$7.974 \times 10^{-3}$	47.33	64.90	$4.6 \times 10^{-5}$	68.10
	20	145.091	$7.185 \times 10^{-3}$	71.43	72.46	$3.0 \times 10^{-5}$	71.43
SS Barks	Blank	05.574	$1.817 \times 10^{-2}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	13.318	$2.470 \times 10^{-3}$	50.29	38.30	$5.4 \times 10^{-5}$	45.95
	10	27.068	$5.995 \times 10^{-4}$	64.70	44.30	$5.9 \times 10^{-4}$	53.27
	15	32.740	$4.139 \times 10^{-4}$	53.94	95.96	$5.3 \times 10^{-5}$	78.42
	20	38.276	$2.917 \times 10^{-4}$	69.85	65.90	$1.0 \times 10^{-5}$	68.58
SS Fruits	Blank	07.642	$6.763 \times 10^{-3}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	21.239	$9.549 \times 10^{-4}$	60.19	36.30	$1.8 \times 10^{-5}$	42.97
	10	22.006	$8.723 \times 10^{-4}$	72.00	46.90	$1.8 \times 10^{-5}$	55.86
	15	15.465	$1.241 \times 10^{-3}$	74.63	94.10	$1.1 \times 10^{-5}$	78.00
	20	31.034	$4.487 \times 10^{-4}$	86.78	121.10	$1.0 \times 10^{-5}$	82.90
SS Seeds	Blank	06.384	$1.162 \times 10^{-3}$	*	20.70	$1.5 \times 10^{-5}$	*
	5	36.672	$3.183 \times 10^{-4}$	68.11	39.00	$1.4 \times 10^{-7}$	50.51
	10	31.751	$4.246 \times 10^{-4}$	39.93	56.90	$1.2 \times 10^{-5}$	63.62
	15	42.888	$2.358 \times 10^{-4}$	70.58	80.90	$2.9 \times 10^{-5}$	74.41
	20	72.732	$8.604 \times 10^{-5}$	49.56	87.90	$5.0 \times 10^{-7}$	76.45



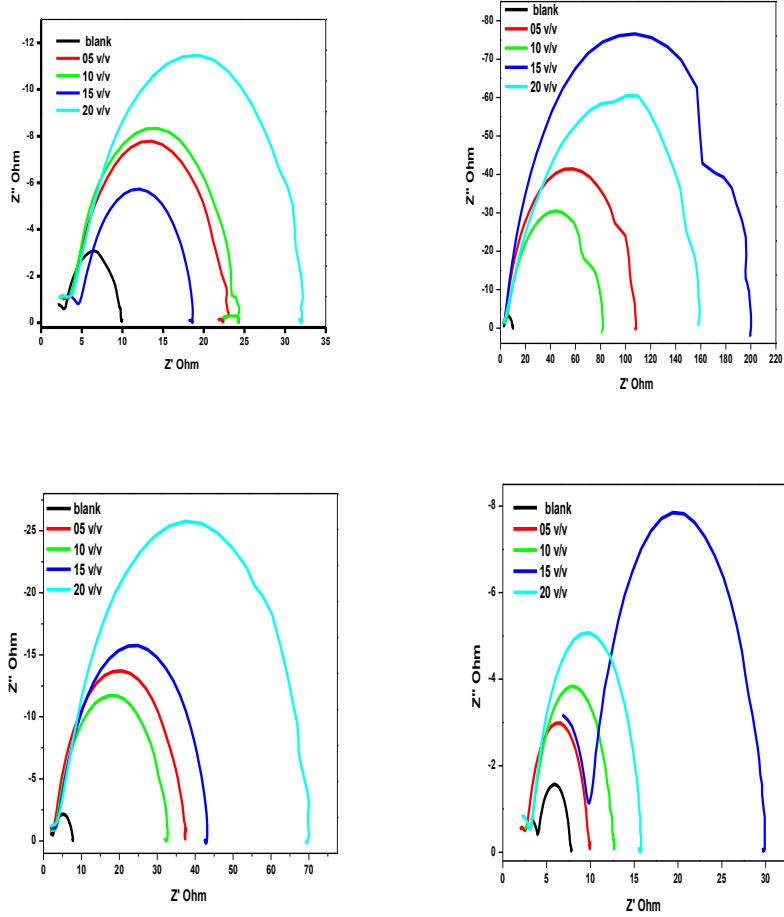
**Fig. 51** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Madhuca Longifolia* (aqueous) extract of (a) leaves (b) bark (c) fruits (d) seeds



**Fig. 52** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Gloriosa superba linn* (aqueous) extract of (a) leaves (b) stems (c) flowers (d) tubers

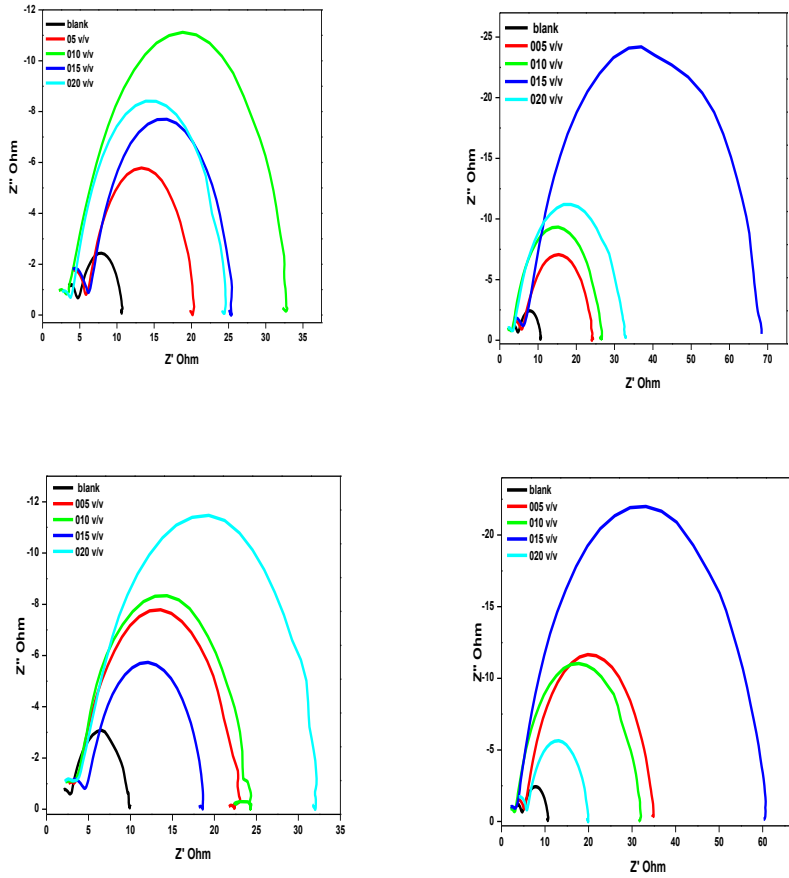


**Fig. 53** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of PD (aqueous) extract of (a) leaves (b) bark (c) fruits (d) seeds

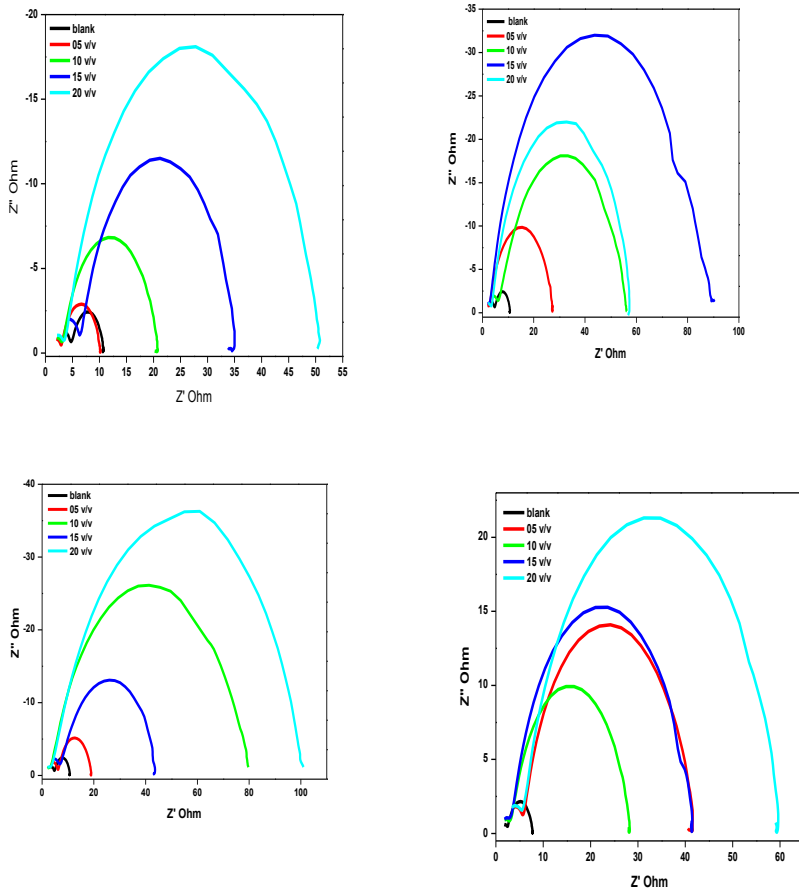


**Fig. 54** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Alangium lamarckii* (aqueous) extract of (a) leaves (b) bark (c) fruits (d) seeds

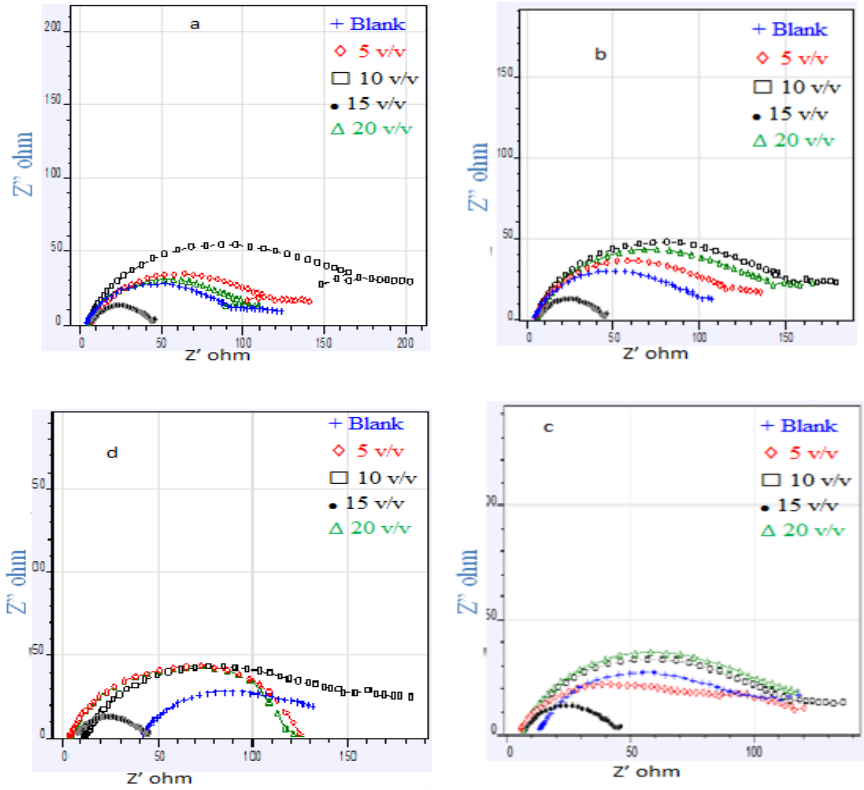




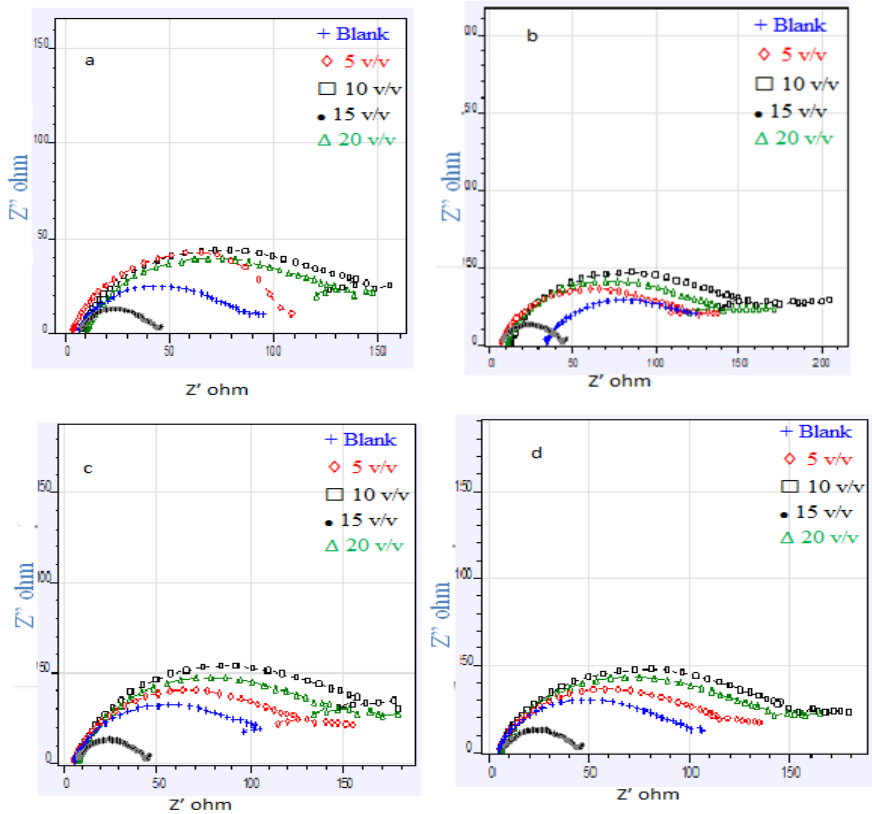
**Fig. 55** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of HI (aqueous) extract of (a) leaves (b) bark (c) flowers (d) seeds



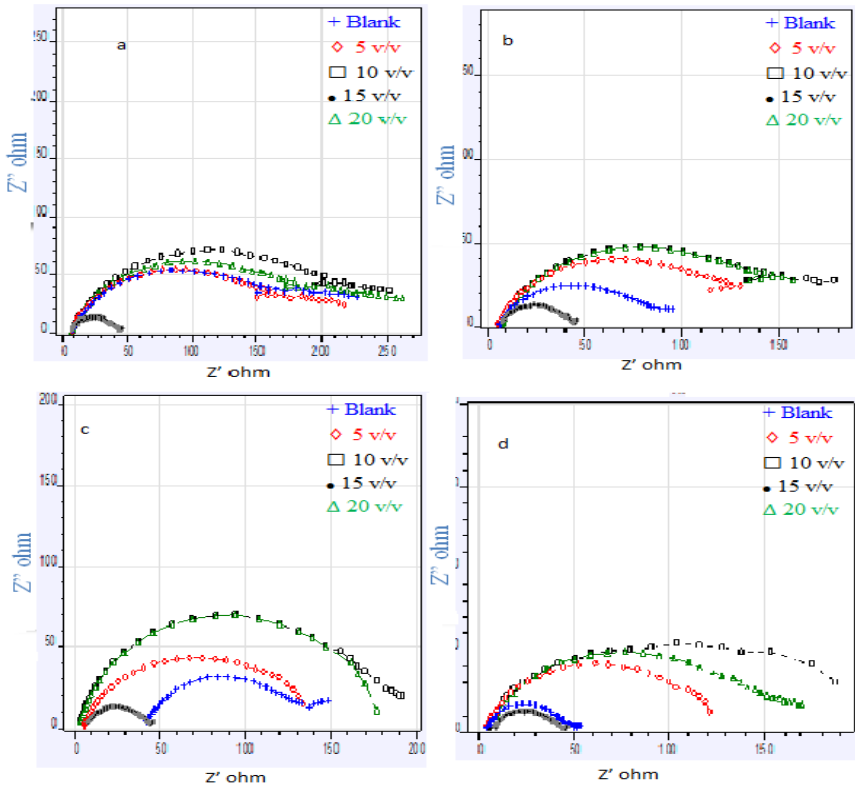
**Fig. 56** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of SS (aqueous) extract of (a) leaves (b) bark (c) fruits (d) seeds



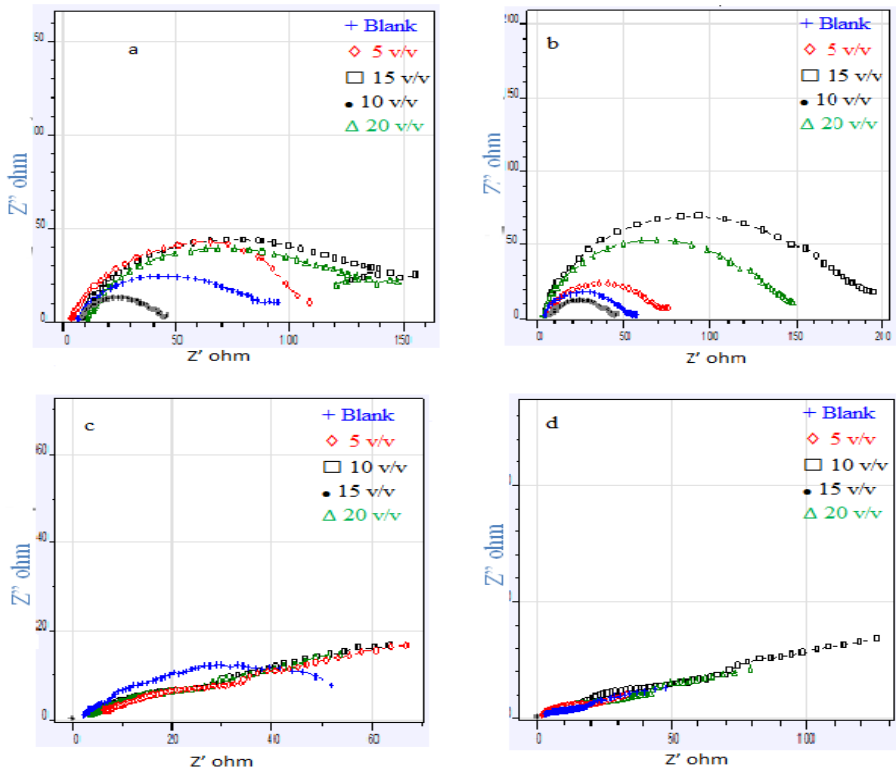
**Fig. 57** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Madhuca Longifolia* (alcoholic) extract of (a) leaves (b) bark (c) fruits (d) seed peels



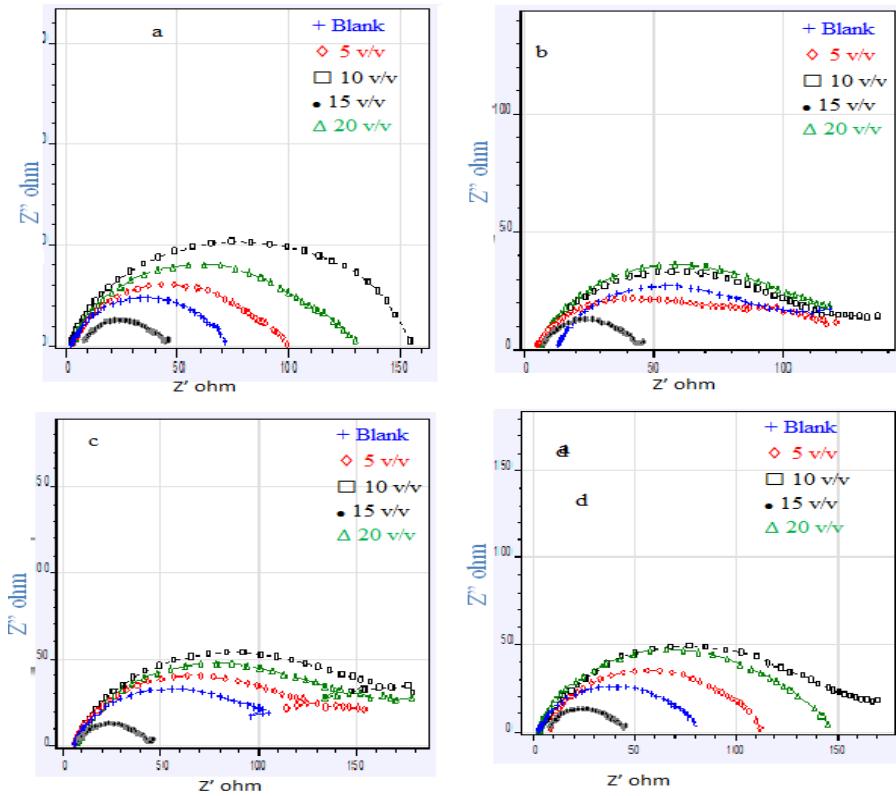
**Fig. 58** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Gloriosa superba* linn (alcoholic) extract of (a) leaves (b) stems (c) flowers (d) tubers



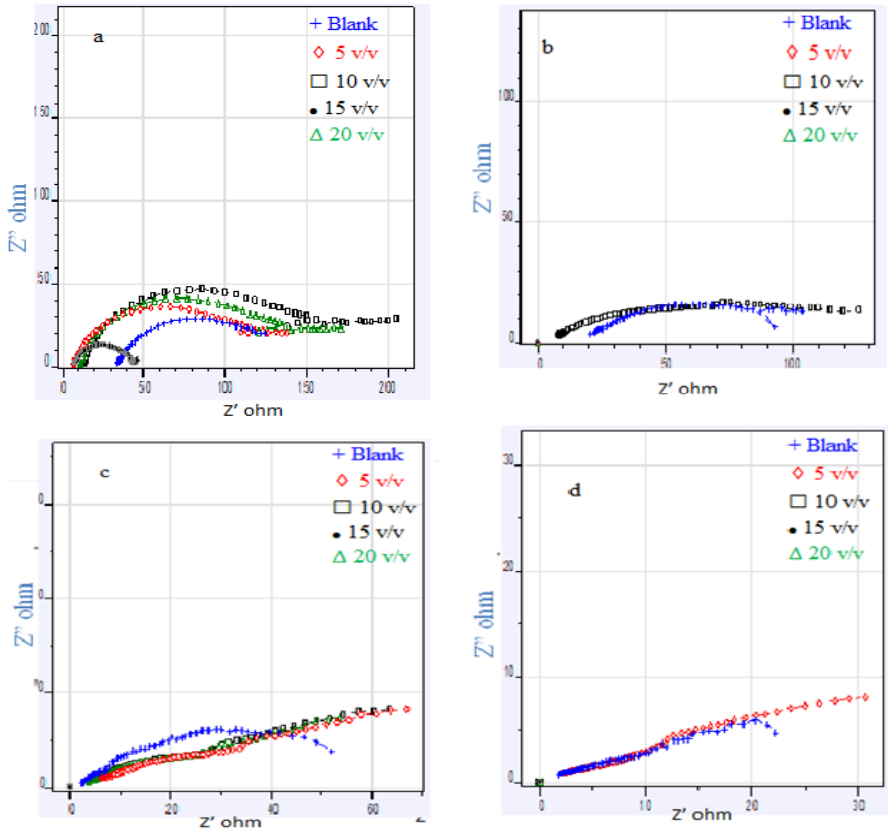
**Fig. 59** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of PD (alcoholic) extract of (a) leaves (b) bark (c) fruits (d) seeds.



**Fig. 60** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Alangium lamarckii* (alcoholic) extract of (a) leaves (b) bark (c) fruits (d) seeds



**Fig. 61** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of HI (alcoholic) extract of (a) leaves (b) bark (c) flowers (d) seeds.



**Fig. 62** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of SS (alcoholic) extract of (a) leaves (b) bark (c) fruits (d) seeds.

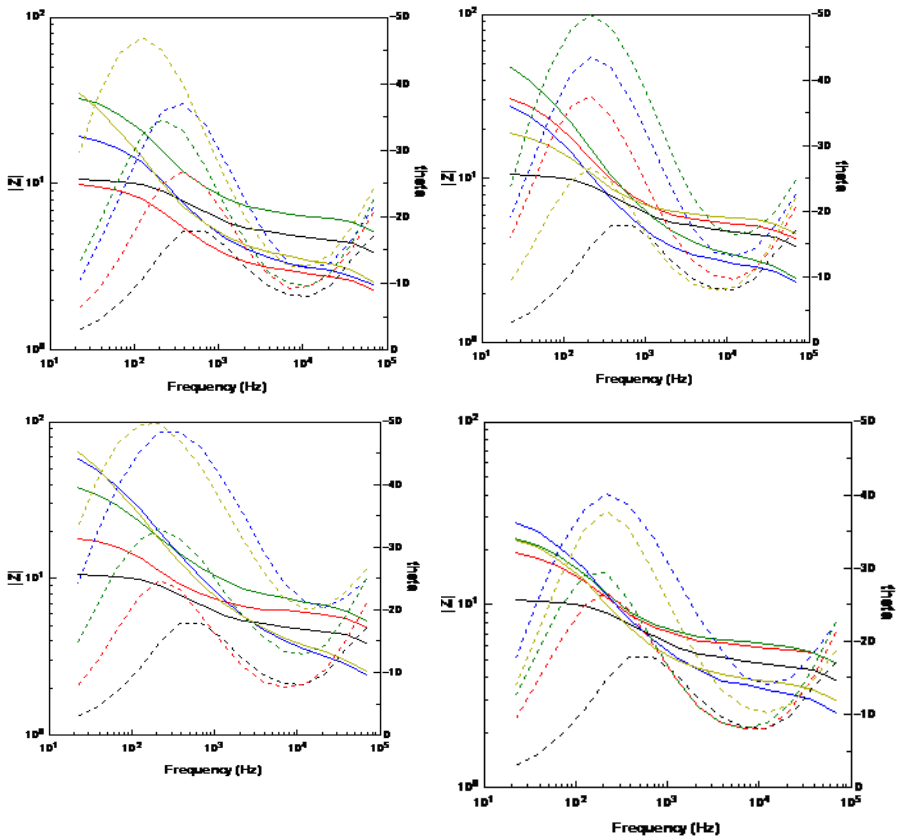
## 5.5 Bode plots

Bode plots (**Figures 63 – 74**) shows resistive region at high frequencies and capacitive region at intermediate frequencies but do not show a clear resistive region (horizontal line and a phase angle =  $0^\circ$ ) at low frequencies. It is reported in literature that the capacitor phase angle and slope value should be  $-90^\circ$  and  $-1$  respectively [567]. These plots showed two overlapped phase maxima at low frequencies. In the bode plot, the impedance is plotted with log of frequencies on the X axis and both the log of absolute value of *the impedance and the phase shift* on the Y-axis. Unlike the Nyquist plot, the *phase angle does not reach  $90^\circ$*  as it is for pure capacitive impedance.

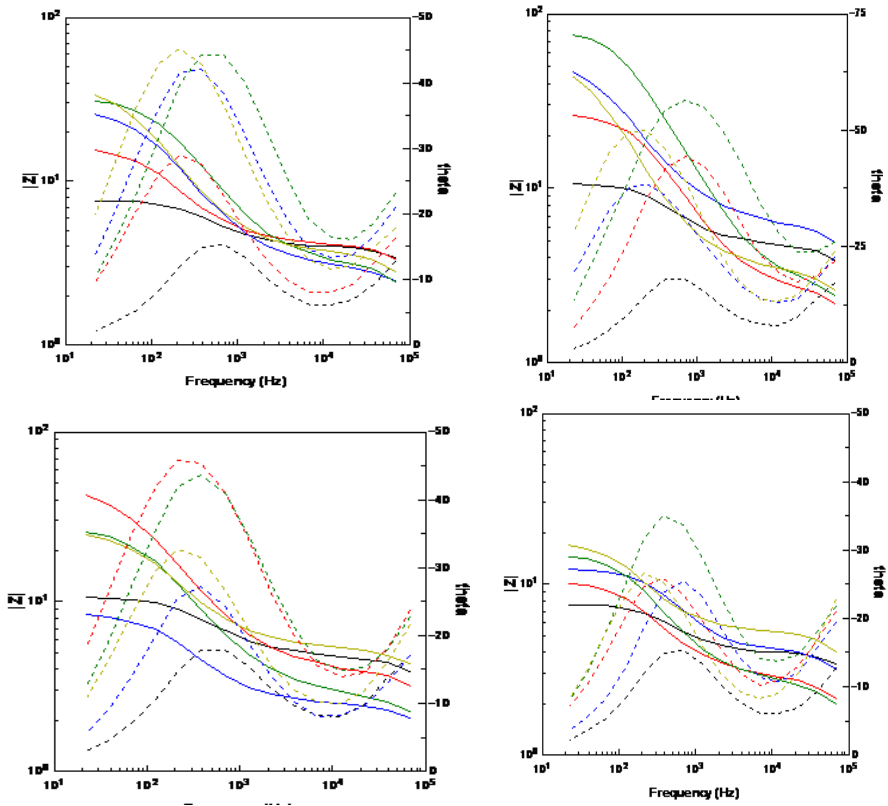
In the bode plot at the highest frequencies,  $\log(R_s + R_{ct})$  appears as a horizontal plateau. However, in our present case deviation occurred from ideal capacitive behavior. This deviation from the ideality is due to the rough electrode



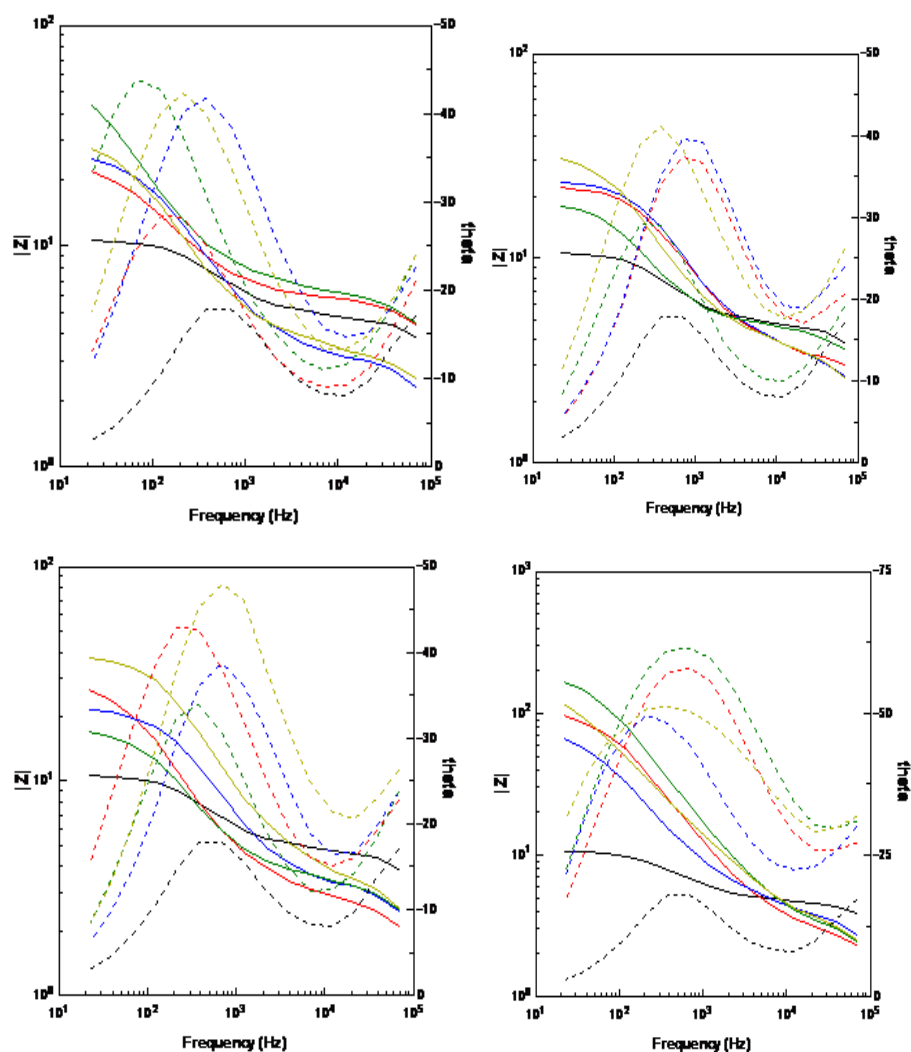
surface. This roughness on the electrode surface is due to accumulation of corrosion products (rust and scale) on the mild steel surface in the acid solution. From the bode plots of the both extract it is *depicted that the phase angle remarkably increased in the presence of inhibitor suggesting that the MS surface* was less corroded in the presence of inhibitor because the inhibitor form a *superior protective film* on MS surface in acid solution and protect free from acid corrosion. From these figure, it was found that the phase angle of the both (aqueous and alcoholic) inhibitor solution is around 50 - 60° respectively.



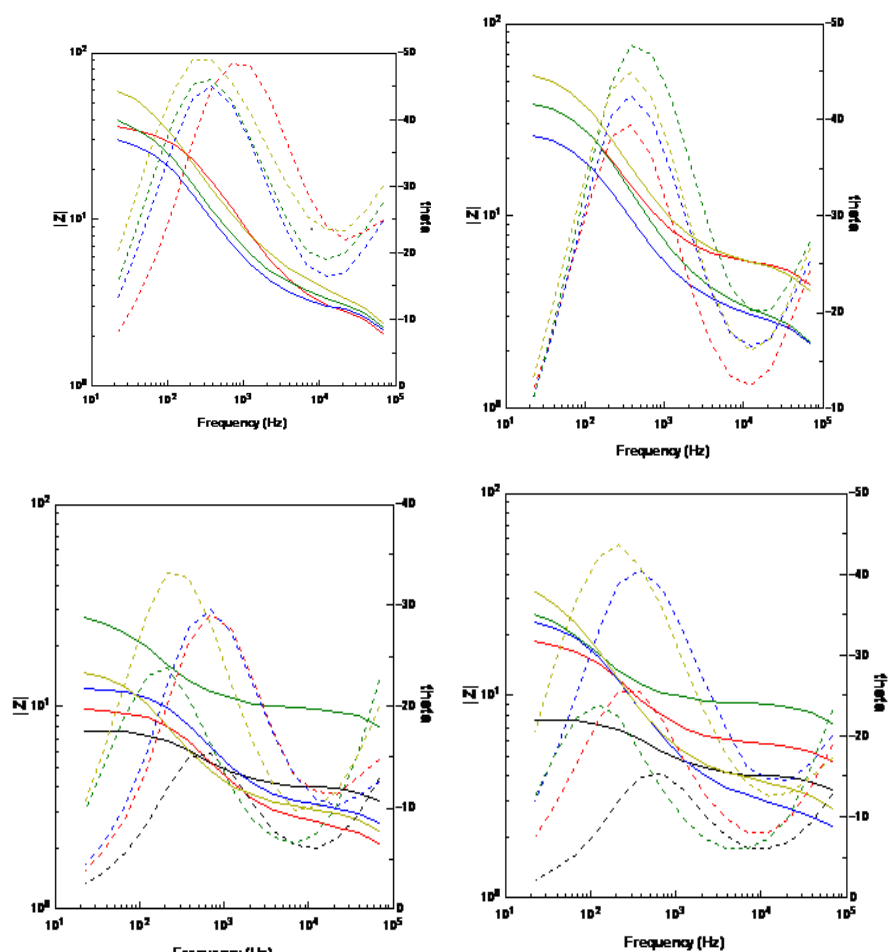
**Fig. 63** Bode plots of mild steel in ML plant (aqueous extract)



**Fig. 64** Bode plots of mild steel in GSL plant (aqueous extract)



**Fig. 65** Bode plots of mild steel in PD plant (aqueous extract)



**Fig. 66** Bode plots of mild steel in AL plant (aqueous extract)

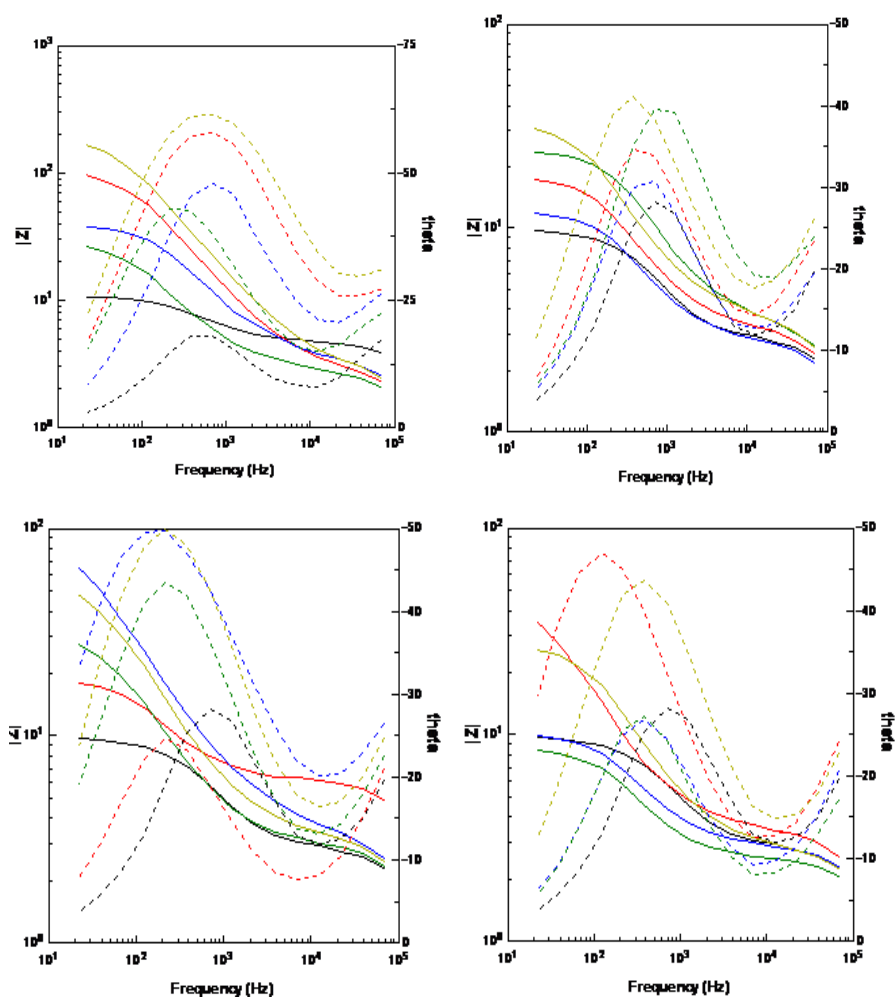


Fig. 67 Bode plots of mild steel in HI plant (aqueous extract)

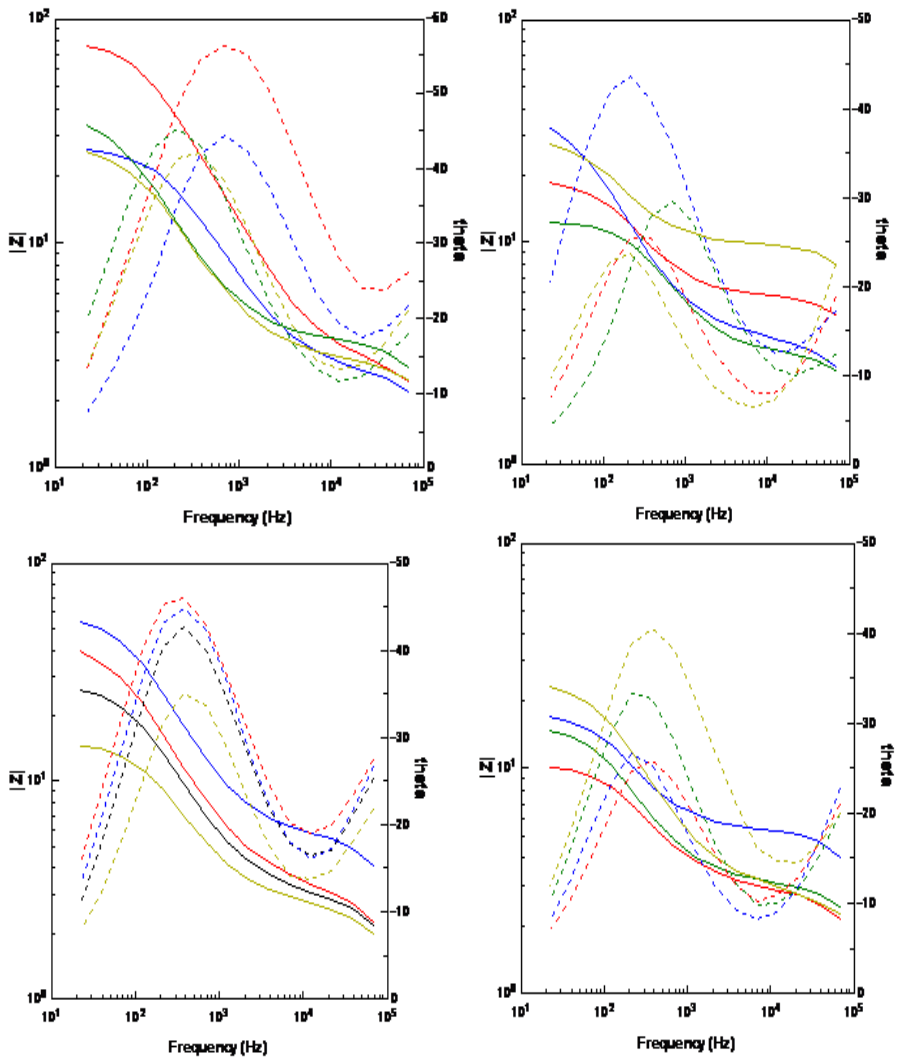


Fig. 68 Bode plots of mild steel in SS plant (aqueous extract)

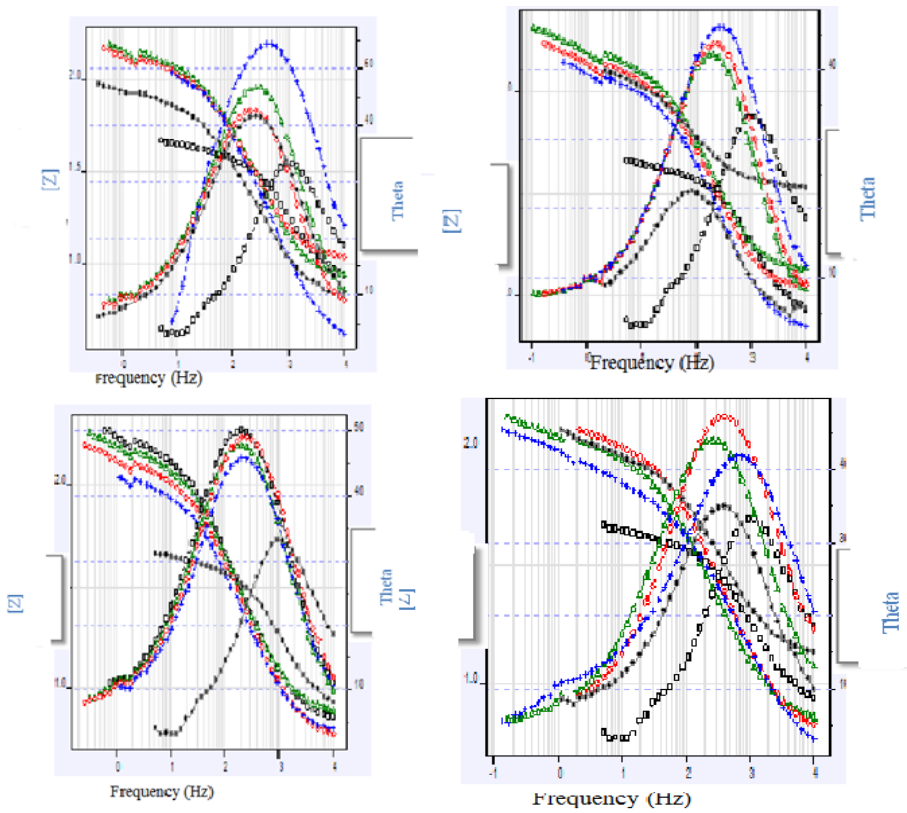
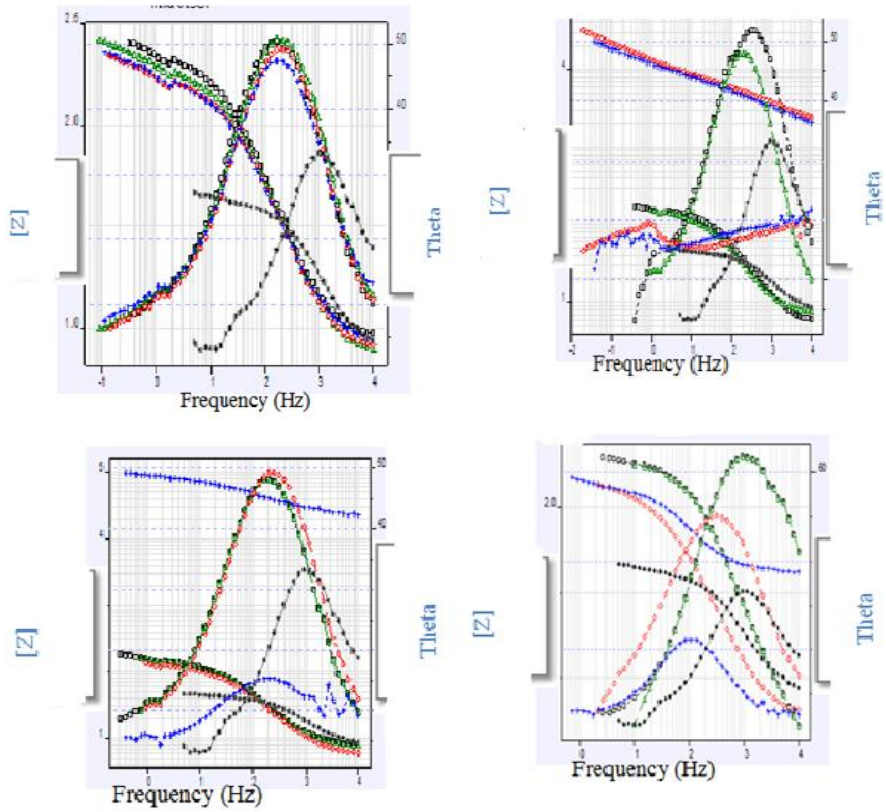
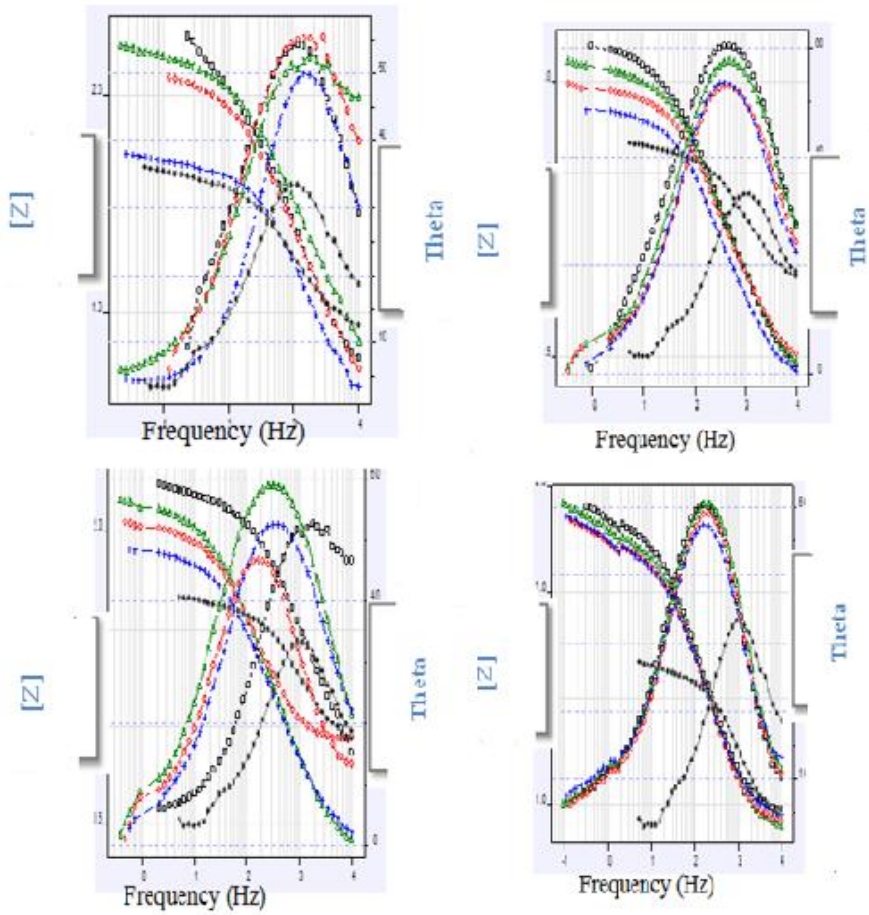


Fig. 69 Bode plots of mild steel in ML plant (alcoholic extract)

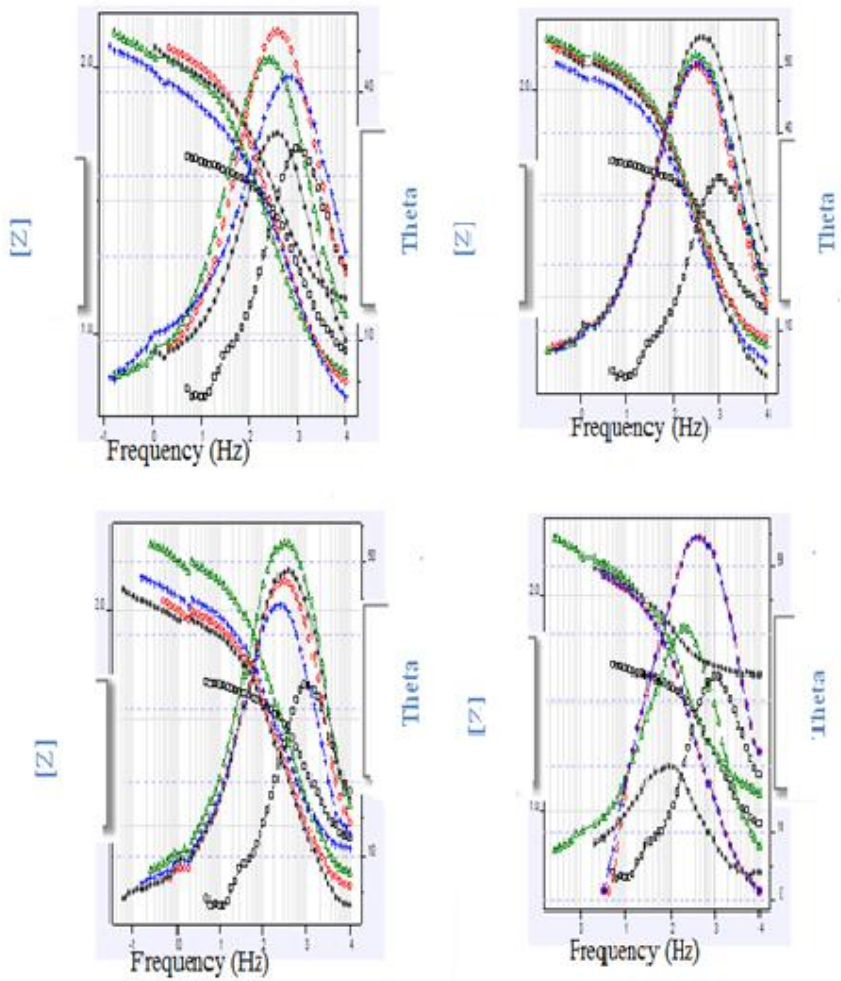


**Fig. 70** Bode plots of mild steel in GSL plant (alcoholic extract)

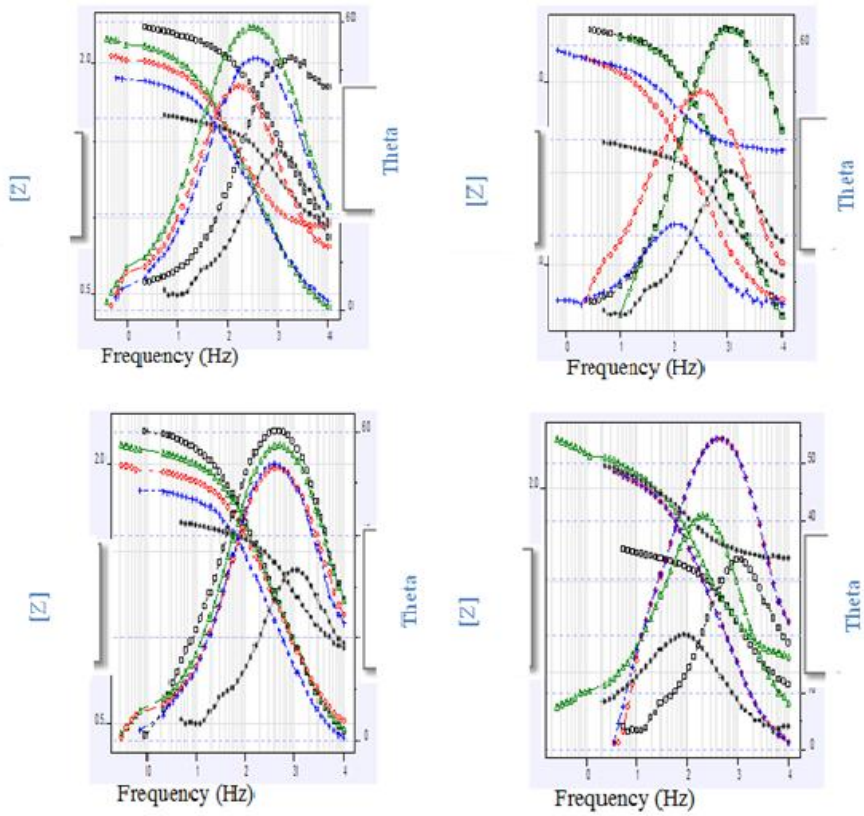




**Fig. 71** Bode plots of mild steel in PD plant (alcoholic extract)



**Fig. 72** Bode plots of mild steel in AL plant (alcoholic extract)



**Fig. 73** Bode plots of mild steel in HI plant (alcoholic extract)

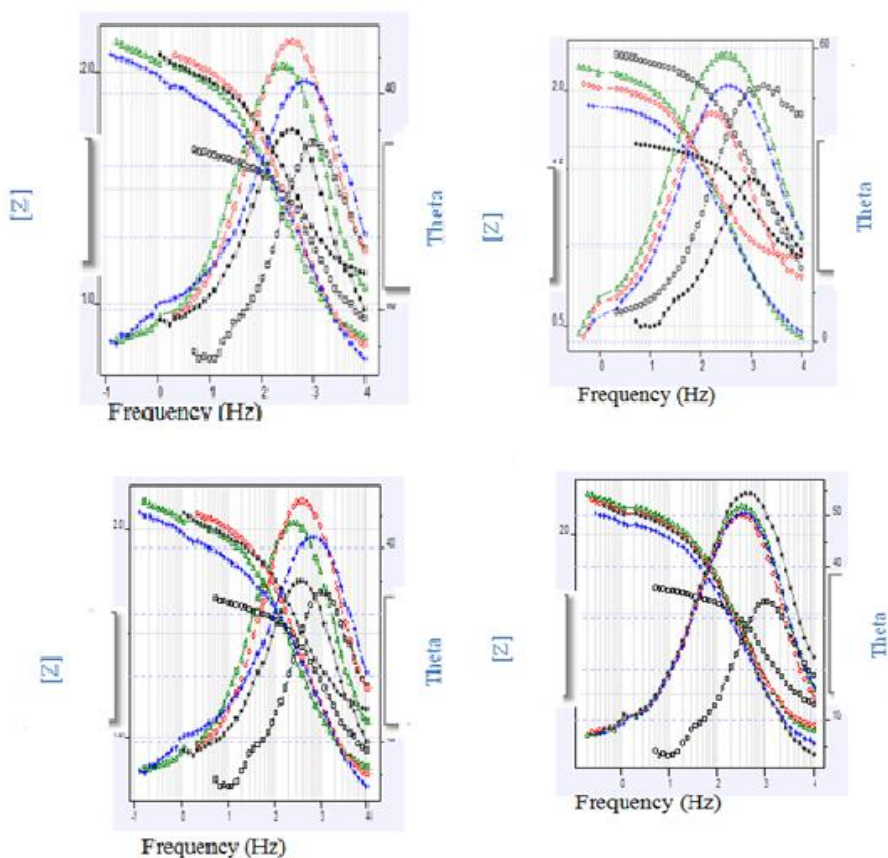


Fig. 74 Bode plots of mild steel in SS plant (alcoholic extract)

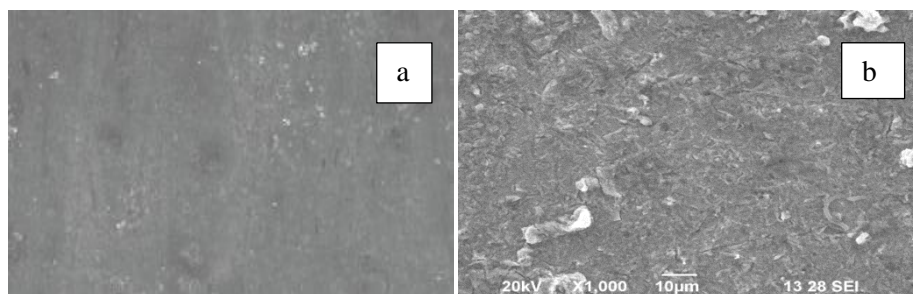
## 5.6 Surface Analysis & EDAX Measurement

It is well known, that the green inhibitor like plants contains numerous organic compounds. It is rather difficultly to understand the mechanism of inhibition for a cluster of different compounds. Present study in the plant extract investigation and observation of the mild steel specimen was carried out by using *scanning electron microscope*. Figures 75-86 shows the SEM image of mild steel surface after immersed in 1N HCl in the absence and presence of selected aqueous and alcoholic extract of six plants (*ML*, *GSL*, *PD*, *AL*, *HI*, *SS*) for 24 hours. Examination of Fig. 75 a observed that the *very strong corroded (pits and crack) and uneven (heavy damage) metal* surface obtained when the metal was kept immersed in 1N HCl in the absence of inhibitor. In the presence of inhibitor (*GSL* plant aqueous) the metal surface shows (Fig. 75 b – d) *smoother (mild steel surface was covered with the protective layer*

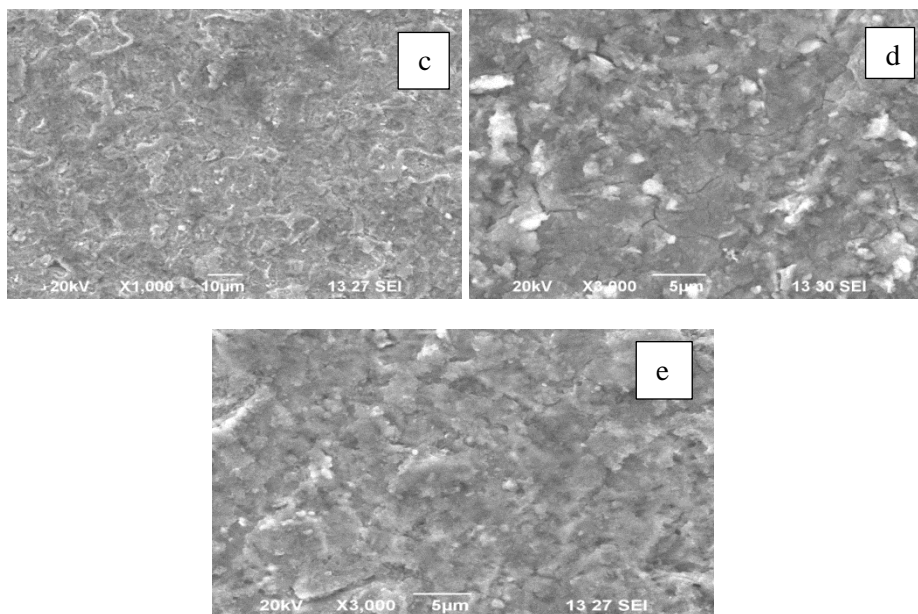
*formed by the inhibitor) with clearly different morphology (surface covered means no pits and cracks).* But, in inhibited solution, the rate of corrosion is suppressed, as the electrode surface is nearly free from corrosion due to the adsorption of the inhibitor on the MS surface.

Examination of **Figure 76 a** showed *very strong corroded (pits and crack) and uneven (heavy damage) metal* surface obtained when the metal was kept immersed in 1N HCl in the absence of inhibitor confirms an attack of the aggressive medium on the mild steel surface. In the presence of inhibitor (GSL plant alcoholic) the metal surface shows (**Fig. 76 b – d**) *smoother (mild steel surface was covered with the protective layer formed by the inhibitor) with clearly different morphology (surface covered means no pits and cracks).*

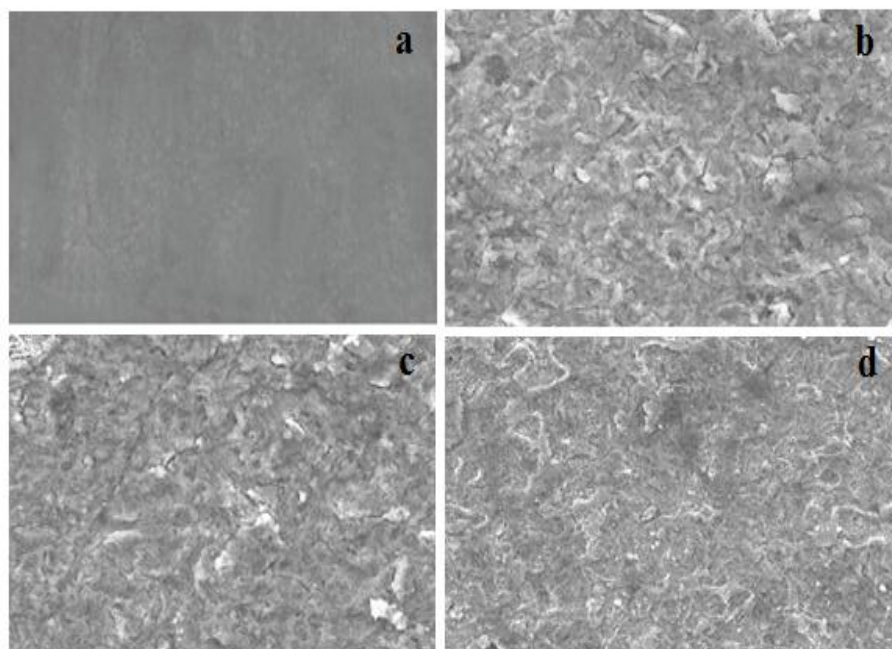
The goal of this section was to confirm the results obtained from chemical and electrochemical measurement that a protective surface film of inhibitor is formed on the electrode surface. The corresponding energy dispersive EDAX profile analysis is presented in **Figures 77 - 86**. The EDAX survey spectra were used to determine which elements of extract components were exposure to acid solution and inhibitor treatment. It is noticed that the existence of the EDAX spectra in the sample exposed to the extract, could be attributed to the adsorption of organic molecules at the mild steel surface. The figure shows that the Fe peaks are considerably suppressed relative to the samples prepared in 1N HCl solution, and this suppression increases with increasing extract concentration and immersion time. The suppression of the Fe lines occurs because of the overlying extract film. These results have been confirmed by those from polarization measurement which suggest that a surface film inhibited the metal dissolution, and it has hence retarded the hydrogen evolution reaction. This surface film also increases the charge transfer resistance of the anodic dissolution of mild steel and down the corrosion rate. Therefore, EDAX examination of the electrode surface supports the results obtained from chemical and electrochemical methods that the plants extract is a good inhibitor for acid solution.

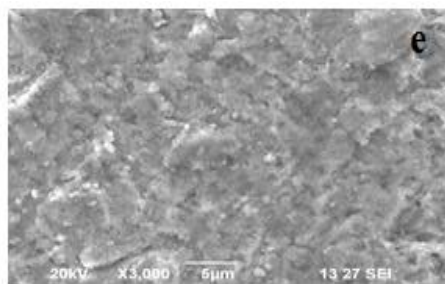




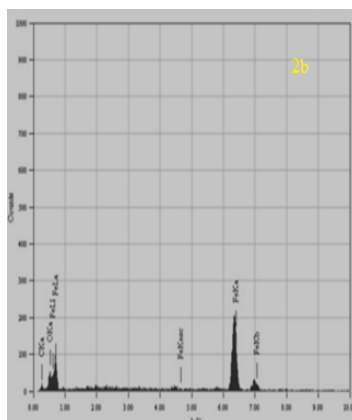
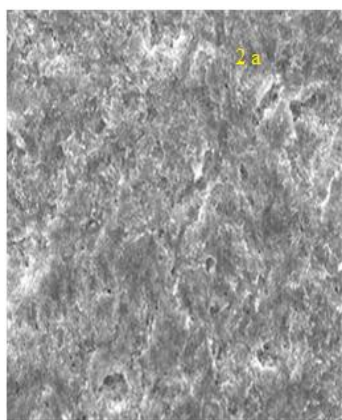
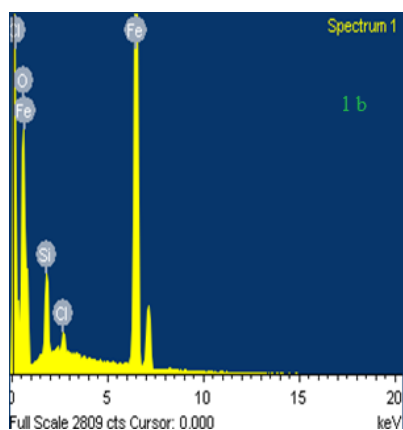
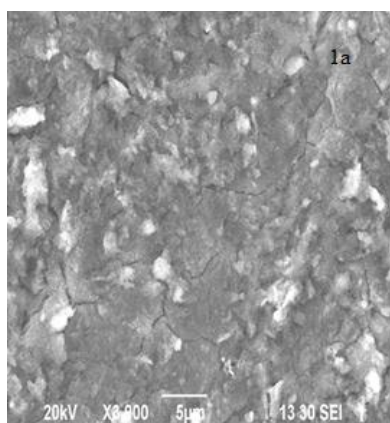


**Fig. 75** SEM image of the surface of mild steel after immersion for 24 hours in 1N HCl solution (a) blank and (ii) in the presence of optimum concentration of the GSL plant aqueous extracts from (b) Stem, (c) Leaves, (d) Flowers and (e) Tubers.

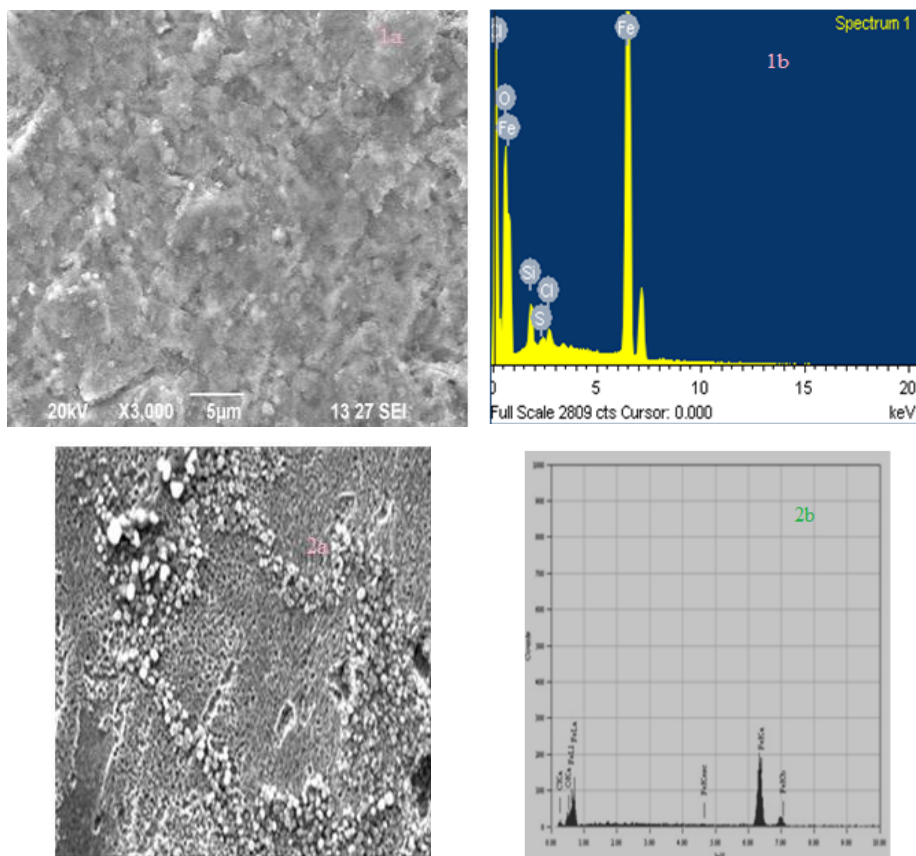




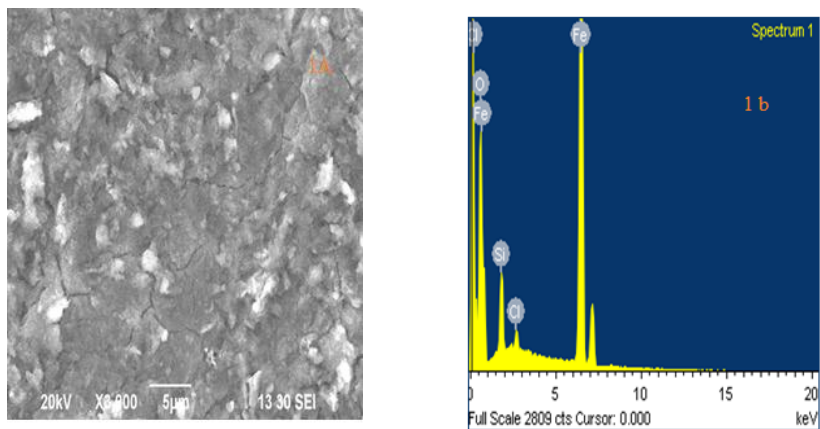
**Fig. 76.** SEM image of the surface of mild steel after immersion for 24 hours in 1N HCl solution (a) blank and (ii) in the presence of optimum concentration of the GSL plant alcoholic extracts from (b) Stem, (c) Leaves, (d) Flowers and (e) Tubers.



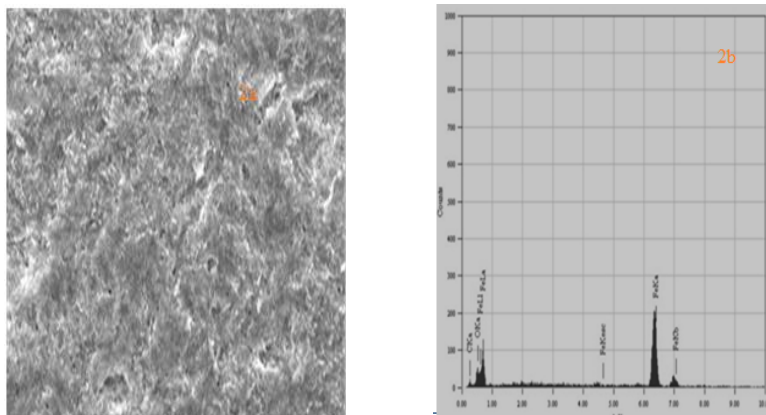
**Fig. 77** SEM with EDAX image of MS in 1N HCl in presence of ML plant (aqueous & alcoholic) 1a and 1b for aqueous and 2a & 2b for alcoholic extract (leaves) at optimum concentration of inhibitor



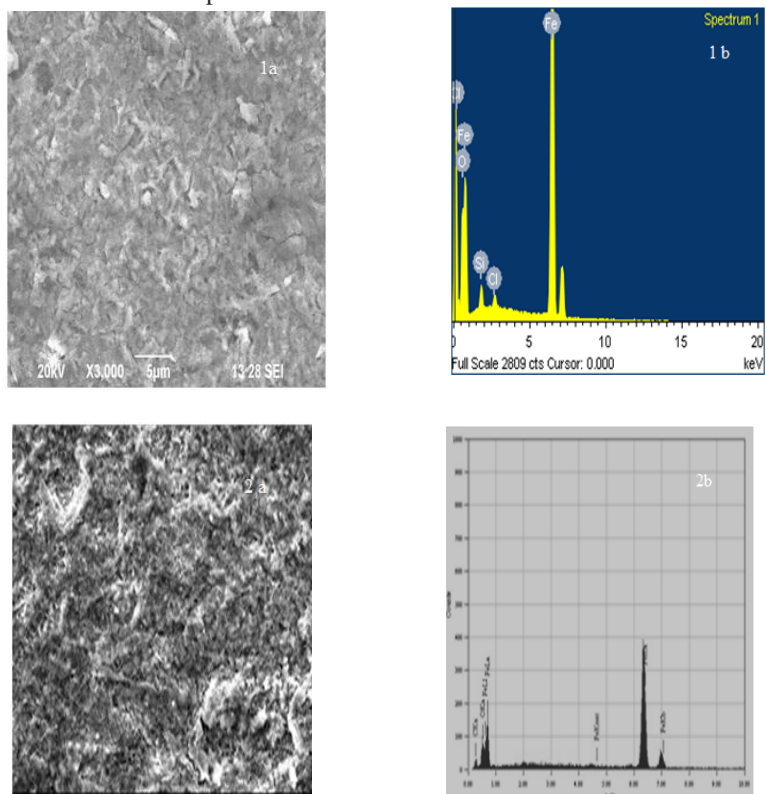
**Fig. 78** SEM with EDAX image of MS in 1N HCl in presence of GSL plant (aqueous & alcoholic) 1a and 1b for aqueous and 2a & 2b for alcoholic extract (leaves) at optimum concentration of inhibitor



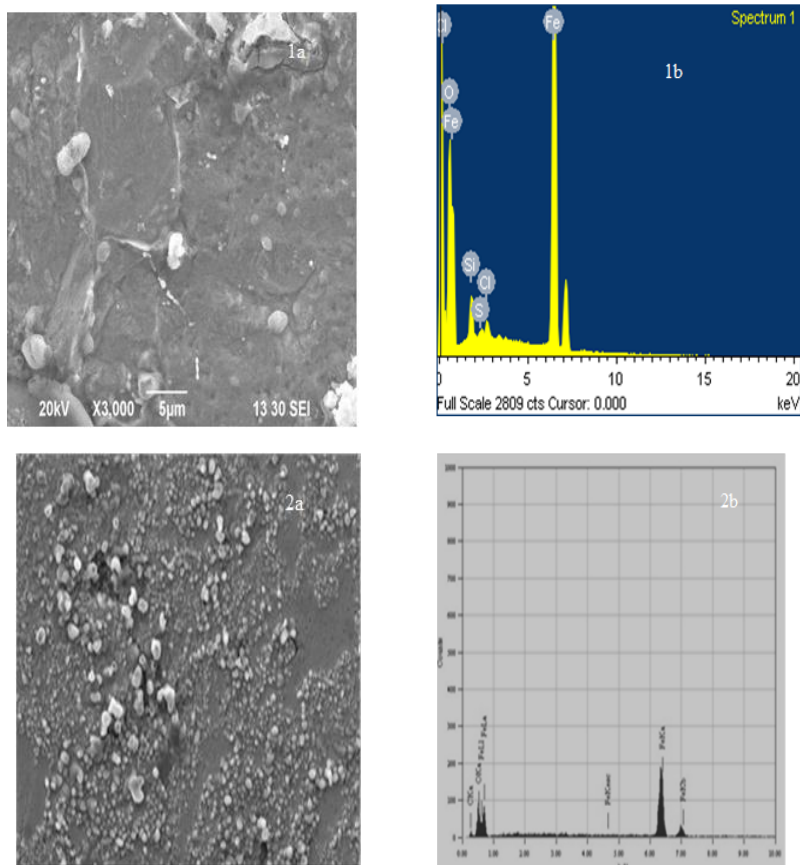




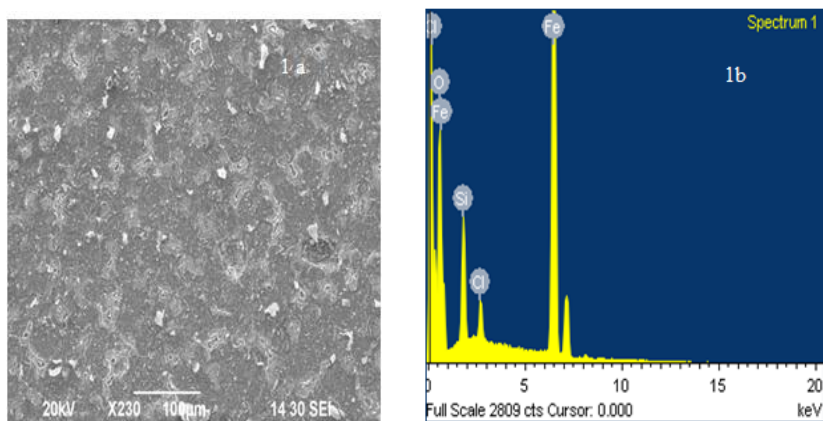
**Fig. 79** SEM with EDAX image of MS in 1N HCl in presence of PD plant (aqueous & alcoholic) 1a and 1b for aqueous and 2a & 2b for alcoholic extract (leaves) at optimum concentration of inhibitor

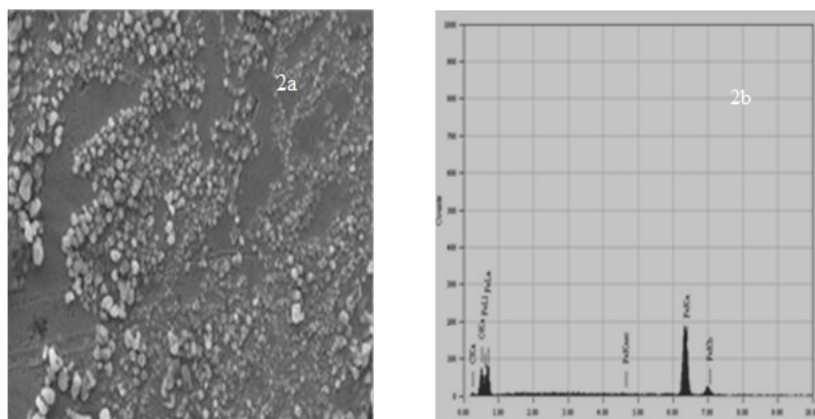


**Fig. 80** SEM with EDAX image of MS in 1N HCl in presence of AL plant (aqueous & alcoholic) 1a and 1b for aqueous and 2a & 2b for alcoholic extract (leaves) at optimum concentration of inhibitor



**Fig. 81** SEM with EDAX image of MS in 1N HCl in presence of HI plant (aqueous & alcoholic) 1a and 1b for aqueous and 2a & 2b for alcoholic extract (leaves) at optimum concentration of inhibitor

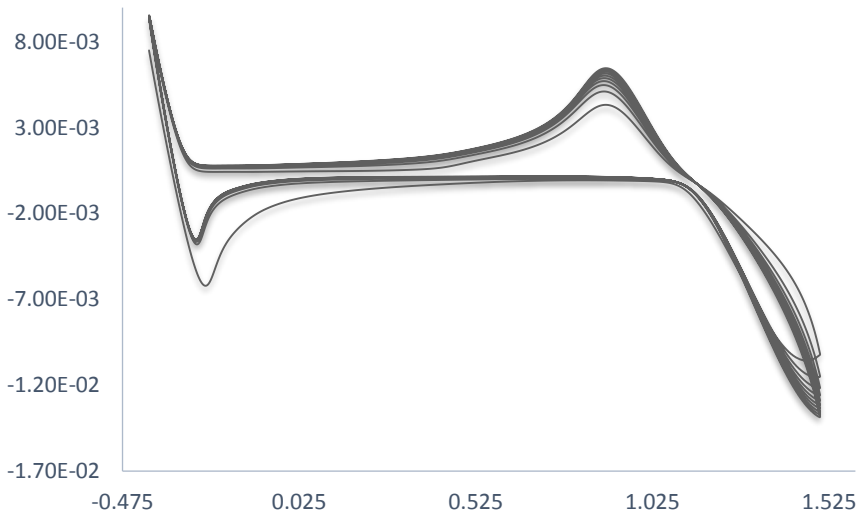




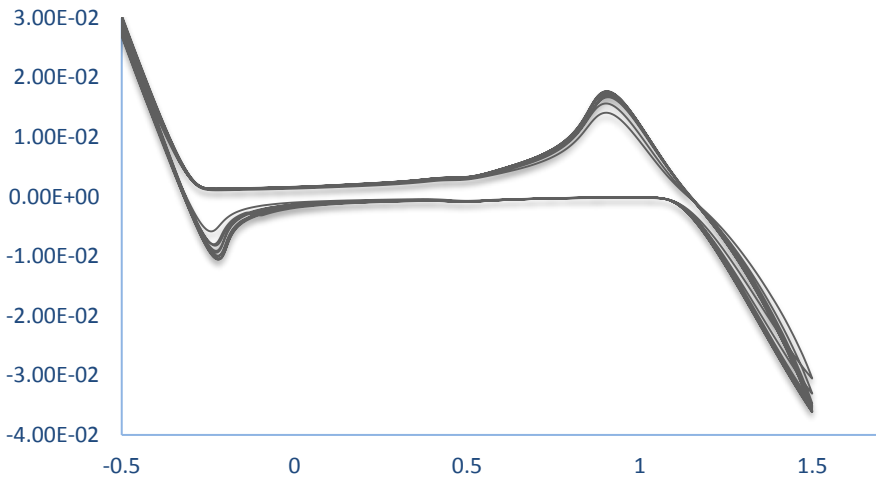
**Fig. 82** SEM with EDAX image of MS in 1N HCl in presence of SS plant (aqueous & alcoholic) 1a and 1b for aqueous and 2a & 2b for alcoholic extract (leaves) at optimum concentration of inhibitor

## 5.7 Cyclic voltammetry measurement

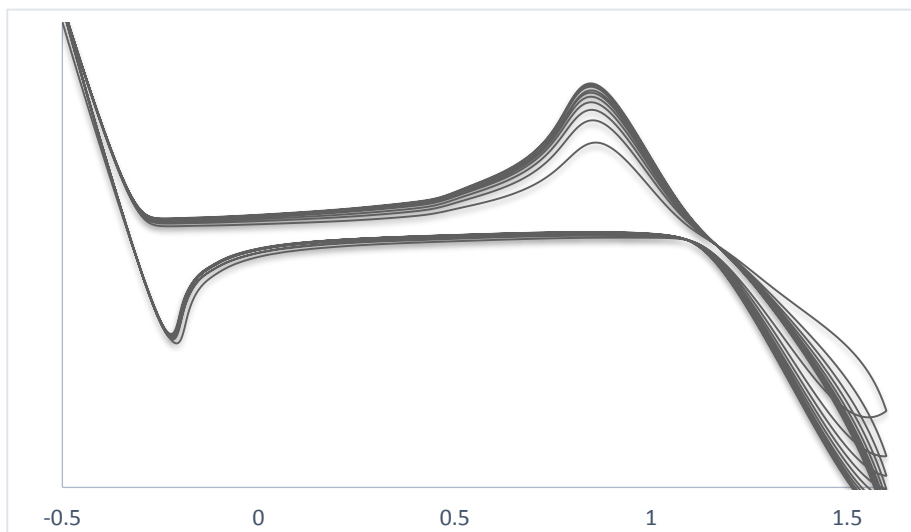
Cyclic voltammetry experiments were carried out in conventional three electrode cell assembly. **Figures 87 – 98** shows the cyclic voltammograms of the mild steel specimens in HCl containing various concentrations of plant extracts. It showed that there are **one anodic current peak and one cathodic peak in the blank solution**. The anodic dissolution of mild steel was occurred by reaction through which can find the first oxidation peak in the CV plots. Consequently, the second oxidation peak represents the process of mild steel to soluble  $\text{Fe}^{2+}$  by reaction. In reserve sweep, the corrosion product of mild steel can be partially reduced as described reaction. On the other hand the corrosion process would be restrained on a certain extent by the increase in film layer. Because of the competition of dissolution and adsorption of the film on mild steel, an anodic current hump appears in CV plots on the reverse sweep at about +1.4 V because the sweep rate is large enough the rate of the film dissolution is hardly compensated by the precipitation of corrosion products so that the anodic current hump becomes clear. Meanwhile, by increasing the inhibitor concentration the potential range of the second anodic peaks change to positive and the peaks gradually diminish. The result indicates that the plant extract is an effective inhibitor for mild steel.



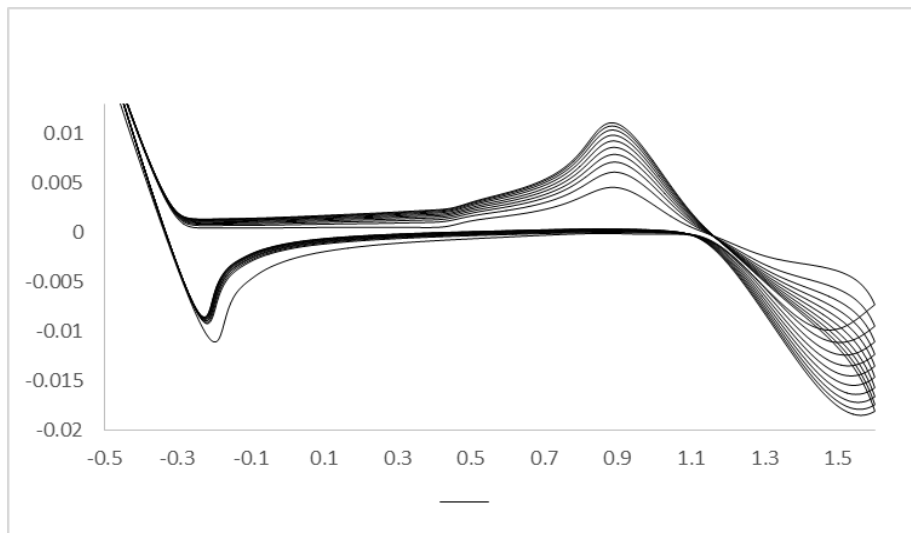
**Fig. 83** Cyclic voltammetry of mild steel in 1N HCl in presence of ML plant (Leaves) aqueous extract at optimum concentration of inhibitor



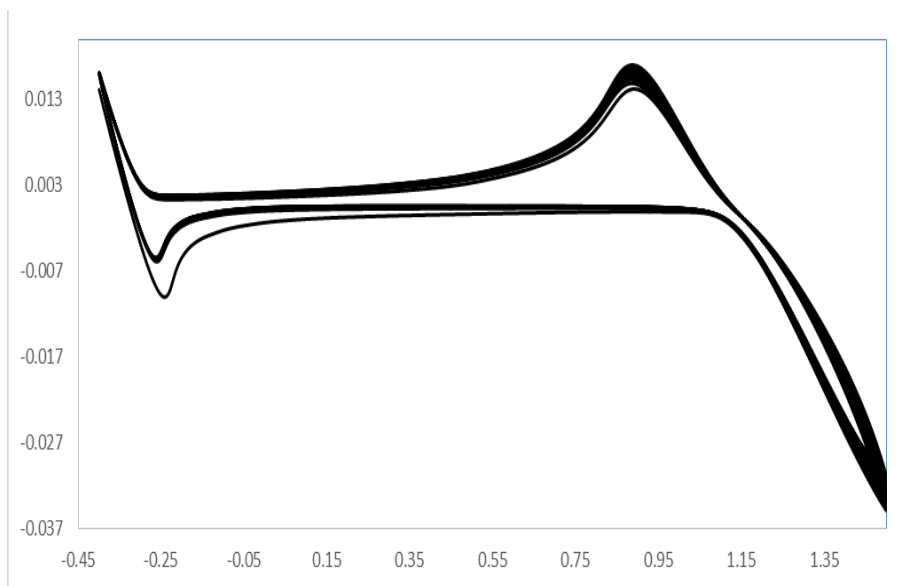
**Fig. 84** Cyclic voltammetry of mild steel in 1N HCl in presence of ML plant (Leaves) alcoholic extract at optimum concentration of inhibitor



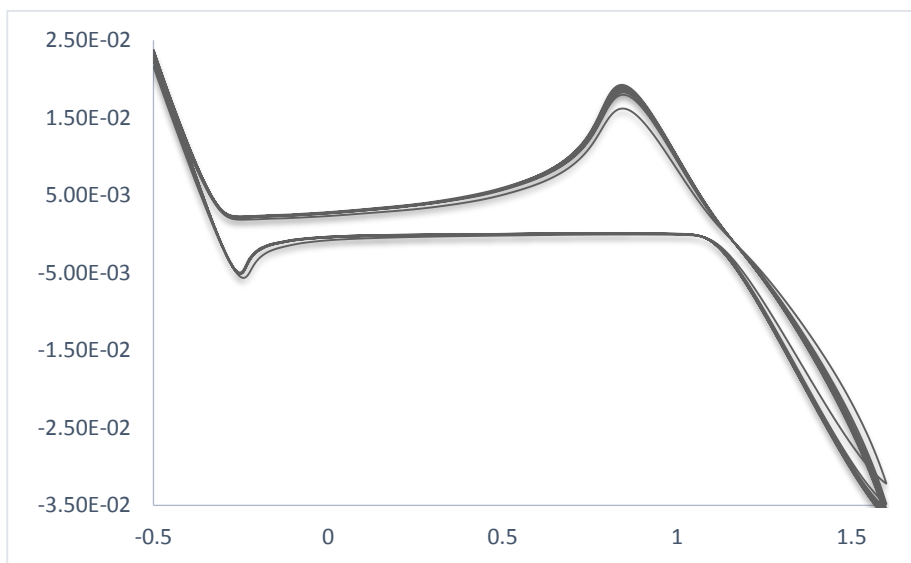
**Fig. 85** Cyclic voltammetry of mild steel in 1N HCl in presence of GSL plant (Leaves) aqueous extract at optimum concentration of inhibitor



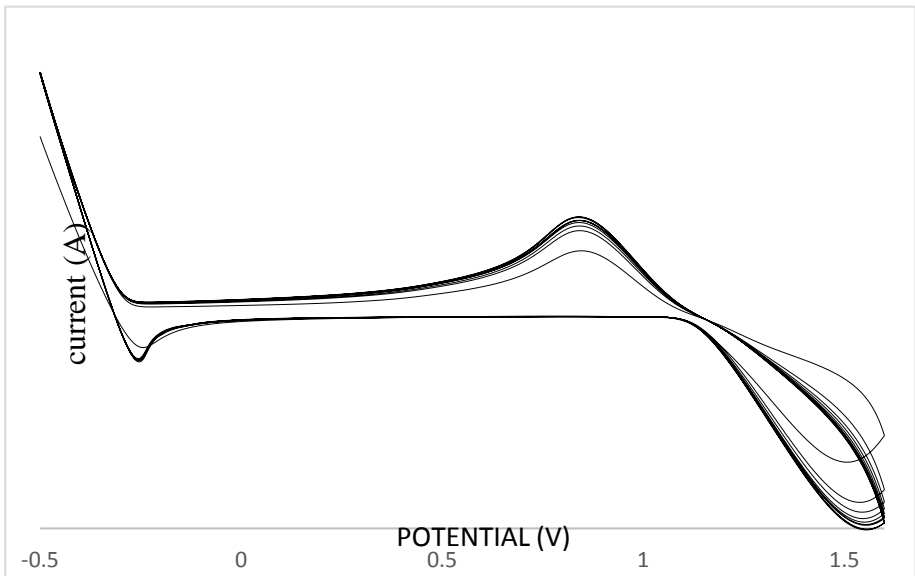
**Fig. 86** Cyclic voltammetry of mild steel in 1N HCl in presence of GSL plant (Leaves) alcoholic extract at optimum concentration of inhibitor



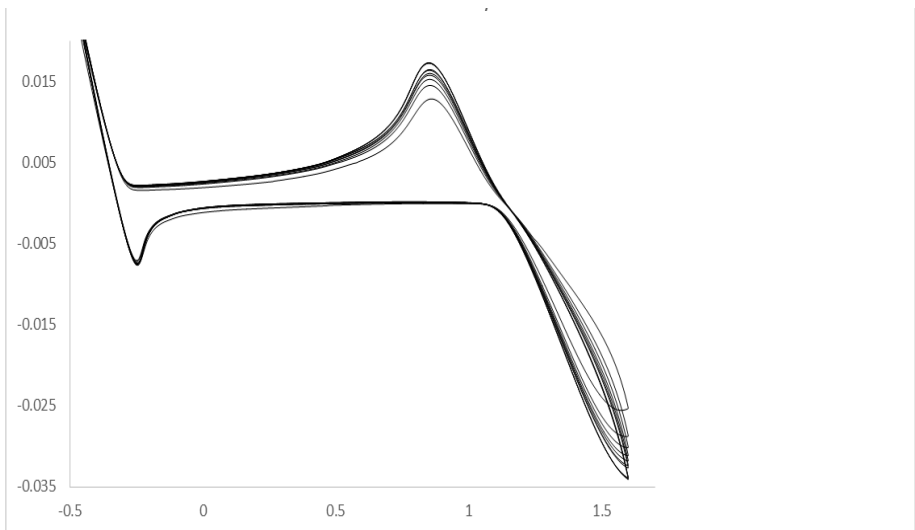
**Fig. 87** Cyclic voltammetry of mild steel in 1N HCl in presence of PD plant (Leaves) aqueous extract at optimum concentration of inhibitor



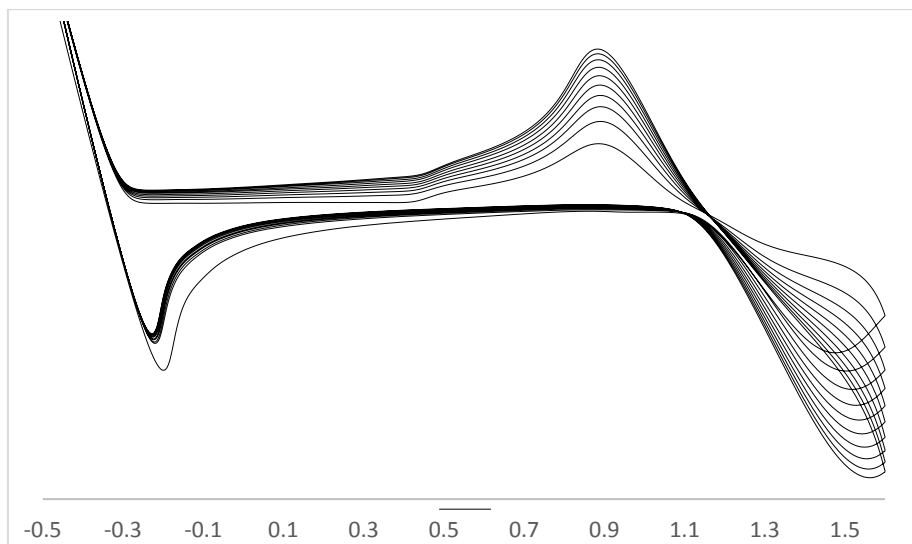
**Fig. 88** Cyclic voltammetry of mild steel in 1N HCl in presence of PD plant (Leaves) alcoholic extract at optimum concentration of inhibitor



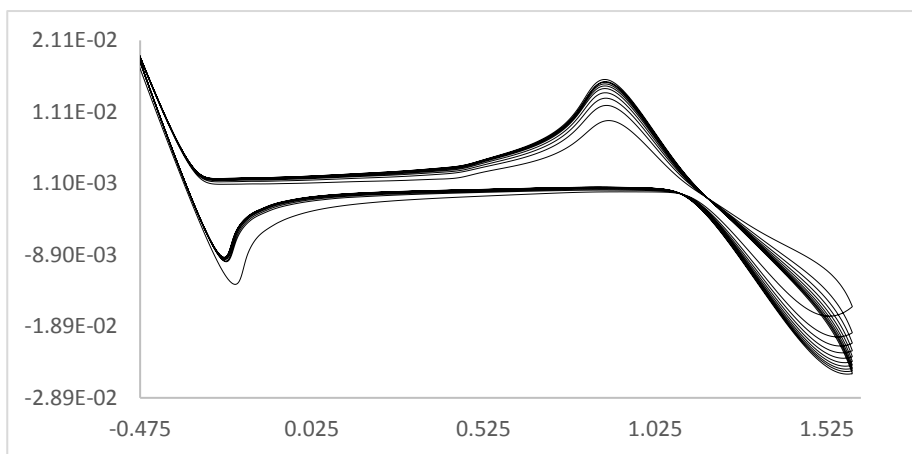
**Fig. 89** Cyclic voltammetry of mild steel in 1N HCl in presence of AL plant (Leaves) aqueous extract at optimum concentration of inhibitor



**Fig. 90** Cyclic voltammetry of mild steel in 1N HCl in presence of AL plant (Leaves) alcoholic extract at optimum concentration of inhibitor

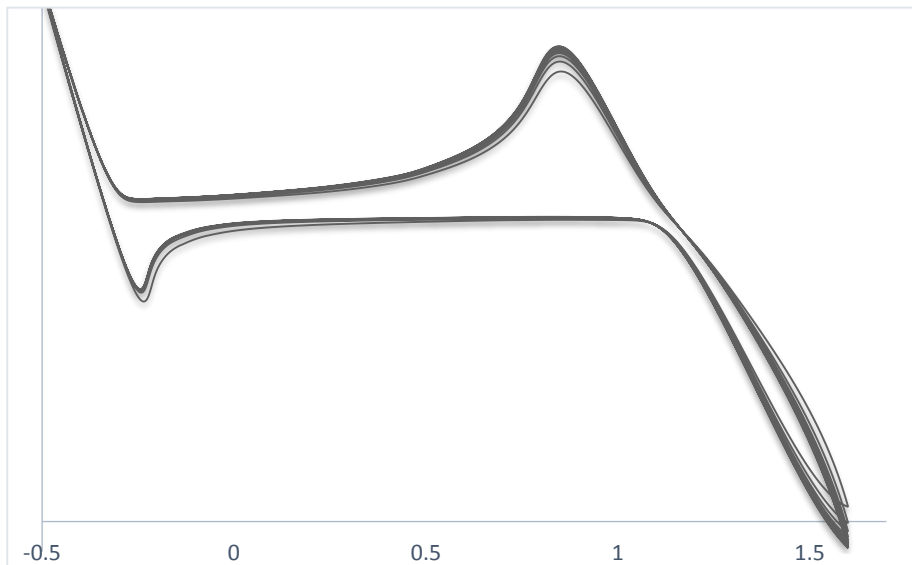


**Fig. 91** Cyclic voltammetry of mild steel in 1N HCl in presence of HI plant (Leaves) aqueous extract at optimum concentration of inhibitor

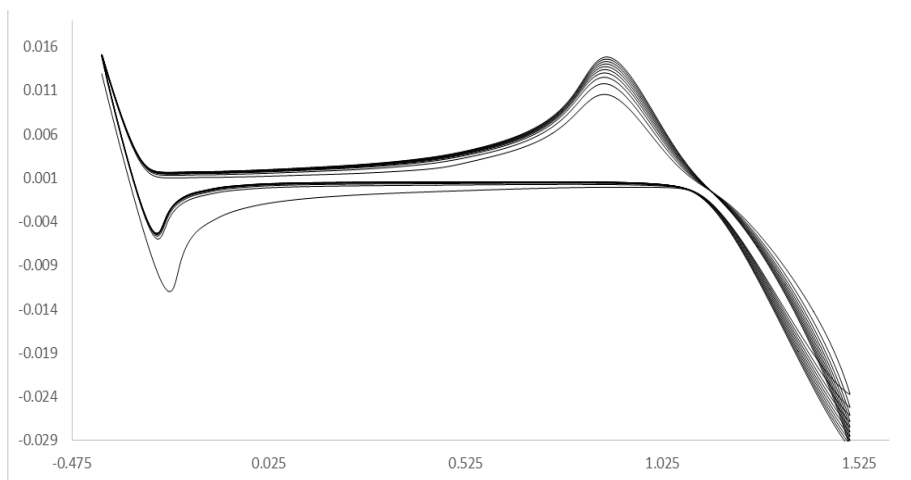


**Fig. 92** Cyclic voltammetry of mild steel in 1N HCl in presence of HI plant (Leaves) alcoholic extract at optimum concentration of inhibitor





**Fig. 93** Cyclic voltammetry of mild steel in 1N HCl in presence of SS plant (Leaves) aqueous extract at optimum concentration of inhibitor



**Fig. 94** Cyclic voltammetry of mild steel in 1N HCl in presence of SS plant (Leaves) alcoholic extract at optimum concentration of inhibitor

## 5.8 Effect of immersion time

Mass loss analysis is one of the easiest and frequently used methods of determining corrosion in metal. In this methods the polished rectangular of mild steel were weighed accurately, fully and separately immersed in 100 ml of 1N HCl in a beaker at room temperature. The inhibition efficiency of plants (aqueous and alcoholic) extract on mild steel as a function of time was presented in **Tables 28 - 39**. It is revealed that the presences of phytochemical constituent in the plant extract are found to be ***bigger molecules to cover a larger surface area on adsorption***. Hence more adsorption takes place on the mild steel surface, the IE increases with an increase in immersion time and inhibitive properties of all the plants extract are fairly good for studied situation.

The influence of duration of immersion and the IE of **ML** (aqueous and alcoholic extracts) is given in **Table 28 and 34**. From the table it is clear that when the immersion period increases the inhibition efficiency decreases and the corrosion rate increases. The inhibition efficiency was found to decrease at longer immersion time, was due to an increase in cathodic or hydrogen evolution kinetics or decreasing strength of adsorption (shifting adsorption – desorption equilibrium towards desorption) This shows that the protective film formed on the metal surface, was broken by the corrosive environment and the film was dissolved.

Weight loss measurement was performed in 1N HCl in the presence and absence of **GSL** extract (both extract) at room temperature for different immersion period from 1-12 h and 3 days, the data is listed in **Table 29 and 35**. The data clearly clarify that the inhibition efficiency increase and after 3 days it decreases. Increase in IE from 1-12 h, showed that the strong adsorption of constituent present in the plant extract on the surface of mild steel giving it a protective layer. Immersion for a longer period (3 days) leads to desorption of plants constituents.

The inhibition efficiency is found to increase from 1-12 hours in 1N HCl medium in the presence of **PD** extract (both extracts) at room temperature; the data are listed in **Table 30 and 36**. The increase of IE up to 12 h reflect the strong adsorption of phytoconstitutens present in the extract onto MS surface, resulting in a more protective layer formed at the steel/acid solution interface. After 3 days, the IE decrease with increasing immersion time in the acid environment. This decrease may be due to the absence of the inactive layer on the MS surface with increasing immersion time.

**Table 31 and 37** gives the values of IE obtained in 1N HCl in the presence and absence of both **AL** extracts. The IE increases with increase in concentration of the inhibitor irrespective of the time of immersion. Maximum IE was observed from the table at 12 h of immersion time. Long-time of immersion (3 days), the IE decreases in the acid environment.

**Table 32 and 38** shows the corrosion parameters of MS in acid solution containing various concentration of **HI** plant of both extract. It is revealed that the mass loss significantly enhanced with increase of exposure time in inhibitor free solution. However, it was slowly declined with rise in immersion time (3 days). This is mainly due to the presence of phytochemical compounds.

In order to assess the stability of adsorbed inhibitor film at MS - acid solution interface with time, mass loss measurements were performed in both extract of *SS* plants. From the **Table 33 and 39** it was noticed that a maximum IE was observed for 12 h of immersion periods. Immersion studies reveal that as the time of immersion increased from 1-12 h the IE also increased. After 3 days there is slightly declined in the IE, this may be explained that decrease (desorption) in inhibition for long periods of immersion can be attributed to the depletion of available inhibitor molecules in the solution due to chelate formation between steel and the inhibitor ligands.

Initially inhibitor efficiency increase from 1 to 12 hours and then there is a decline in inhibitor effect at 3 days. This behavior may be attributed due to the increase in corrosion loss with increase in the time of immersion may be ascribed to change occurring in the inhibitor and built up of metal salts in solution. Many researcher points out rather strongly the fact that the rate increases in active surface area as the metal attached. Nevertheless it was a decrease in the inhibition efficiency with further exposure time, showing that the inhibition was brought about by the physical absorption of the reactive constituents of the solution extract to the test metal's surface. Thus with increase *in exposure time, the interfacial bond between the extracts active molecular constituents (due to contamination) and weakened, thereby decreasing the inhibition efficiency.*

In discussing corrosion inhibition by surface – active organic compounds, various factors are taken into consideration including the number and types of adsorbing group and their electron structure. The selected six plant extract under investigation contains different organic substance with proven corrosion inhibiting capabilities such as alkaloids and terpenoids are shown in **Fig. 21-26**. It is very difficult to assign the observed inhibiting effect to a particular constituent. The net adsorption of the organic compounds on the corroding steel surface creates a barrier that isolates the metal from the corrodent. IE increases with an increase in the metal surface fraction occupied by the organic matter.

**Table 28** Inhibition efficiency of aqueous extract of ML plants at various immersion time

Parts of Madhuca Longifolia plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3days
Madhuca Longifolia leaves	Blank	*	*	*	*	*	*	*
	5	59.78	64.83	72.54	76.54	90.86	85.02	55.90
	10	62.00	70.29	76.05	80.96	84.00	90.72	50.78
	15	68.75	75.09	82.19	85.42	90.69	96.25	43.09
	20	92.31	95.14	96.57	96.88	94.30	99.04	43.03
Madhuca Longifolia barks	5	10.31	60.29	74.93	85.02	88.78	89.13	59.04
	10	35.81	66.59	80.88	90.29	89.88	92.78	49.42
	15	44.05	78.06	88.19	95.75	95.02	97.92	41.66
	20	63.18	92.83	95.03	97.79	97.73	98.12	40.75

(Continued)

**Table 28 (Continued)**

Madhuca Longifolia <b>fruits</b>	5	31.81	41.24	56.24	74.11	84.29	88.76	32.09
	10	36.95	55.85	86.60	76.32	86.89	92.05	22.74
	15	59.84	88.55	92.97	86.68	90.38	94.15	22.56
	20	84.17	90.29	94.10	94.98	95.49	96.69	22.47
Madhuca Longifolia <b>seed peels</b>	5	31.75	45.03	51.33	74.86	80.81	92.01	63.04
	10	40.21	66.24	65.89	81.98	92.37	95.69	53.48
	15	75.88	78.38	74.51	89.79	94.15	96.21	44.90
	20	89.02	89.01	90.56	94.98	96.03	97.14	43.21

**Table 29** Inhibition efficiency of aqueous extract of GSL plants at various immersion time

Parts of GSL plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
<i>Gloriosa Superba Linn leaves</i>	Blank	-	-	-	-	-	-	-
	5	16.10	32.13	46.36	56.72	73.36	84.28	56.78
	10	36.56	48.38	62.72	71.39	79.93	88.36	44.20
	15	49.57	60.39	66.36	82.18	89.03	90.71	40.09
	20	65.35	72.12	80.18	87.73	90.24	96.39	38.78
<i>Gloriosa Superba Linn stems</i>	5	31.45	39.37	53.27	60.17	72.97	80.72	65.29
	10	43.13	56.75	67.38	72.52	78.17	81.21	53.90
	15	52.24	60.09	69.20	74.08	80.26	82.82	41.87
	20	69.30	74.14	86.16	89.32	94.15	96.27	23.90
<i>Gloriosa SuperbaLinn flowers</i>	5	53.15	62.29	65.29	74.19	85.89	91.09	44.20
	10	66.29	69.71	74.40	75.69	89.13	92.59	38.67
	15	74.86	79.46	82.34	89.17	90.73	94.57	30.48
	20	94.95	80.25	88.90	89.99	94.65	96.23	26.17
<i>Gloriosa Superba Linn tubers</i>	5	32.29	60.73	76.16	78.28	90.49	94.99	39.12
	10	53.28	84.65	84.96	87.34	91.64	96.05	35.33
	15	69.75	85.48	88.59	88.90	93.37	96.35	27.07
	20	72.58	86.53	90.27	91.90	94.10	96.89	19.39

**Table 30** Inhibition efficiency of aqueous extract of PD plants at various immersion time

Parts of Pithecellobium Dulce plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
Pithecellobium Dulce leaves	Blank	-	-	-	-	-	-	-
	5	46.17	50.23	74.66	74.88	82.56	89.96	53.20
	10	57.55	59.28	79.00	82.79	89.76	92.32	48.67
	15	70.90	72.94	80.28	84.65	90.54	93.93	40.30
	20	81.58	82.62	87.93	88.84	93.28	96.45	33.78

**Table 30 (Continued)**

Pithecellobium Dulce barks	5	42.76	74.18	81.32	78.09	90.87	94.22	47.89
	10	48.19	76.57	85.87	88.78	94.45	95.13	39.63
	15	63.23	78.32	87.69	89.09	95.04	95.49	33.09
	20	74.02	83.98	93.96	94.67	96.36	96.20	24.97
Pithecellobium Dulce fruits	5	37.34	59.53	64.17	71.35	70.87	80.83	49.38
	10	43.06	64.78	73.96	75.78	83.33	89.76	47.90
	15	59.06	73.96	74.09	79.89	88.52	91.89	38.94
	20	70.45	74.76	79.74	83.54	90.23	96.98	28.67
Pithecellobium Dulce seeds	5	49.65	78.20	78.04	70.87	85.78	90.23	38.94
	10	57.96	82.59	81.76	84.89	87.32	93.18	29.07
	15	77.09	84.22	86.90	87.45	93.89	94.87	20.78
	20	86.91	89.93	89.07	93.57	94.71	96.99	20.78

**Table 31** Inhibition efficiency of aqueous extract of AL plants at various immersion time

Parts of Alangium Lamarckii Plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
Alangium lamarckii Leaves	5	57.98	59.48	64.56	72.39	84.22	70.56	53.89
	10	65.39	69.59	70.54	66.76	70.14	78.72	46.92
	15	74.95	81.36	77.16	77.96	82.49	87.95	38.04
	20	83.16	92.16	84.15	80.37	93.76	98.19	38.01
Alangium Lamarckii barks	5	70.11	70.30	60.53	76.46	65.78	72.12	47.90
	10	74.08	85.19	77.28	83.12	66.28	83.38	39.87
	15	79.35	91.06	86.19	87.22	77.92	92.02	28.65
	20	91.93	93.83	95.05	90.09	89.78	96.91	28.13
Alangium Lamarckii Fruits	5	70.81	78.90	72.44	74.21	80.89	75.02	40.73
	10	76.15	86.16	77.63	76.78	89.28	79.53	36.29
	15	87.34	94.56	84.60	82.59	94.19	88.98	28.18
	20	94.21	97.89	92.19	93.65	95.66	97.16	28.14
Alangium Lamarckii Seeds	5	68.10	70.93	72.65	75.78	76.87	79.21	38.20
	10	79.98	84.24	85.33	86.98	82.96	83.56	34.68
	15	88.98	89.94	89.89	87.48	89.08	91.33	28.30
	20	95.62	96.37	97.25	93.09	94.54	98.60	27.89

**Table 32** Inhibition efficiency of aqueous extract of HI plants at various immersion time

Parts of <i>Holoptelea Integrifolia</i> plant	Conc. of the extract (v/v)	Inhibition Efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
<i>Holoptelea Integrifolia</i> leaves	Blank	-	-	-	-	-	-	-
	5	24.10	51.13	36.79	54.89	59.72	65.56	46.20
	10	44.43	60.29	58.14	66.70	69.16	78.72	38.17
	15	57.50	72.33	66.76	77.36	85.29	96.95	34.09
	20	66.29	80.45	83.15	89.37	90.87	98.13	26.33
<i>Holoptelea Integrifolia</i> barks	5	30.31	44.90	50.43	56.16	65.78	69.62	39.29
	10	45.08	56.19	67.88	77.72	69.18	84.70	30.15
	15	58.85	68.94	74.19	82.45	87.22	93.22	26.99
	20	64.93	82.63	85.52	90.09	92.78	94.18	26.99
<i>Holoptelea Integrifolia</i> flowers	5	52.81	58.90	56.40	50.51	53.89	48.09	37.89
	10	65.25	70.60	69.13	66.48	67.34	69.33	33.08
	15	72.34	74.16	79.40	80.57	77.19	88.89	24.11
	20	79.21	81.09	89.29	93.17	95.80	97.16	24.08
<i>Holoptelea Integrifolia</i> seeds	5	38.06	44.81	50.23	58.98	66.71	69.11	36.18
	10	46.68	50.54	55.33	64.02	78.06	89.36	27.49
	15	67.34	73.73	76.41	78.12	89.45	93.38	22.80
	20	72.62	79.34	81.05	82.05	92.50	97.72	22.80

**Table 33** Inhibition efficiency of aqueous extract of SS plants at various immersion time

Parts of <i>Schreabera swietenoids</i> plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
<i>Schreabera swietenoids</i> leaves	Blank	-	-	-	-	-	-	-
	5	16.34	40.37	56.16	54.32	45.56	82.90	43.89
	10	65.78	60.57	72.12	60.44	68.27	86.27	36.98
	15	71.50	83.12	77.98	83.95	84.23	88.55	28.67
	20	74.98	90.44	95.16	91.30	94.02	93.90	18.55
<i>Schreabera swietenoids</i> barks	5	39.22	56.83	60.03	66.23	75.06	81.04	45.22
	10	53.50	65.24	63.90	78.07	84.56	85.38	48.99
	15	60.28	76.23	73.70	83.88	89.02	90.34	39.66
	20	73.31	89.34	89.03	90.67	92.11	93.02	32.87
<i>Schreabera swietenoids</i> fruits	5	27.90	59.09	84.05	80.64	77.55	85.73	35.15
	10	54.17	70.06	86.72	87.09	84.03	92.11	30.44
	15	68.83	79.81	92.45	88.24	90.04	92.87	24.48
	20	74.36	88.73	94.89	92.58	93.75	94.09	20.78

(Continued)

**Table 33 (Continued)**

Schreabera swietenioids seeds	5	37.89	40.19	67.70	82.33	88.24	80.36	27.90
	10	59.20	58.83	84.69	85.07	91.27	88.97	24.88
	15	68.06	69.90	89.91	91.38	92.60	89.34	26.90
	20	82.38	80.74	93.47	92.65	93.04	94.45	26.89

**Table 34** Inhibition efficiency of alcoholic extract of ML plants at various immersion time

Parts of Madhuca Longifolia plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
Madhuca longifolia leaves	Blank	*	*	*	*	*	*	*
	5	52.21	65.12	69.14	71.67	70.06	74.89	50.39
	10	59.01	74.21	72.30	80.23	80.21	86.71	48.30
	15	64.72	81.61	79.95	84.09	89.45	93.01	48.28
	20	89.32	86.73	89.32	92.09	91.79	93.98	48.28
Madhuca longifolia bark	5	39.16	44.87	59.21	69.92	69.09	70.32	37.29
	10	42.09	50.32	64.72	77.32	74.89	75.22	35.90
	15	56.32	67.34	75.02	88.05	92.90	86.32	34.91
	20	64.72	88.96	90.18	89.09	93.01	94.17	34.90
Madhuca longifolia fruits	5	60.71	72.43	66.24	79.38	64.34	86.54	42.78
	10	77.02	87.94	75.95	81.12	72.71	93.09	40.29
	15	78.97	93.35	84.94	82.34	86.36	94.38	39.40
	20	89.98	94.41	94.92	90.28	95.25	96.49	39.37
Madhuca longifolia seeds peel	5	66.21	45.35	59.29	52.32	66.14	74.96	47.90
	10	76.11	60.62	73.13	69.19	78.22	88.12	46.38
	15	78.09	77.30	75.52	80.34	84.19	89.90	46.38
	20	89.98	89.12	88.19	92.36	95.25	96.32	46.30

**Table 35** Inhibition efficiency of alcoholic extract of GSL plants at various immersion time

Parts of Gloriosa Superba Linn plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
Gloriosa Superba linn leaves	Blank	-	-	-	-	-	-	-
	5	27.09	40.35	54.32	63.79	66.76	71.53	47.90
	10	29.34	47.67	60.79	66.67	68.10	78.10	46.78
	15	40.35	55.89	64.09	75.77	77.96	80.72	45.87
	20	53.49	66.21	73.51	81.89	80.78	93.92	45.87

(Continued)

**Table 35 (Continued)**

Gloriosa Superba linn <b>stems</b>	5	23.56	35.90	49.57	75.86	76.36	79.06	58.00
	10	27.89	41.43	62.12	78.03	80.84	89.72	57.35
	15	38.07	49.67	64.75	79.56	88.90	94.17	55.90
	20	53.25	59.72	70.09	89.90	93.05	96.75	55.90
Gloriosa Superba linn <b>flowers</b>	5	40.54	50.23	61.23	76.98	88.45	89.39	47.89
	10	53.90	59.46	66.44	78.54	89.04	90.07	40.55
	15	63.72	69.03	70.96	87.02	91.90	93.56	33.90
	20	80.43	88.34	89.37	94.76	92.09	97.49	33.89
Gloriosa Superba linn <b>tubers</b>	5	49.34	58.38	60.11	71.34	79.56	88.88	41.20
	10	56.90	70.17	72.54	76.09	84.00	89.45	37.39
	15	66.75	72.64	78.96	85.23	88.73	90.92	28.90
	20	88.80	89.97	96.37	97.17	97.43	97.52	28.87

**Table 36** Inhibition efficiency of alcoholic extract of PD plants at various immersion time

Parts of Pithecellobium Dulce plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
Pithecellobium Dulce leaves	Blank	-	-	-	-	-	-	-
	5	40.23	79.66	80.91	79.50	70.12	52.16	50.23
	10	78.10	82.81	86.60	76.76	80.14	73.17	49.90
	15	85.04	85.96	90.46	87.96	90.93	85.12	47.92
	20	94.18	88.14	94.91	90.37	91.80	94.23	34.84
Pithecellobium Dulce barks	5	70.31	79.12	40.30	24.27	85.78	16.36	49.30
	10	85.95	80.12	58.12	59.17	58.82	36.27	41.28
	15	93.37	94.12	74.10	84.12	69.27	95.73	38.96
	20	95.21	96.01	88.12	95.16	91.32	46.98	28.90
Pithecellobium Dulce fruits	5	19.29	43.12	41.25	71.18	69.70	89.45	42.89
	10	29.54	52.59	62.70	72.19	72.18	35.21	35.67
	15	47.70	63.61	66.75	82.95	84.80	70.12	26.59
	20	79.12	74.05	79.69	85.80	85.50	79.18	26.59
Pithecellobium Dulce seeds	5	56.76	26.61	50.49	33.74	63.87	84.27	36.99
	10	74.16	44.50	61.50	42.76	78.69	79.12	30.87
	15	74.96	56.17	75.19	58.43	90.81	80.12	30.87
	20	82.16	80.17	82.18	86.66	94.72	95.14	29.45



**Table 37** Inhibition efficiency of alcoholic extract of AL plants at various immersion time

Parts of Alangium lamarckii Plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3days
Alangium lamarckii Leaves	Blank	-	-	-	-	-	-	-
	5	68.10	71.53	66.76	64.39	54.32	45.56	38.90
	10	78.22	80.25	78.54	76.76	60.12	68.72	33.12
	15	87.50	89.99	86.16	87.96	82.49	86.95	24.87
	20	90.2	92.16	93.15	90.37	91.30	94.10	24.70
Alangium lamarckii Barks	5	70.31	74.90	80.33	86.16	85.78	90.12	37.12
	10	75.08	86.59	87.88	87.72	86.88	94.78	36.49
	15	78.85	88.90	89.19	89.15	87.22	95.92	35.22
	20	84.93	92.03	93.05	94.09	90.78	96.91	35.20
Alangium lamarckii Fruits	5	72.81	78.90	76.14	74.21	83.89	78.90	47.21
	10	75.95	80.16	85.33	76.78	87.28	89.13	37.29
	15	78.84	84.56	87.60	82.59	87.99	92.98	37.10
	20	93.21	91.89	92.69	90.17	93.89	94.16	37.10
Alangium lamarckii Seeds	5	78.90	74.93	80.23	83.78	86.87	89.21	44.23
	10	86.98	80.54	85.33	84.98	88.96	90.56	40.21
	15	87.98	83.44	86.59	88.98	89.18	92.21	40.21
	20	92.62	90.34	94.25	92.09	91.54	94.60	40.20

**Table 38** Inhibition efficiency of alcoholic extract of HI plants at various immersion time

Parts of <i>Holoptelea</i> <i>Integrifolia</i> plant	Conc. of the extract (v/v)	Inhibition Efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
<i>Holoptelea</i> <i>Integrifolia</i> leaves	Blank	-	-	-	-	-	-	-
	5	63.12	67.33	73.98	79.29	82.90	84.42	46.28
	10	66.27	70.29	76.09	85.67	89.34	90.89	40.12
	15	68.76	79.30	83.81	86.90	90.95	93.67	40.12
	20	78.34	82.10	88.54	90.06	94.23	96.22	39.99
<i>Holoptelea</i> <i>Integrifolia</i> barks	5	20.13	34.67	46.90	62.10	78.01	89.99	52.95
	10	54.80	65.40	76.99	78.28	88.90	91.90	50.67
	15	68.23	76.33	80.18	88.22	91.47	94.93	50.60
	20	70.21	79.89	83.05	90.98	93.78	95.22	50.60
<i>Holoptelea</i> <i>Integrifolia</i> flowers	5	52.19	60.57	73.89	76.31	84.20	89.09	48.29
	10	62.90	74.65	79.67	84.22	89.37	92.11	42.18
	15	66.29	79.56	84.95	86.07	92.16	93.87	42.18
	20	79.54	80.19	88.38	90.65	93.84	95.90	40.70

(Continued)

**Table 38 (Continued)**

<i>Holoptelea Integrifolia</i> seeds	5	58.38	61.11	67.25	81.83	89.30	93.28	51.38
	10	67.89	70.25	80.12	84.74	93.95	94.76	49.97
	15	79.34	80.90	88.19	92.11	94.36	96.98	38.77
	20	82.34	84.35	90.34	93.29	96.84	97.95	30.28

**Table 39** Inhibition efficiency of alcoholic extract of SS plants at various immersion time

Parts of Schreabera swietenioids plant	Conc. of the extract (v/v)	Inhibition efficiency (%)						
		1h	3h	5h	7h	9h	12h	3 days
Schreabera swietenioids leaves	Blank	-	-	-	-	-	-	-
	5	33.08	38.11	44.24	48.28	50.78	64.37	49.73
	10	59.67	48.34	57.57	69.78	68.24	72.89	45.29
	15	62.66	64.93	65.23	73.90	75.10	88.42	45.29
	20	67.88	69.43	71.45	77.64	88.43	93.12	45.29
Schreabera swietenioids barks	5	59.92	60.76	65.23	70.26	71.94	89.90	51.90
	10	66.72	64.06	77.12	81.34	83.73	92.48	47.21
	15	78.82	65.27	80.34	87.79	90.45	94.79	47.19
	20	88.71	88.23	89.90	90.28	93.21	97.72	45.89
Schreabera swietenioids fruits	5	59.43	64.65	66.10	67.29	70.19	88.23	38.11
	10	65.03	77.35	83.04	85.12	87.34	90.06	35.90
	15	71.28	88.90	89.72	89.99	88.90	91.66	35.90
	20	75.87	90.24	94.18	95.29	93.90	93.02	35.78
Schreabera swietenioids seeds	5	70.92	72.10	77.21	79.05	90.28	92.65	49.18
	10	73.47	74.29	87.79	89.74	92.22	93.38	42.11
	15	76.89	80.78	89.34	92.18	96.07	94.99	40.84
	20	80.22	89.30	91.78	94.29	97.31	97.92	40.84

## 5.9. Effect of temperature

Temperature is one of the main factors like to modify the behavior of materials in a corrosion medium. The adsorption of organic compounds on the corroding system by physical or chemical adsorption was described by studying the effect of temperature.

The effect of temperature on the corrosion inhibition properties of all plant (both extract) was studied by exposing the mild steel in 1 N HCl containing 5, 10, 15, 20 v/v of the selected six plant (both extract) in the temperature range of 303-323 K and the data obtained are presented in **Tables 40 - 45**. The data obtained suggest that the plant extract get observed on the metal surface in both extracts studied, corrosion rate increased with increase in temperature (corrosion of metal is generally

accompanied with evolution of  $H_2$  gas) in acid solution. However, in temperature variation the *inhibition efficiency decreases with increase of temperature* indicates that the inhibitor film which formed on the metal surface is *less protective in nature at higher temperature* because of desorption (de-shielded) of inhibitor molecules from the metal surface. The result indicates that the adsorption of main active phytochemical constituents present in the inhibitors shields the metal surface at room temperature. This observation has been explained to be due to reduction in stability of adsorbed film at high temperature as temperature increases, Gibbs free energy and enthalpy rise to a higher value, so that some of the chemical bonds joining the molecules onto metallic surface are impaired and film stability reduced. This indicates that adsorption of selected six plants (both extract) extract is spontaneous and occurs via physical adsorption.

The decrease in IE with rise in temperature, as illustrated in **Table 40**, suggests that the possible desorption of some of the adsorbed inhibitor from the metal surface at high temperature. From this occurrence, it can be said that the decrease in IE with increase in temperature could be traceable to the fact that, at lower temperature, inhibitor molecules have the tendency to adsorb themselves on the steel surface. So, at lower temperature, the inhibitor has the tendency to establish stronger interaction to the surface of the mild steel than at high temperature. Also the adsorption of the **ML** plant (both extract) onto the mild steel surface at lower temperature prevents the breakdown of the passive film, hence higher corrosion resistance of mild steel.

To evaluate the adsorption of **GSL** in both extract in HCl acid media, mass loss data were investigated in the range of 303-323 K and the results are depicted in **Table 41**. Further rise in temperature, decreases the IE at higher concentration. This observation established the effectiveness of GSL extract in reducing corrosion of mild steel in the temperature range of 313K. It results that the lower IE at high temperature.

Weight loss measurement was carried out over range of 303-323 K in the presence and absence of **PD** plant (both extract) for an immersion period of 1h, to evaluate the stability of the adsorbed film on the mild steel. The results obtained are listen in **Table 42**. The IE increase up to 313 K and thereafter decrease. Also, with increased desorption of inhibitor at high temperature, more surface area of mild steel come in contact with acid environment, resulting in decrease in IE with increase in temperature.

Weight loss experiment was carried out at different temperature in the presence and absence of **AL** plant (both extract) to evaluate the stability of the adsorbed film on the mild steel plates. The results obtained are shown in **Table 43**. At elevated temperature, the rate of dissolution of mild steel increases as time lag between adsorption and desorption decrease and hence the inhibition efficiency decreases. Metal surface remaining exposed to acid environment for a longer period increase the rate of corrosion and thus decreases the IE.

Weight loss studies were carried out at three different temperatures in presence and absence of **HI** plant (both extract) and the inhibition efficiency values calculated are presented in **Table 44**. From the table, it is noted that the IE increases steadily with increasing concentration of the inhibitor. The IE decrease with increasing

temperature, though it is not so significant. The data represents the dependence of inhibitor concentration for improved protection.

Temperature change of the system involving mild steel in HCl acid solution is a function of time in the absence and presence of different concentration of *SS* plants (both extract) and the IE values calculated are presented in **Table 45**. Addition of the inhibitor caused a decreased in the high temperature and an increase in the time required reaching it. The effectiveness of the *SS* plant extract is attributable to the presence of pi electron in aromatic ring and lone pair of electron on the nitrogen and oxygen atom. This indicates that adsorption of *SS* plants (both extract) is spontaneous and occurs via physical adsorption.

**Table 40** The percentage inhibition efficiency of ML plants (both extracts) at various temperatures

Aqueous extract					Alcoholic extract			
Parts of Madhuca Longifolia plant	Conc. of the extract (v/v)	IE (%)			Conc. of the extract (v/v)	IE (%)		
		303K	313K	323K		303K	313K	323K
Madhuca Longifolia leaves	Blank	*	*	*	Blank	*	*	*
	5	44.10	46.20	40.70	5	50.64	45.15	46.66
	10	57.60	58.60	44.80	10	68.83	52.72	43.01
	15	62.20	62.80	32.20	15	69.22	57.27	30.95
	20	63.10	57.30	26.10	20	70.90	66.36	38.88
Madhuca Longifolia barks	5	47.40	43.10	48.61	5	45.90	38.39	33.80
	10	51.50	49.40	35.71	10	52.45	36.79	28.33
	15	56.20	51.60	20.15	15	68.85	32.83	26.87
	20	64.30	59.15	16.18	20	71.80	28.82	22.95
Madhuca Longifolia fruits	5	44.35	41.85	31.00	5	24.92	39.96	6.34
	10	48.69	53.97	49.59	10	38.20	52.15	26.98
	15	54.55	57.60	54.84	15	44.04	63.67	32.06
	20	59.10	60.10	56.50	20	70.59	67.21	55.55
Madhuca Longifolia seed peels	5	53.84	43.47	34.59	5	25.97	20.25	27.63
	10	66.43	59.56	46.76	10	55.32	42.02	35.78
	15	74.40	69.56	57.42	15	74.41	58.48	45.00
	20	80.41	73.69	60.12	20	82.20	76.87	62.10

**Table 41** The percentage inhibition efficiency of GSL plants (both extracts) at various temperatures.

Aqueous extract of GSL plants					Alcoholic extract of GSL plants			
Parts of <i>Gloriosa Superba</i> Linn (GSL) plant	Conc. of the extract (v/v)	IE (%)			Conc. of the extract (v/v)	IE (%)		
		303K	313K	323K		303K	313K	323K
<i>Gloriosa Superba</i> Linn <b>Leaves</b>	Blank	-	-	-	Blank	-	-	-
	5	34.13	39.12	26.76	5	39.48	40.24	36.48
	10	57.60	50.67	42.54	10	59.59	57.54	41.36
	15	62.28	57.95	50.16	15	71.36	63.74	48.04
	20	76.65	62.12	53.15	20	81.02	77.22	53.66
<i>Gloriosa Superba</i> Linn <b>Stems</b>	5	66.66	65.50	64.55	5	65.71	56.58	49.58
	10	71.11	69.40	68.54	10	73.89	62.24	54.86
	15	81.48	75.97	74.76	15	77.48	74.41	47.24
	20	82.22	79.05	77.79	20	80.45	77.13	45.50
<i>Gloriosa Superba</i> Linn <b>Flowers</b>	5	44.35	49.85	51.67	5	66.12	59.90	47.41
	10	48.69	53.97	59.59	10	67.90	61.55	60.55
	15	54.55	57.64	60.29	15	73.65	66.86	66.27
	20	68.76	61.48	65.65	20	74.97	72.12	69.80
<i>Gloriosa Superba</i> Linn <b>Tubers</b>	5	47.40	12.15	26.81	5	39.25	50.29	40.02
	10	50.37	59.13	34.37	10	64.48	60.73	54.82
	15	60.01	68.17	58.36	15	71.49	66.69	58.18
	20	71.10	74.70	69.03	20	77.59	74.78	63.10

**Table 42** The percentage inhibition efficiency of PD plants (both extracts) at various temperatures.

Aqueous extract of PD plants					Alcoholic extract of PD plants			
Parts of <i>Pithecellobium Dulce</i> plant	Conc. of the extract (v/v)	IE (%)			Conc. of the extract (v/v)	IE (%)		
		303K	313K	323K		303K	313K	323K
<i>Pithecellobium Dulce</i> <b>leaves</b>	Blank	-	-	-	Blank	-	-	-
	5	57.01	64.00	32.10	5	17.56	15.94	19.67
	10	62.50	71.00	37.08	10	59.45	40.56	36.04
	15	79.10	77.79	59.14	15	60.81	46.57	37.26
	20	84.64	81.16	61.00	20	73.24	51.30	48.52
<i>Pithecellobium Dulce</i> <b>barks</b>	5	72.67	69.26	65.36	5	17.24	38.80	16.17
	10	83.44	78.48	72.18	10	31.03	70.14	30.29
	15	87.65	82.19	79.21	15	70.68	72.08	36.17
	20	88.04	86.79	81.76	20	81.03	78.58	42.35

(Continued)

**Table 42 (Continued)**

Pithecellobium Dulce fruits	5	40.52	46.18	82.10	5	20.83	34.24	18.66
	10	52.64	55.72	46.89	10	58.33	64.38	53.33
	15	62.18	61.47	58.91	15	75.00	78.08	69.33
	20	72.10	71.36	62.38	20	84.72	81.78	70.66
Pithecellobium Dulce seeds	5	30.24	39.34	35.21	5	21.40	35.33	24.69
	10	48.72	49.15	40.84	10	39.43	40.00	46.91
	15	60.11	59.53	52.59	15	60.56	66.66	61.60
	20	70.27	68.21	66.39	20	84.50	78.00	65.18

**Table 43** The percentage inhibition efficiency of AL plants (both extracts) at various temperatures.

Parts of Alangium lamarckii plant	Conc. of the extract (v/v)	Aqueous extract IE (%)			Conc. of the extract (v/v)	Alcoholic extract IE (%)		
		303K	313K	323K		303K	313K	323K
Alangium lamarckii leaves	Blank	*	*	*	Blank	*	*	*
	5	59.48	40.24	26.48	5	53.16	26.38	14.06
	10	61.59	57.54	35.36	10	69.62	34.72	44.06
	15	69.36	63.74	68.04	15	72.15	77.77	65.00
	20	89.02	87.22	73.66	20	86.07	78.88	70.50
Alangium lamarckii barks	5	65.71	56.58	59.58	5	22.97	23.61	32.53
	10	73.89	62.24	64.86	10	43.24	27.77	63.85
	15	77.48	74.41	69.24	15	60.81	73.61	69.13
	20	80.45	77.13	70.50	20	89.18	78.88	70.36
Alangium lamarckii fruits	5	46.12	59.90	47.41	5	30.12	25.97	44.26
	10	67.90	61.55	60.55	10	60.12	51.20	51.02
	15	73.65	66.86	66.31	15	78.01	64.56	63.56
	20	74.97	72.12	69.80	20	86.48	81.23	73.41
Alangium lamarckii seeds	5	39.25	50.29	40.02	5	35.23	32.15	23.09
	10	64.48	60.73	54.82	10	44.52	39.54	40.56
	15	71.49	66.69	60.18	15	66.03	58.90	56.81
	20	77.59	74.78	70.10	20	80.83	76.65	69.31

**Table 44** The percentage inhibition efficiency of HI plants (both extracts) at various temperatures.

Aqueous extract of HI plants					Alcoholic extract of HI plants			
Parts of <i>Holoptelea Integrifolia</i> plant	Conc. of the extract (v/v)	IE (%)			Conc. of the extract (v/v)	IE (%)		
		303 K	313 K	323 K		303 K	313 K	323 K
<i>Holoptelea</i>	Blank	-	-	-	Blank	-	-	-
	5	22.18	18.12	17.23	5	74.35	10.00	48.46

<i>Integrifolia</i> <b>leaves</b>	10	41.06	30.42	25.69	10	89.74	50.90	50.38
	15	58.60	38.41	32.71	15	92.30	61.90	65.38
	20	69.51	52.20	46.22	20	92.30	78.18	68.84
<i>Holoptelea</i> <i>Integrifolia</i> <b>barks</b>	5	38.24	32.18	29.10	5	43.18	48.27	45.16
	10	56.42	40.36	32.32	10	65.90	51.72	34.51
	15	68.25	50.22	43.98	15	79.54	68.96	50.96
	20	69.16	70.33	51.71	20	84.09	79.31	67.41
<i>Holoptelea</i> <i>Integrifolia</i> <b>flowers</b>	5	18.56	15.14	10.21	5	58.92	38.09	30.43
	10	21.96	19.32	17.54	10	62.50	52.38	36.95
	15	25.97	21.73	19.06	15	73.21	57.14	63.04
	20	29.43	28.81	22.19	20	85.71	80.95	72.60
<i>Holoptelea</i> <i>Integrifolia</i> <b>seeds</b>	5	38.33	34.08	28.69	5	38.46	48.00	36.81
	10	54.02	49.25	43.46	10	69.23	68.00	59.09
	15	74.02	51.12	46.46	15	73.09	74.00	70.45
	20	85.56	60.53	52.67	20	84.23	79.00	69.72

**Table 45** The percentage inhibition efficiency of SS plants (both extracts) at various temperatures.

Parts of Schreabera swietenioids plant	Conc. of the extract (v/v)	IE (%)			Conc. of the extract (v/v)	IE (%)		
		303K	313K	323K		303K	313K	323K
Schreabera swietenioids <b>leaves</b>	Blank	-	-	-	Blank	*	*	*
	5	74.49	70.63	64.00	5	13.75	40.24	21.91
	10	85.15	77.40	71.50	10	27.50	71.95	56.16
	15	89.15	80.16	76.50	15	76.25	78.04	62.19
	20	91.13	82.04	80.00	20	85.00	89.02	78.04
Schreabera swietenioids <b>barks</b>	5	47.10	44.00	42.00	5	16.25	42.66	44.04
	10	62.50	56.50	47.88	10	40.00	58.66	53.80
	15	76.48	70.60	67.83	15	78.75	69.33	59.76
	20	80.28	77.50	75.66	20	81.25	74.00	62.14
Schreabera swietenioids <b>fruits</b>	5	57.20	45.59	33.05	5	34.11	10.95	18.05
	10	71.16	60.06	56.07	10	57.64	46.57	50.00
	15	75.13	62.30	59.72	15	65.88	54.38	69.16
	20	77.16	69.16	64.82	20	71.76	73.56	70.27
Schreabera swietenioids <b>seeds</b>	5	34.74	31.57	38.21	5	26.38	34.21	26.38
	10	42.25	36.31	39.67	10	61.11	59.21	38.88
	15	57.31	47.89	44.45	15	65.27	72.36	62.50
	20	61.43	53.68	54.45	20	70.27	74.58	71.22

## 5.10 Adsorption isotherm

The primary step in the action of inhibitors in acid solution is generally agreed to be adsorption on the MS surface. In order to clarify the nature of adsorption, temperature dependence of corrosion rates in uninhibited and inhibited solution, weight loss measurement were carried out in the temperature range 303 – 323 K. The

information on the collaboration between inhibitor molecules (organic adsorbate) and mild steel surface can be provided by adsorption isotherm. In order to obtain the isotherm, the fractional surfaces coverage ( $\theta$ ) as a function of inhibitor concentration must be obtained. Recent researches have looked into action of the adsorption from a purely mechanistic kinetic point of view.

It is well established that the first step in corrosion inhibition of metal and alloys is the adsorption of organic inhibitor molecules at the metal/solution interface. The extent of adsorption on many factors, such as the nature of metal, conditions of metal surface, the chemical structure of the inhibitors and nature of its functional groups, pH and type of corrosion medium and temperature. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitor on the steel surface. Several adsorption isotherm viz., *Frumkin*, *Hasley*, *Langmuir*, *Temkin*, *Freundlich*, *flory-Huggins* were tested and the adsorption isotherm was found to provide the best description of the behaviour of this inhibitor. The mass loss measurements are tested graphically for fitting three isotherms like *Hasley*, *Langmuir and Temkin*. Attempts were made to fit surface coverage values determined from weight loss measurements into different adsorption isotherms models *figures 94-129*. The alcoholic and aqueous data plot showed [see *Fig. 94-129*] a straight line with regression coefficient almost equal to 1. The adsorption indicating major components (heterocyclic), compounds usually contains polar function with hetero atom such as *N, S, O, and P and have double or triple bond or aromatic ring* have more active sites (electron donor and possibility of centre of adsorption) in the all plants is strongly adsorbed on the metal surface by mutual attraction of the molecules. The adsorption studied suggested that all the six plants (both extract) obeyed the following adsorption isotherm:

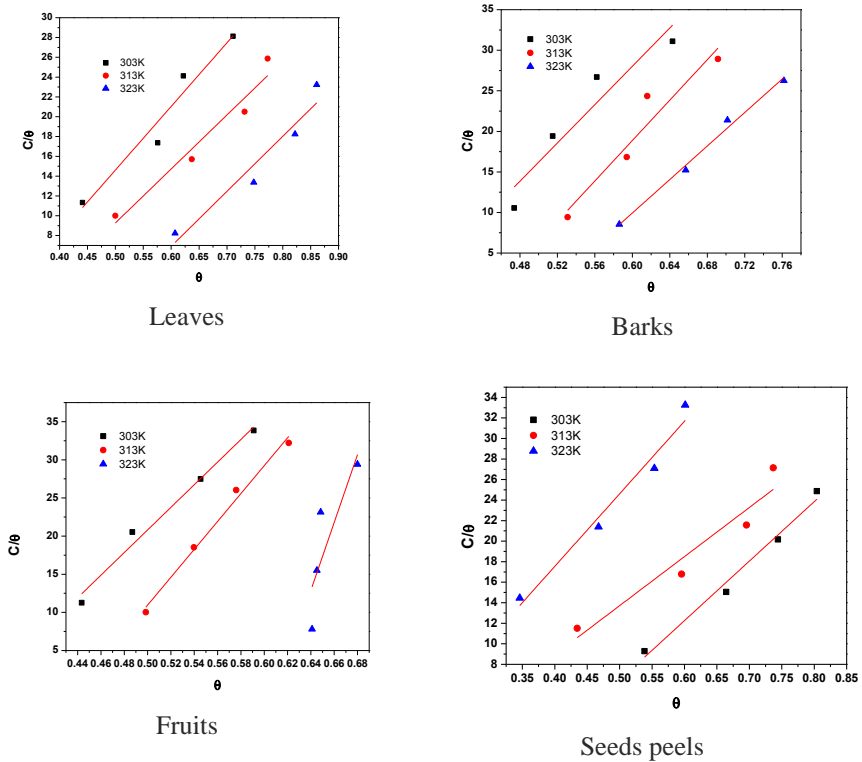
**Langmuir isotherm:** The plots of  $\log (\theta/(1-\theta))$  vs  $\log C$  yield a straight line, where  $C$  is the inhibitor concentration, proving that the inhibition is due to the adsorption of the active compounds onto the metal surface and obeys the *Langmuir isotherm* [Figures 95, 98.,]. From the results obtained, it is significant to note that these plots are linear with slopes equal to unity, which indicates a strong adherence of the adsorption data to the assumptions confirming Langmuir adsorption isotherm.

**Temkin isotherm:** The plots of  $\theta$  against  $\log C$  as shown in figures [see 97, 100] gave a linear relationship indicating that the adsorption of the compounds on the mild steel surface from acid followed Temkin adsorption isotherm, supporting the hypothesis that corrosion inhibition by these compounds results from adsorption on the metal surface. The applicability of Temkin's adsorption isotherm verifies the assumption of monolayer adsorption on a uniform, homogeneous metal surface with an interaction in the adsorption layer.

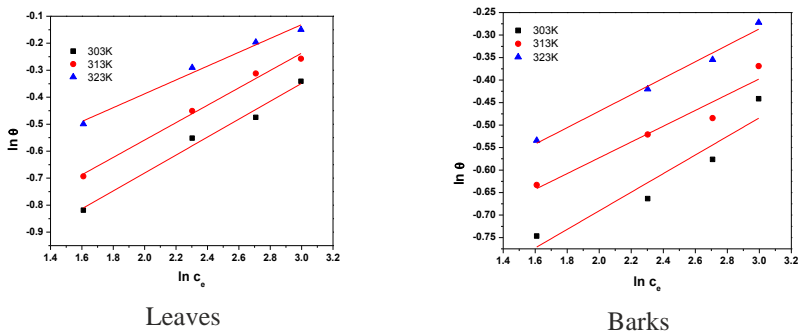
**Hasley isotherm:** the plots of  $\log \theta$  against  $\ln C$  as shown [96, 99.,] in linear lines confirm that obeys Hasley isotherm. In the action mechanism of inhibitor in acid media the first step is adsorption on the metal surface. The formation of donor-acceptor surface complexes between pi-electron of inhibitor and the vacant d-orbital of metal was postulated in most of the inhibition studies. These isotherms are very important in determining the mechanism of *Organo-electrochemical reaction* and it provides important clues to the nature of the *metal-inhibitor interaction*. The

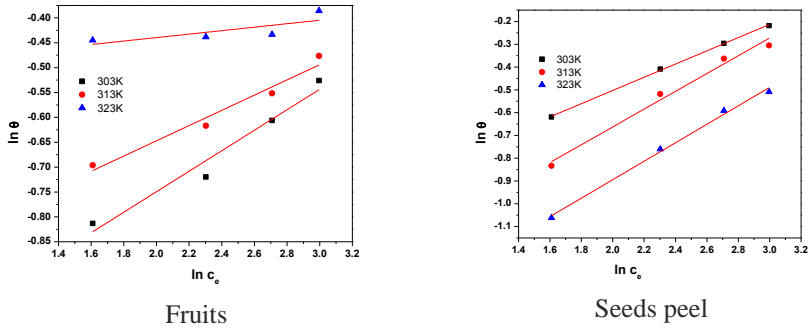


metal/solution interface is due to the formation of either *electrostatic or covalent bonding between the adsorbates and the metal surface atom*. Good correlation between plant water and alcoholic soluble constituent and suggest *physical adsorption mechanism* was obtained.

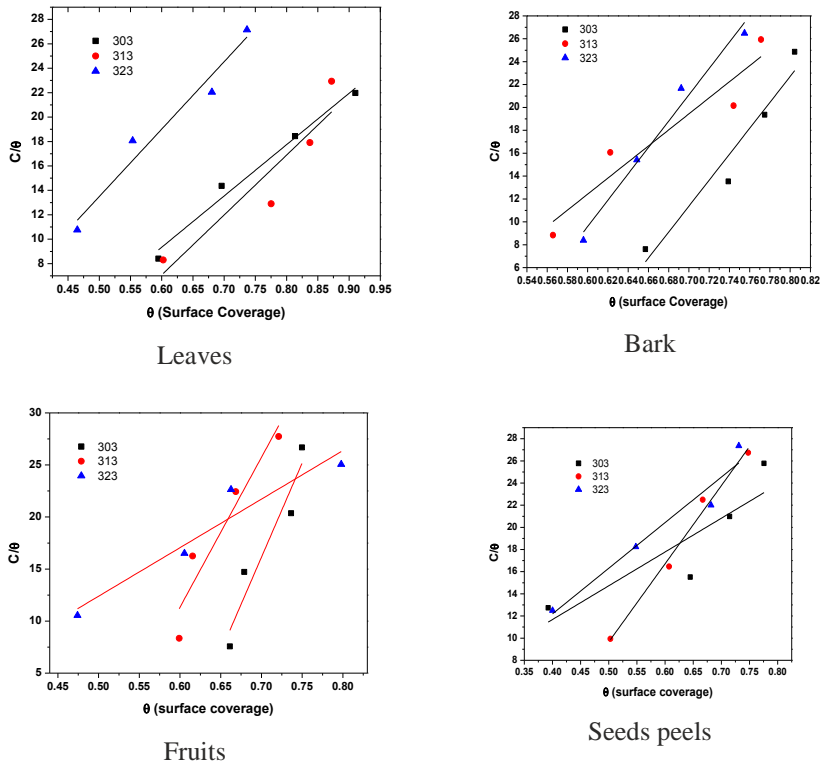


**Fig. 95** Langumir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of ML plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds peels.

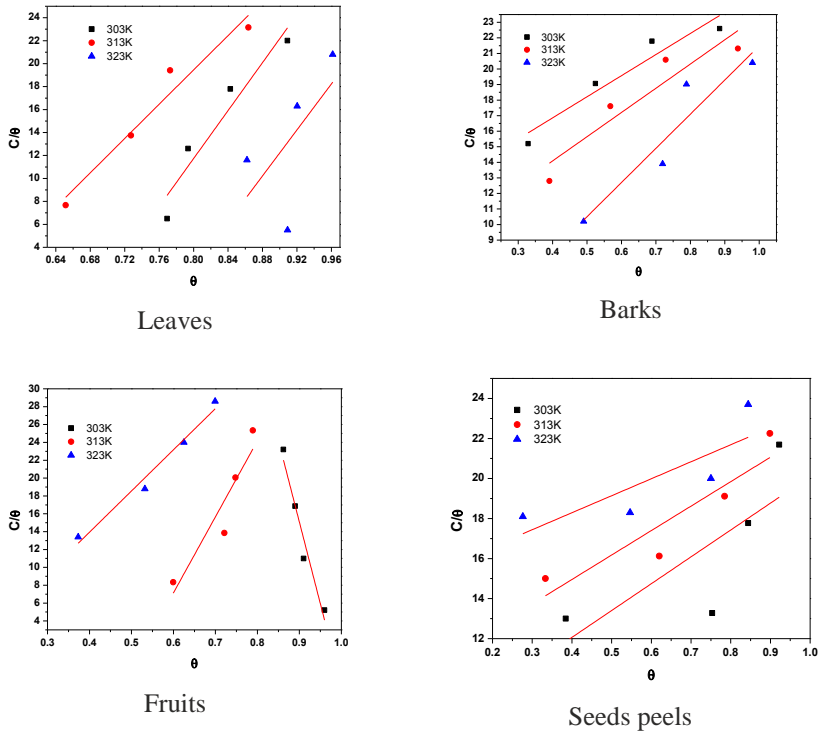




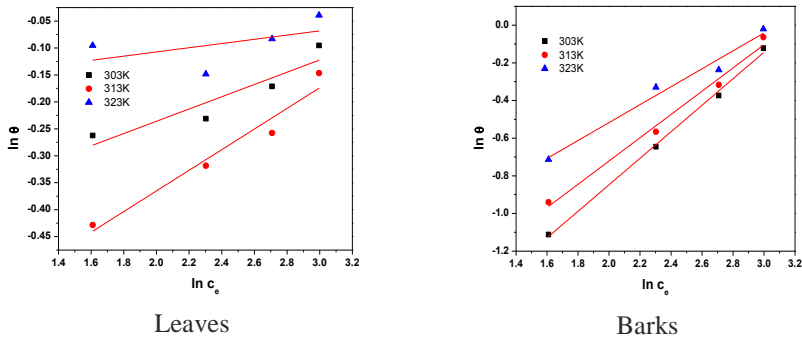
**Fig. 96** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of ML plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds peels.

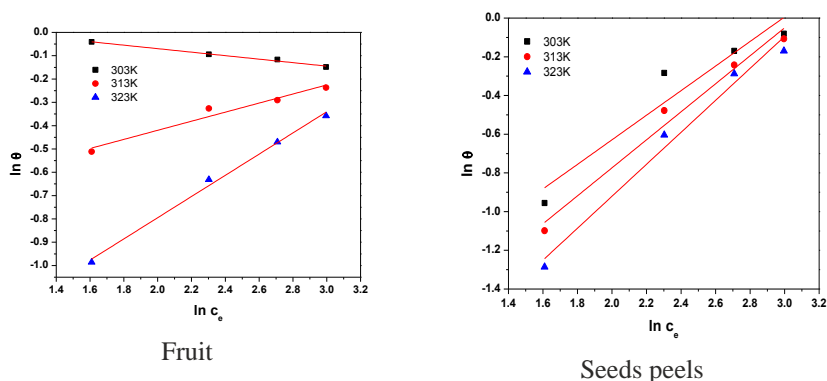


**Fig. 97** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of ML plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds peels.

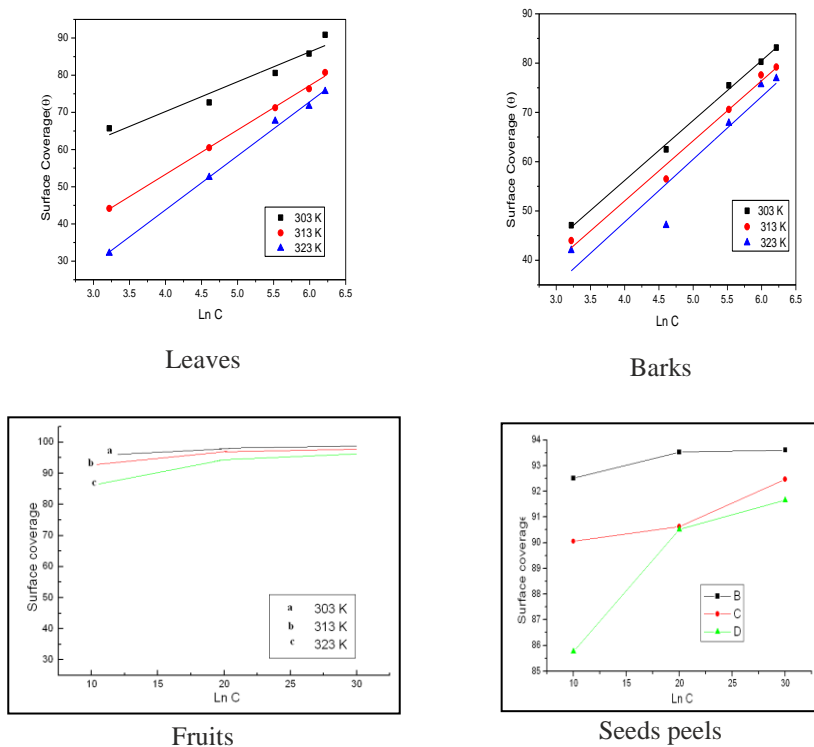


**Fig. 98** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of ML plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds peels.

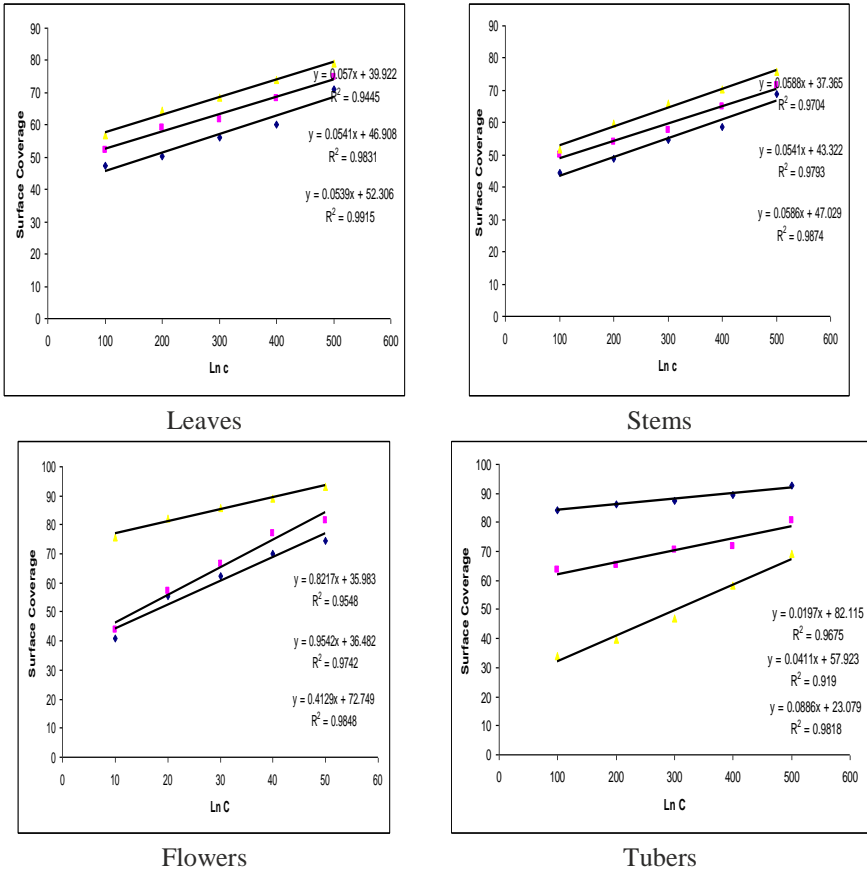




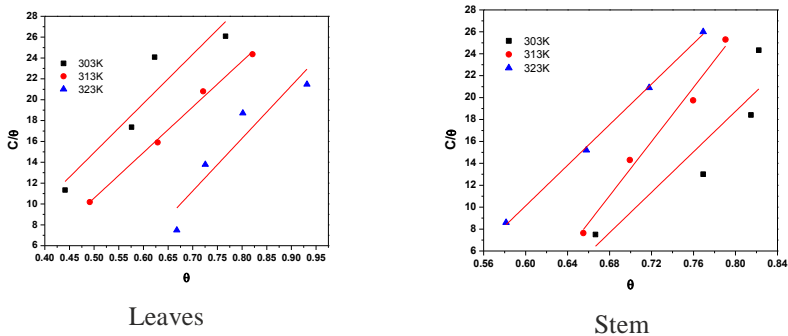
**Fig. 99** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of ML plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds peels.

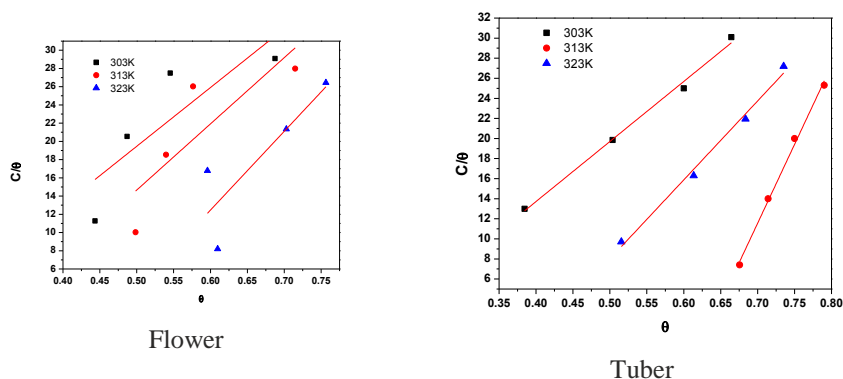


**Fig. 100** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of ML plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds peels.

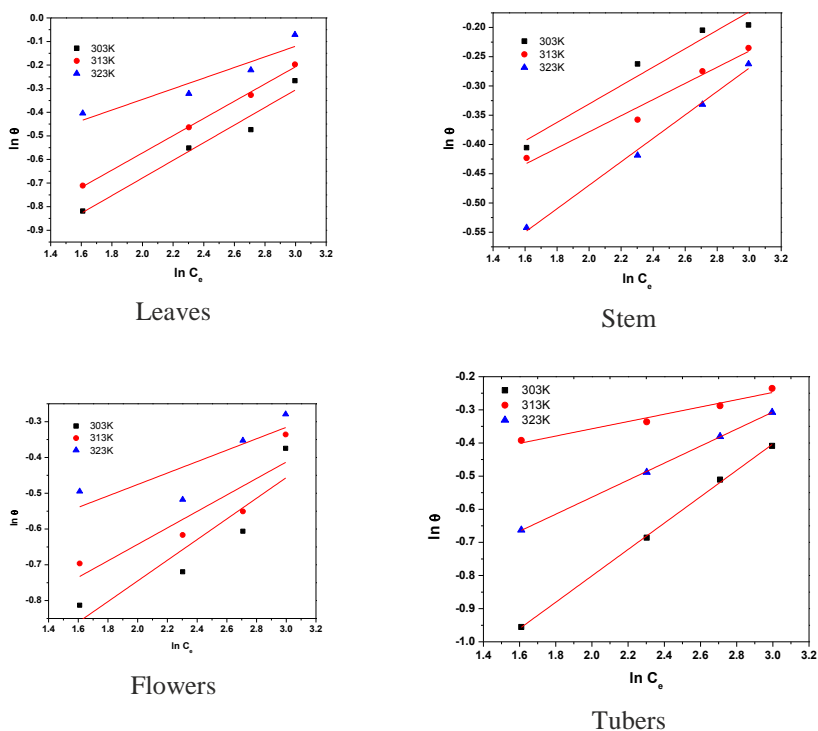


**Fig. 101** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Gloriosa superba* linn plant aqueous extracts (a) leaves (b) stems (c) flowers and (d) tubers.

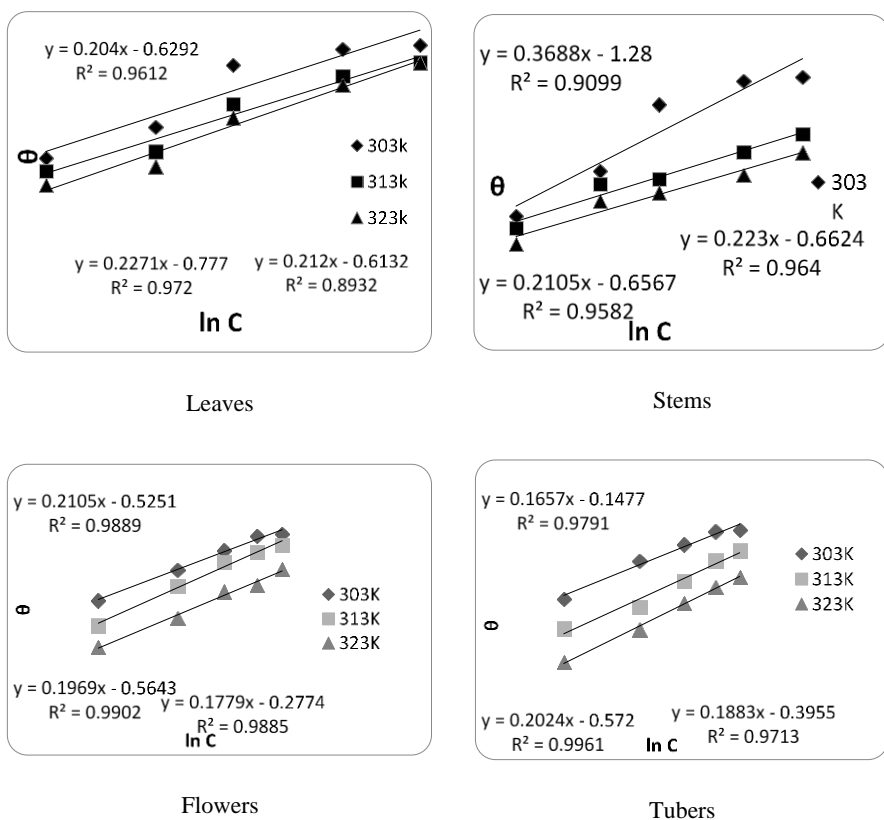




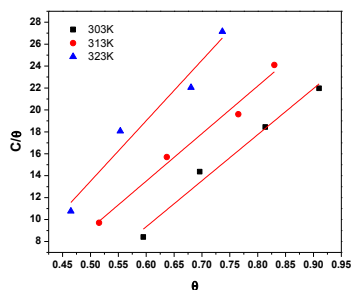
**Fig. 102** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Gloriosa superba* linn plant aqueous extracts (a) leaves (b) stems (c) flowers and (d) tubers.



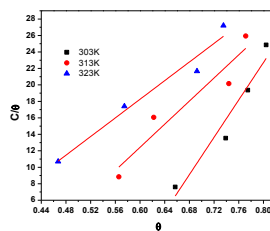
**Fig. 103** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Gloriosa superba* linn plant aqueous extracts (a) leaves (b) stems (c) flowers and (d) tubers.



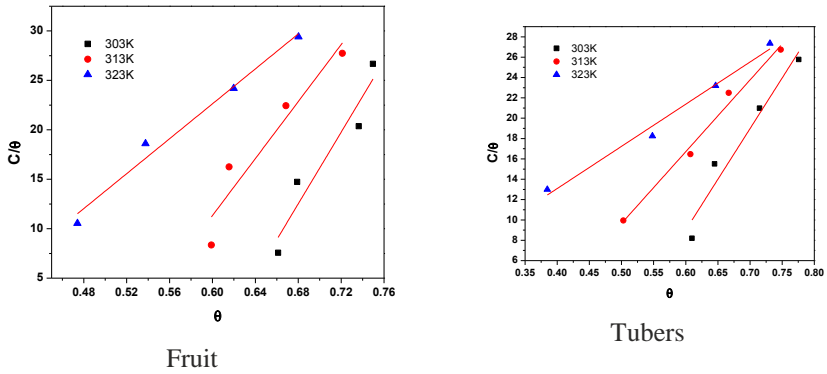
**Fig. 104** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Gloriosa superba* linn plant alcoholic extracts (a) leaves (b) stems (c) flowers and (d) tubers.



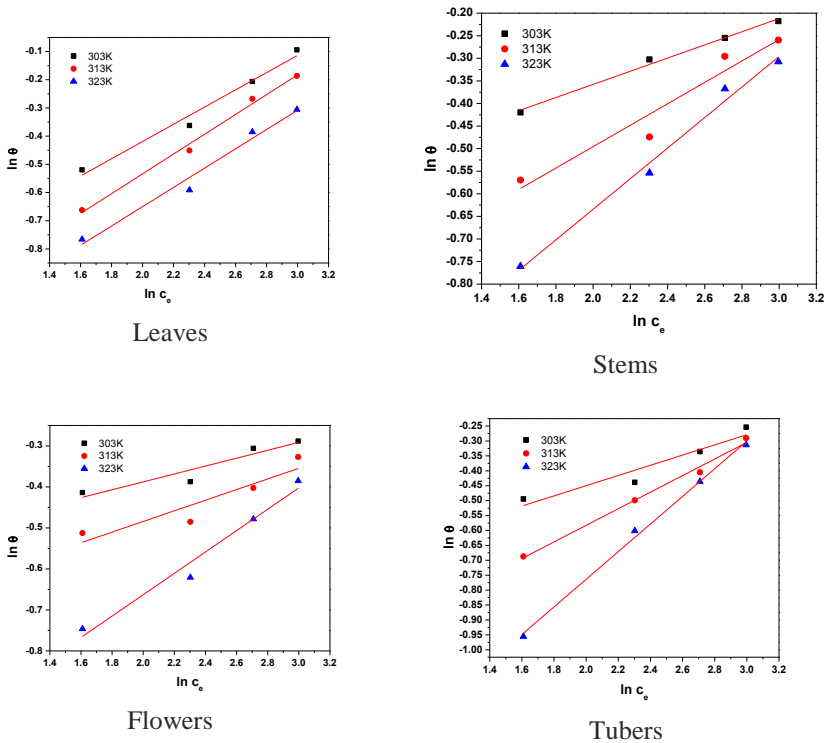
Leaves



Stems

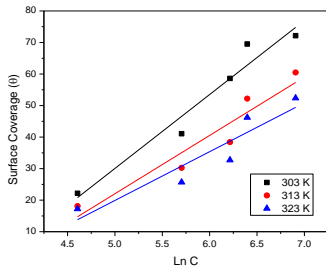


**Fig. 105** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Gloriosa superba* linn plant alcoholic extracts (a) leaves (b) stems (c) flowers and (d) tubers.

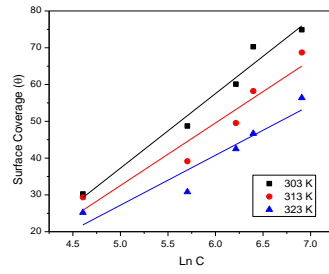


**Fig. 106** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Gloriosa superba* linn plant alcoholic extracts (a) leaves (b) stems (c) flowers and (d) tubers.

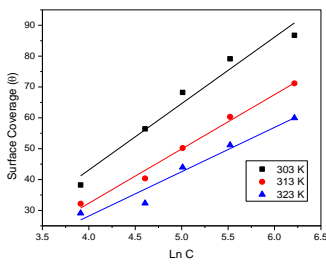




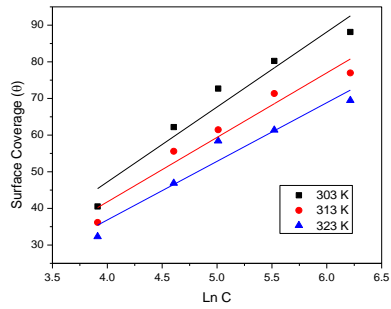
Leaves



Barks

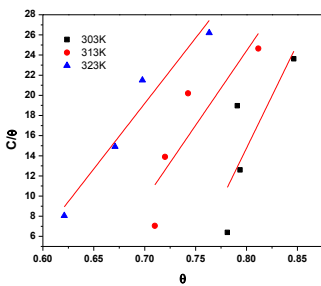


Fruits

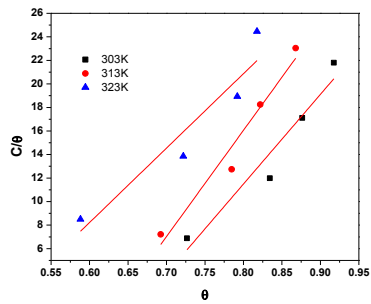


Seeds

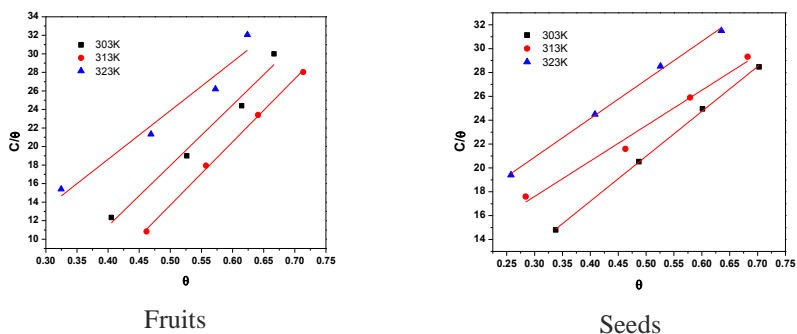
**Fig. 107** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of PD plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.



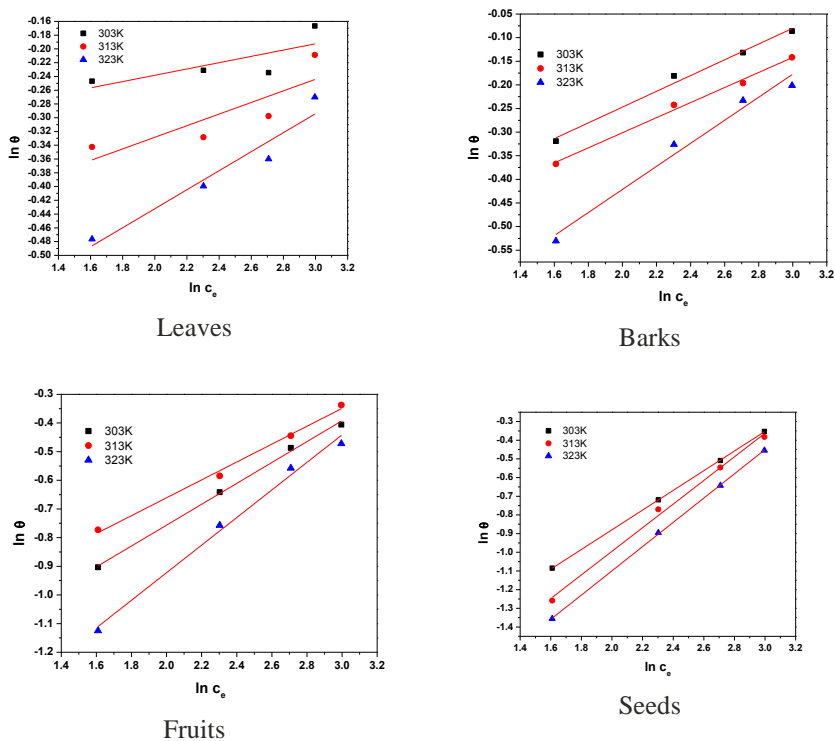
Leaves



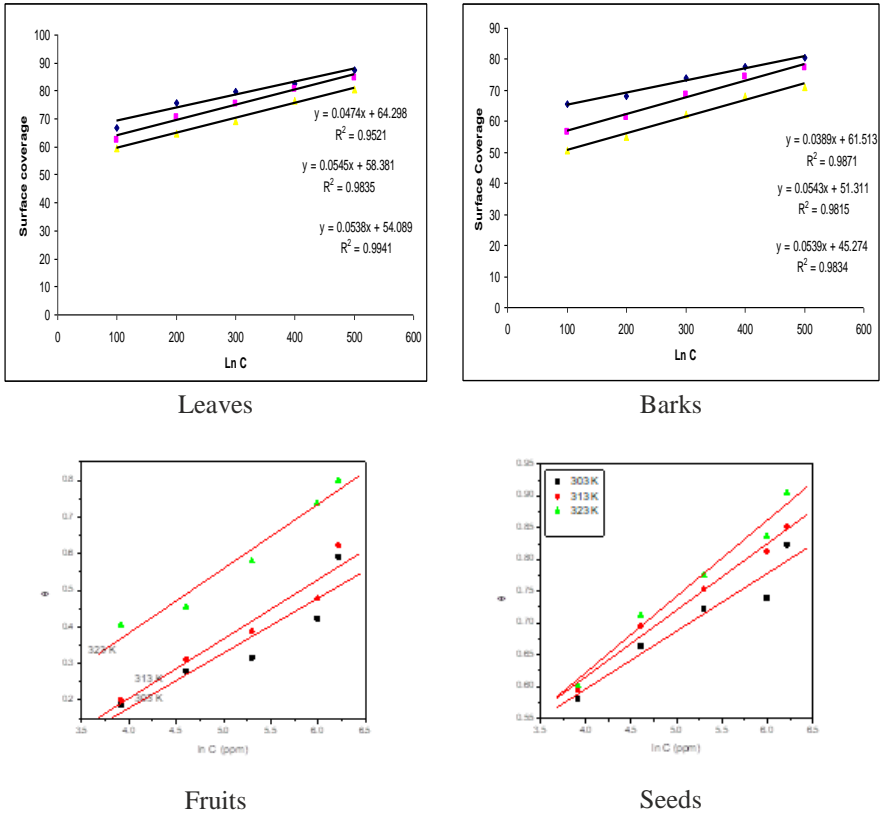
Barks



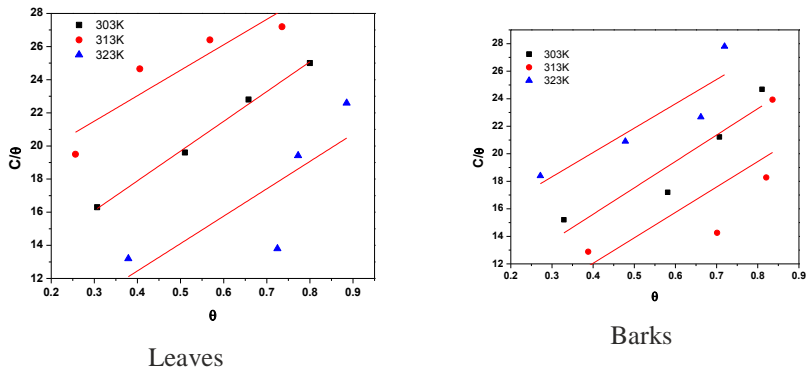
**Fig. 108** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of PD plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.

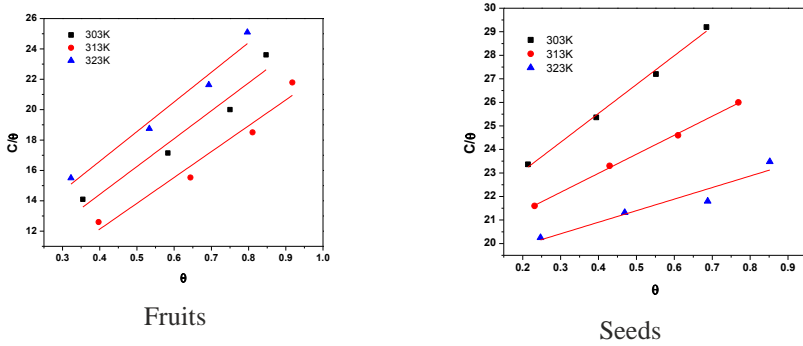


**Fig. 109** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of PD plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.

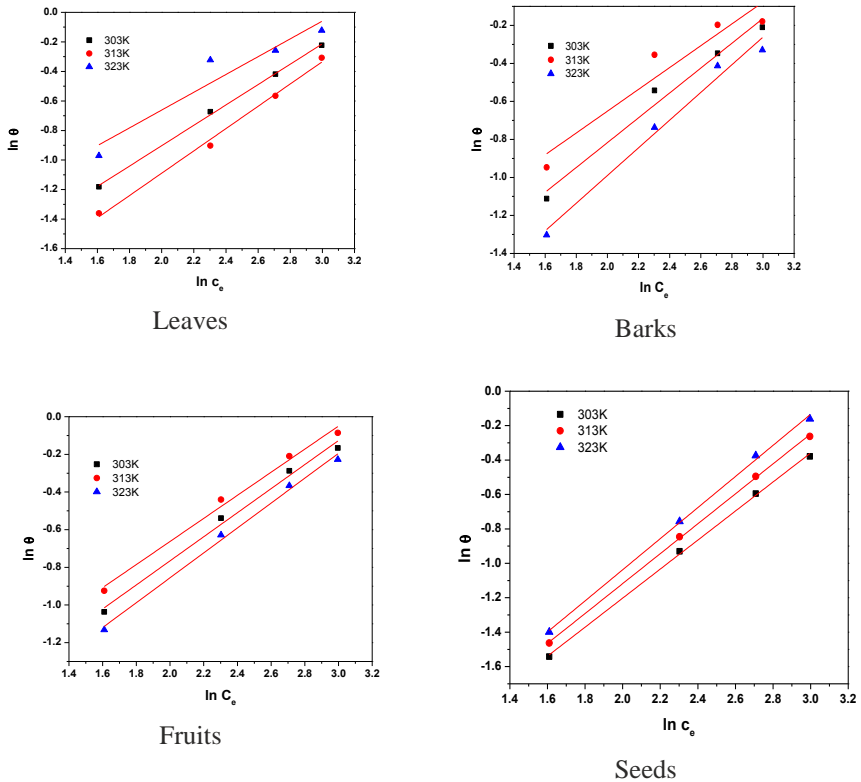


**Fig. 110** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of PD plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.

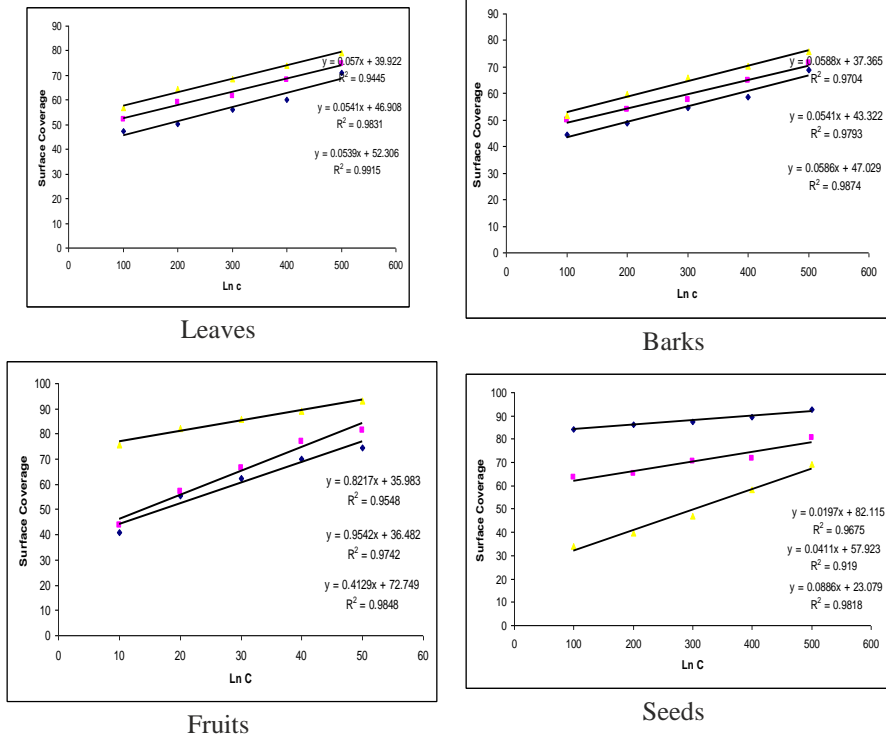




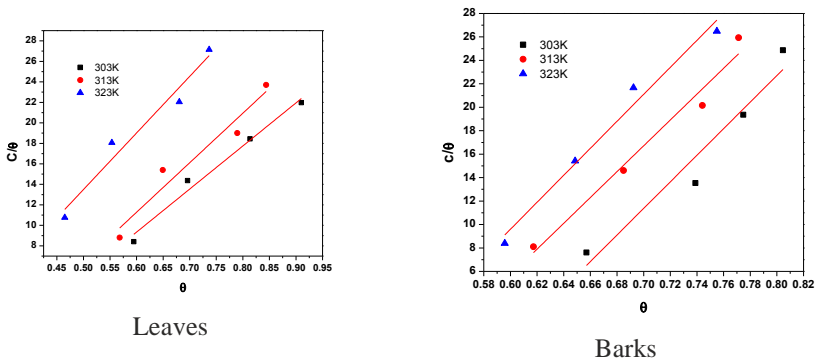
**Fig. 111** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of PD plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.

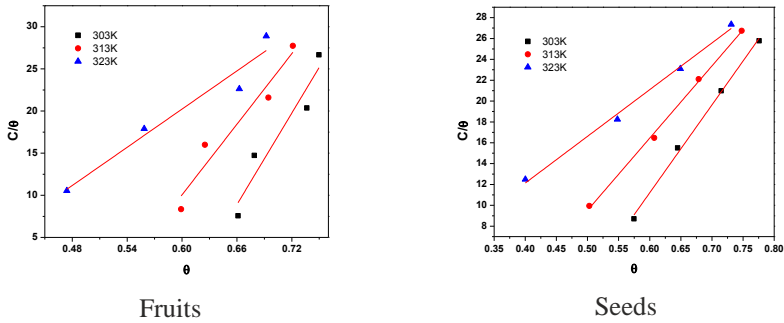


**Fig. 112** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of PD plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.

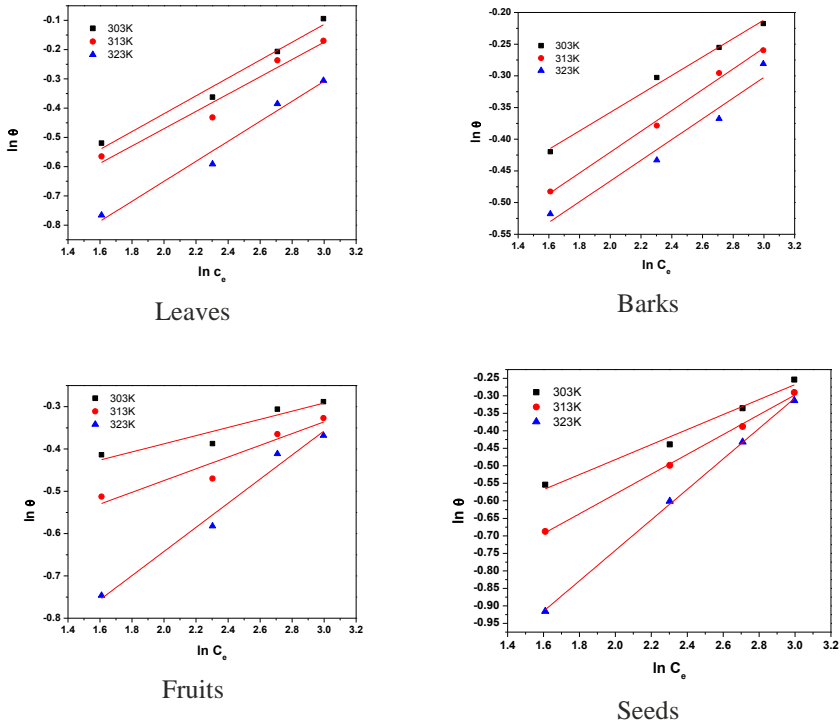


**Fig. 113** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Alangium lamarckii* plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.

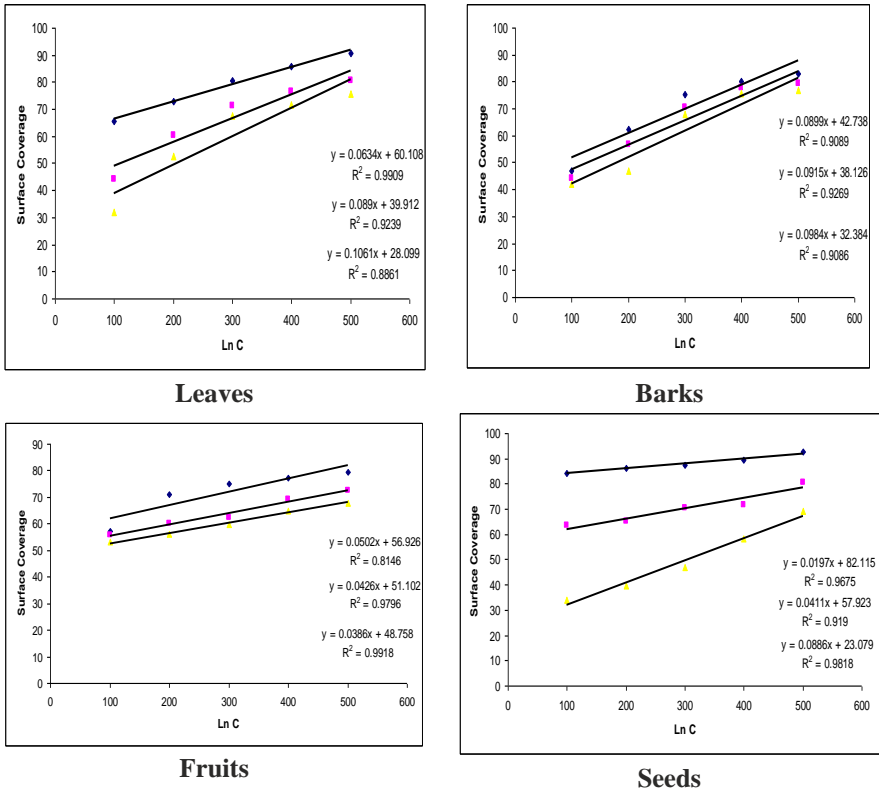




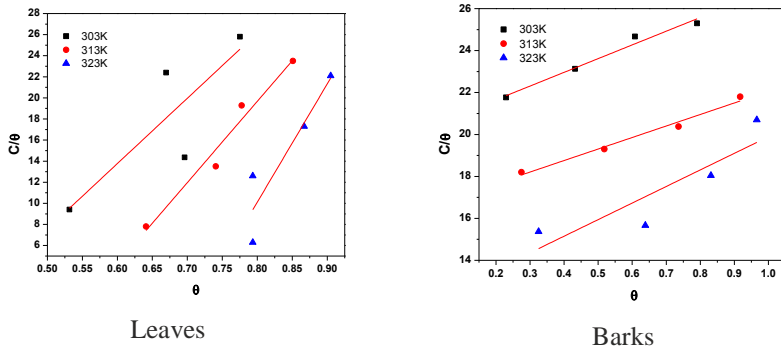
**Fig. 114** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Alangium lamarckii* plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.

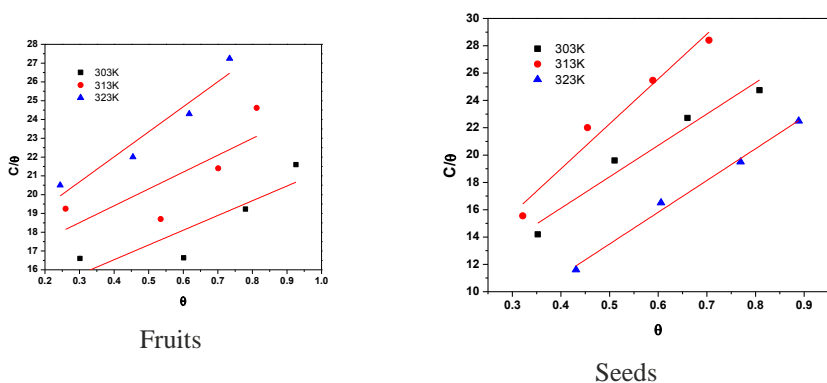


**Fig. 115** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Alangium lamarckii* plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.

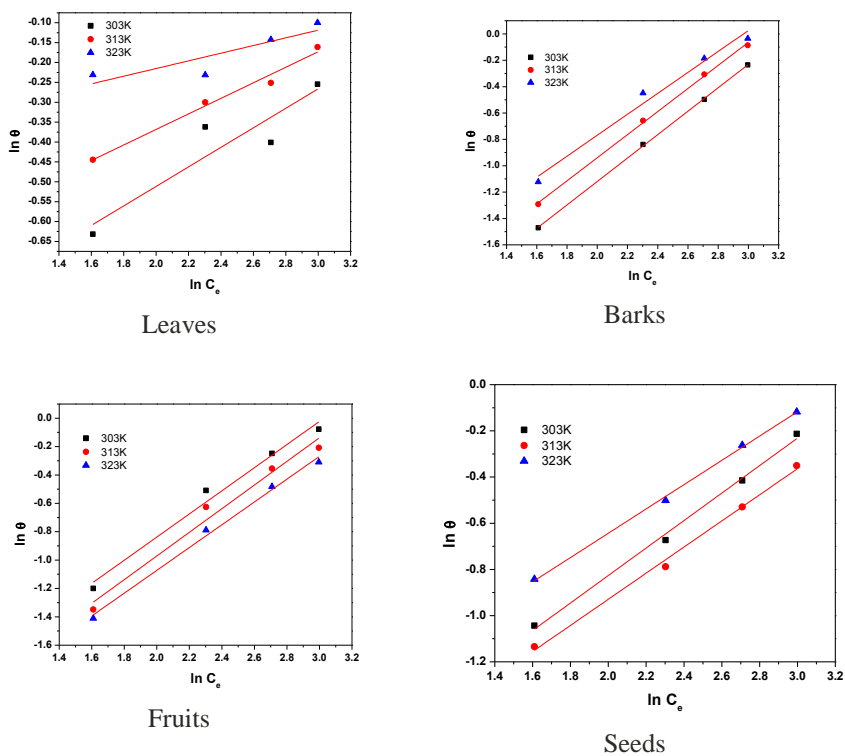


**Fig. 116** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Alangium lamarckii* plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.



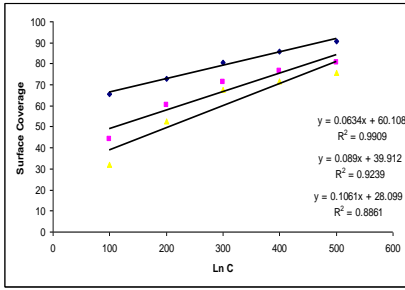


**Fig. 117** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Alangium lamarckii* plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.

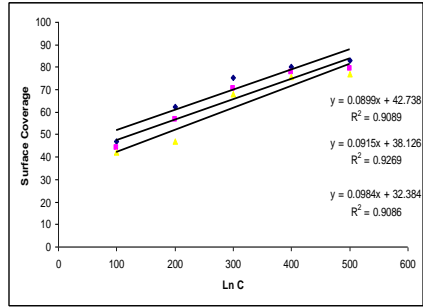


**Fig. 118** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of *Alangium lamarckii* plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.

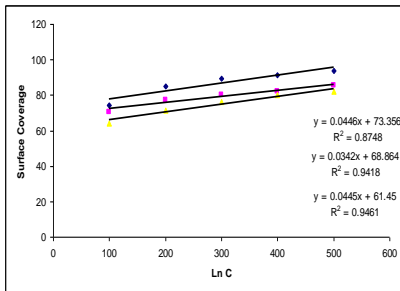




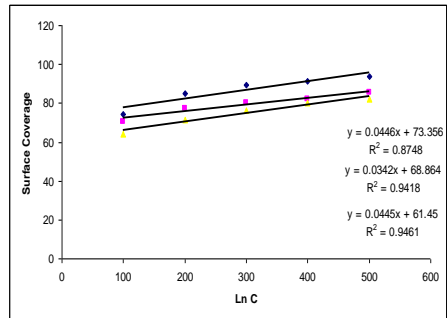
Leaves



Barks

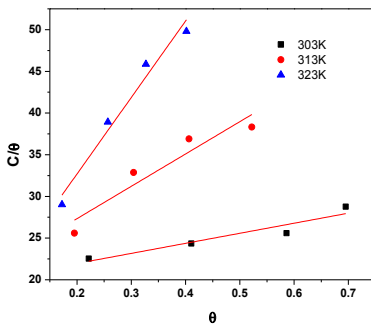


Flowers

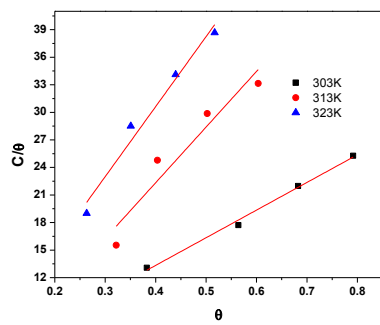


Seeds

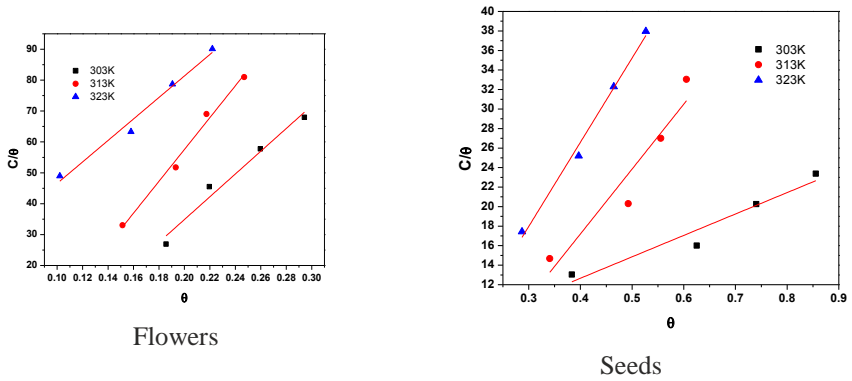
**Fig. 119** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of HI plant aqueous extracts (a) leaves (b) barks (c) flowers and (d) seeds.



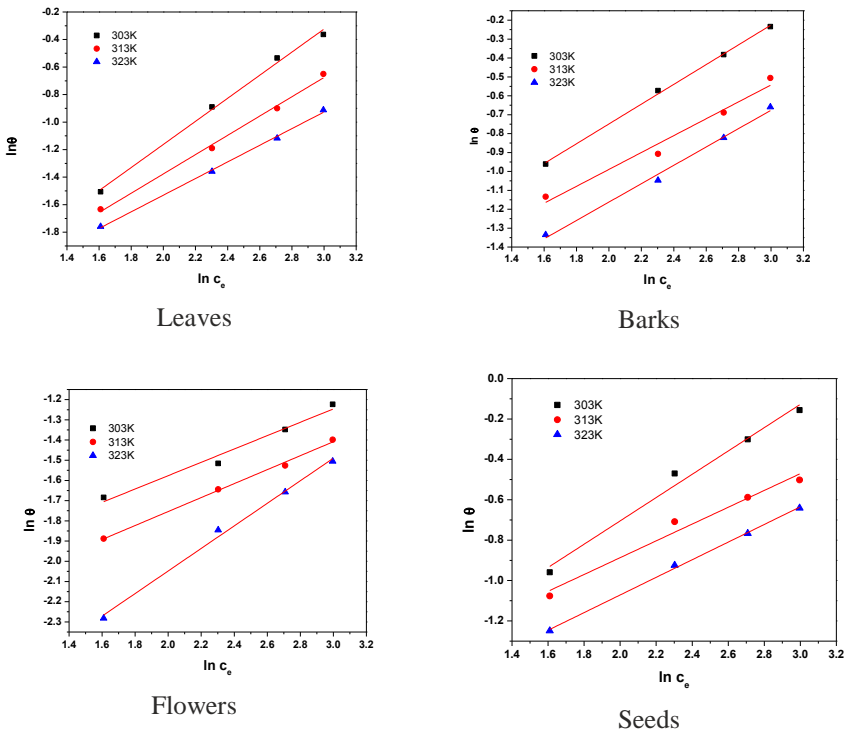
Leaves



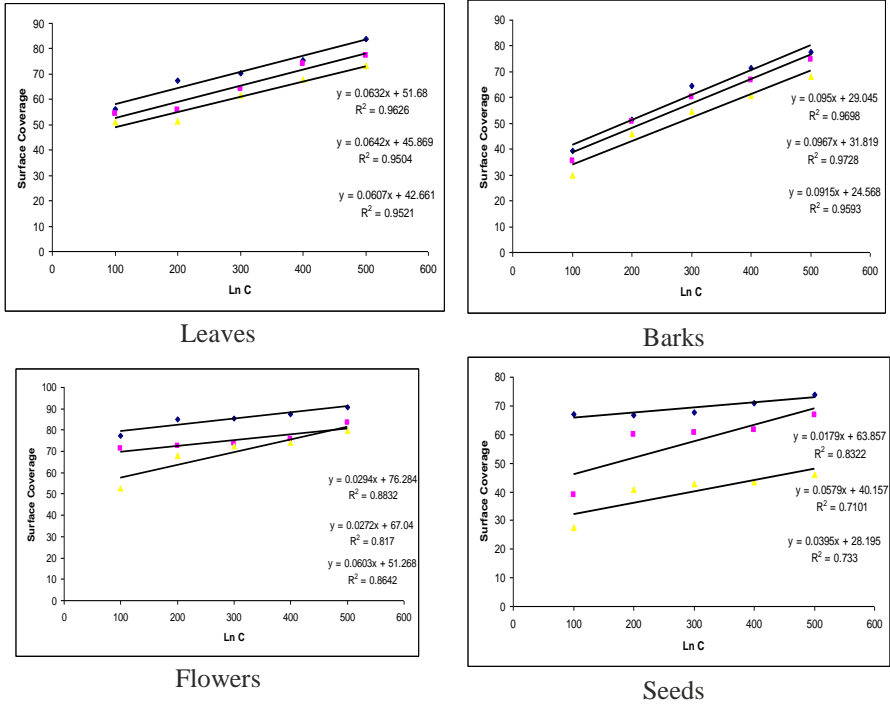
Barks



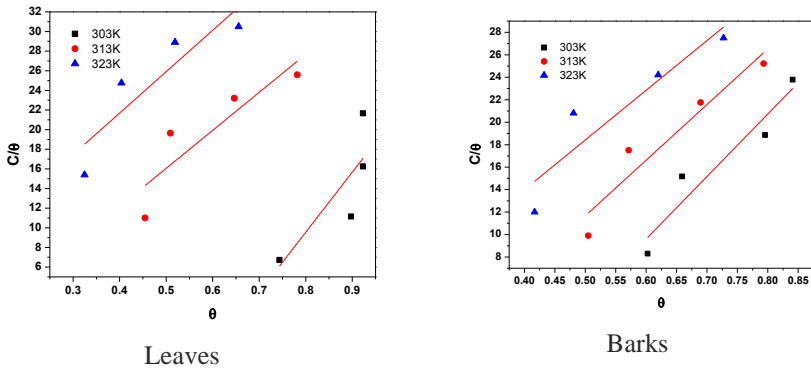
**Fig. 120** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of HI plant aqueous extracts (a) leaves (b) barks (c) flowers and (d) seeds.

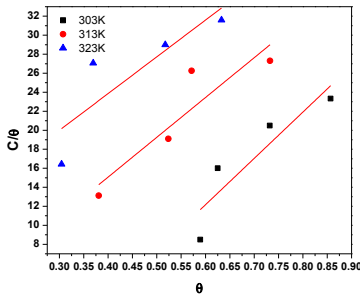


**Fig. 121** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of HI plant aqueous extracts (a) leaves (b) barks (c) flowers and (d) seeds.

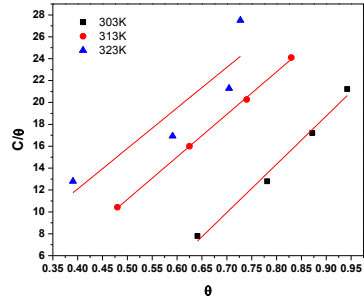


**Fig. 122** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of HI plant alcoholic extracts (a) leaves (b) barks (c) flowers and (d) seeds.



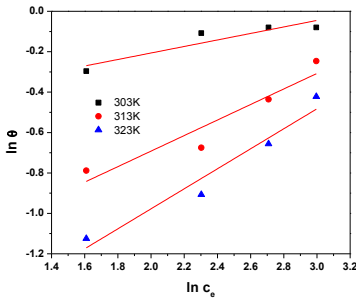


Flower

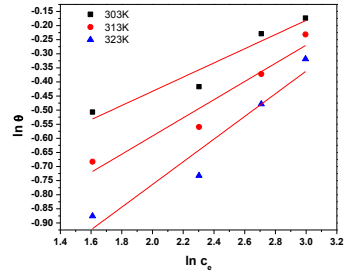


Seeds

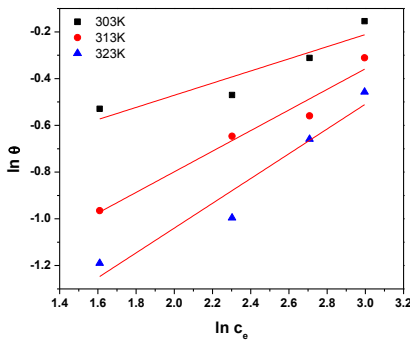
**Fig. 123** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of HI plant alcoholic extracts (a) leaves (b) barks (c) flowers and (d) seeds.



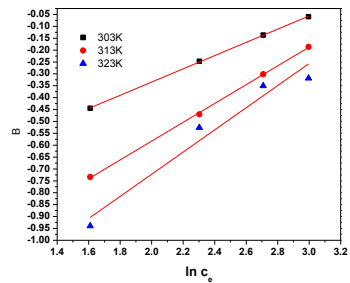
Leaves



Barks

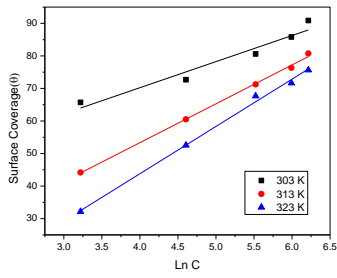


Flowers

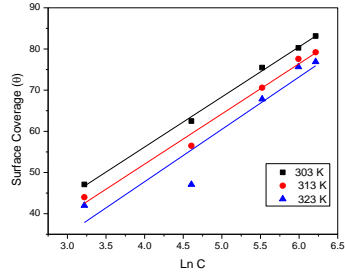


Seeds

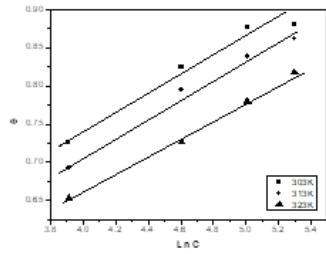
**Fig. 124** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of HI plant alcoholic extracts (a) leaves (b) barks (c) flowers and (d) seeds.



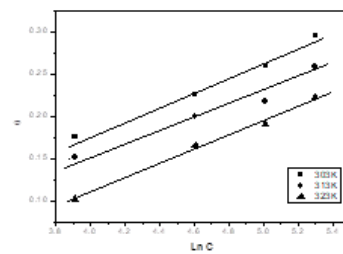
Leaves



Barks

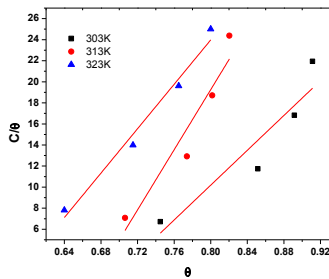


Fruits

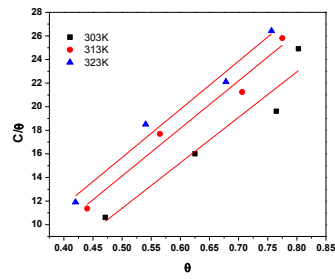


Seeds

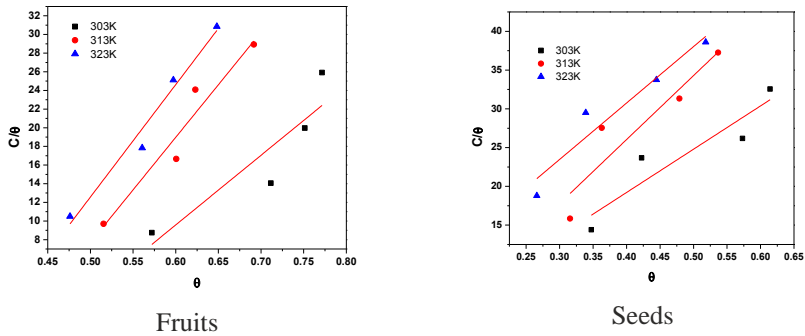
**Fig. 125** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of SS plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.



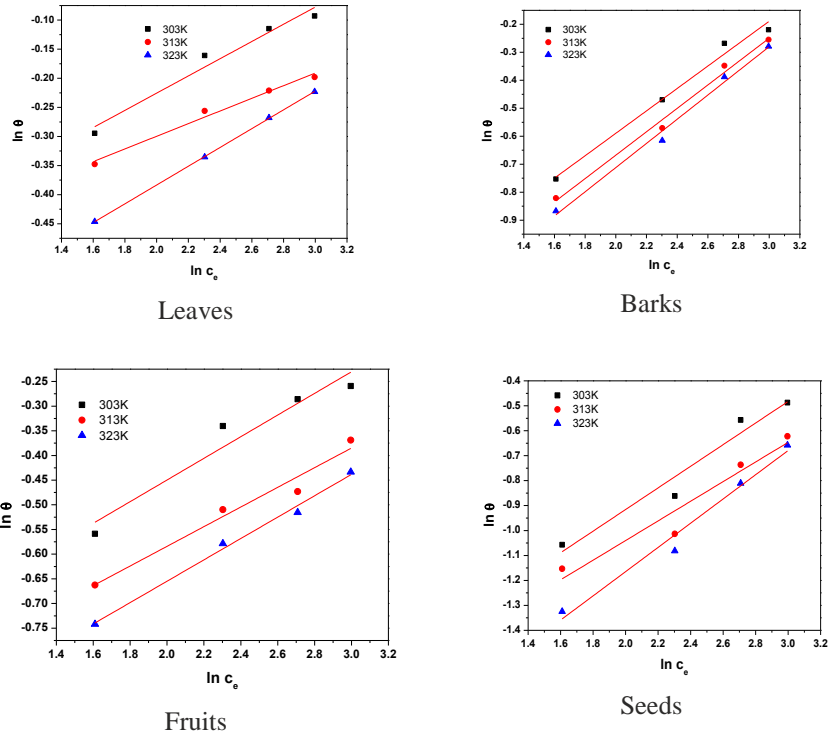
Leaves



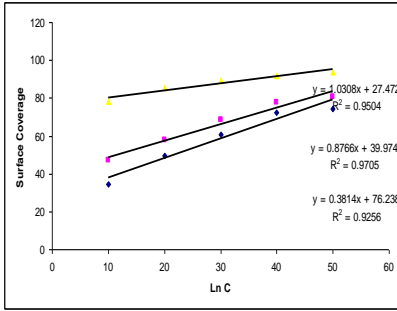
Barks



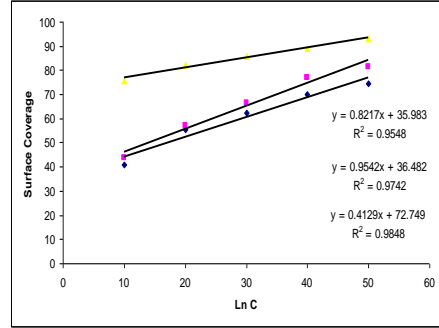
**Fig. 126** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of SS plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.



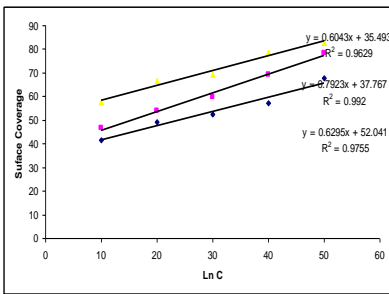
**Fig. 127** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of SS plant aqueous extracts (a) leaves (b) barks (c) fruits and (d) seeds.



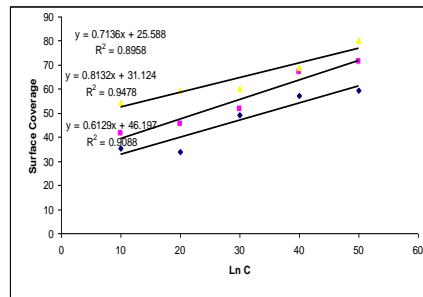
Leaves



Barks

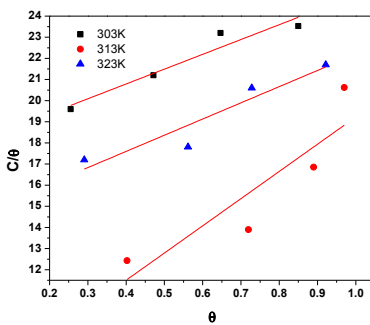


Fruits

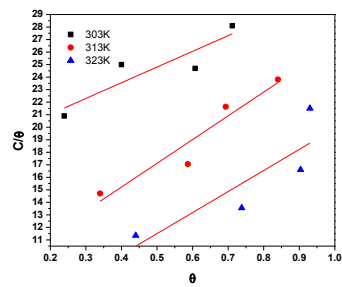


Seeds

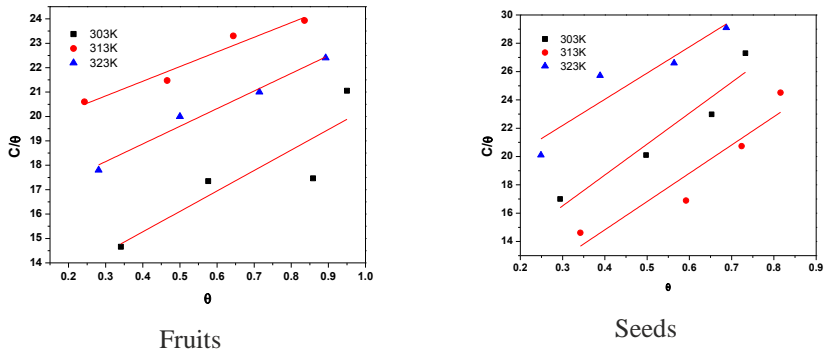
**Fig. 128** Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of SS plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.



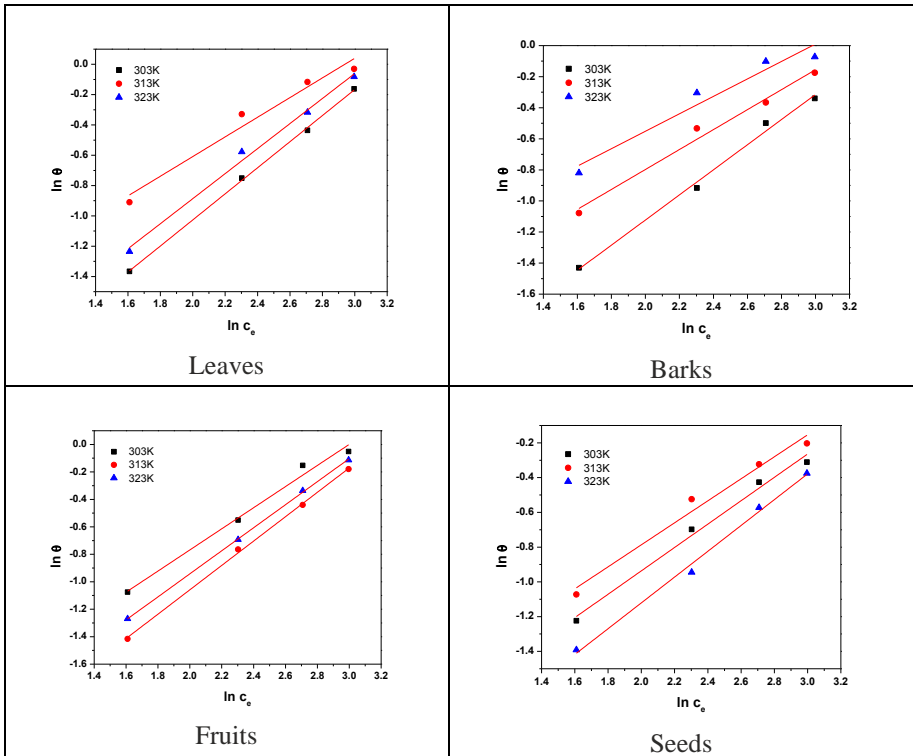
Leaves



Barks



**Fig. 129** Langmuir adsorption isotherm plot for mild steel in 1N HCl containing different concentration of SS plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.



**Fig. 130** Hasley adsorption isotherm plot for mild steel in 1N HCl containing different concentration of SS plant alcoholic extracts (a) leaves (b) barks (c) fruits and (d) seeds.



## 5.11 Thermodynamic considerations

From the temperature study results, thermodynamic parameters such as  $E_a$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were calculated. Values of  $E_a$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$  were obtained at different temperature of ML leaves of both extract is presented in **Tables 46 - 47**. The activation parameters play an important role in understanding the inhibitive mechanism of the inhibitor. The activation energies ( $E_a$ ) for the corrosion of mild steel in the absence and presence of different concentration of the plants extracts were calculated by using Arrhenius-type equation.

$$\ln R_c = \ln A - \frac{E_a}{RT}$$

Where  $E_a$  is the activation energy,  $R$  is universal gas constant,  $A$  is the Arrhenius pre-exponential factor,  $T$  is absolute temperature and  $R_c$  is corrosion rate. The values of  $E_a$  were evaluated from the slope of the plots of  $R_c$  versus  $1/T$  (not shown) and it is given in **Tables 46 - 47**. The enthalpy of activation ( $\Delta H^*$ ) and the entropy of activation ( $\Delta S^*$ ) for the corrosion of mild steel in 1N HCl solution was estimated using the transition state equation.

$$R_c = KT/h \exp(\Delta S/R) \exp(-\Delta H/RT)$$

Where  $K$  is the Boltzmann constant,  $h$  is the Plank constant,  $A$  is Arrhenius pre-exponential factor,  $T$  is the absolute temperature and  $R_c$  is corrosion rate.

$$E_{a(ads)} = E_{a(system)} - E_{a(blank)}$$

$E_{a(blank)}$  is the apparent activation energy in the absence of the inhibitor,  $E_{a(system)}$  is the apparent activation energy in the presence of the inhibitor and  $E_{a(ads)}$  is the apparent activation energy of adsorption.

The data in **Tables 46 - 47** indicates that the addition of plant extract leads to increase in  $E_a$  and ( $\Delta H^*$ ) to values greater than that of the free solution. The average difference values of ( $E_a - \Delta H^*$ ) is 2.69 KJ/mol which is approximately equal to the value of  $RT$  (i.e.  $8.314 \times 326.5 = 2.71$ ) KJ/mol at the average temperature studied. This result agrees that the corrosion process is uni-molecular reaction defined by the perfect gas equation given by

$$E_a - \Delta H^* = RT$$

Positive values of enthalpies  $\Delta H^*$  reflect endothermic nature of mild steel dissolution. The presence of inhibitor increases  $\Delta H^*$  and the reaction becomes more endothermic when compared to blank. Large and positive values of entropies showed that the activated complex in the rate determining step represents a dissociation step meaning that an increase in disordering takes place on going from reactants to the activated complex. A negative value for  $\Delta S$  also indicates spontaneity of the adsorption process, the increase of  $\Delta S$  (**-62.90 to -35.76 and -116.89 to -97.94**) with increasing inhibitor concentration, reveals that an increase in disordering takes place on going from reactant to the activated complex. However physical adsorption was the major contributor while chemisorption only slightly contributed to the adsorption mechanism judging from the decrease in percentage of inhibition efficiency with increase in temperature. Chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The values of  $\Delta G$  up to **-20 KJ/mol** are consistent with electrostatic interaction between charged molecules and a charged metal and the process indicates physical adsorption, while

those more negative than **-40 KJ/mol** involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond that indicates chemical adsorption. According to the data of  $\Delta G$  obtained (**-8.782 to -11.794 and -15.77 to -10.79 KJ/mol**) in the present study indicates that the adsorption mechanism of plant extract on mild steel is simply physisorption, thus inhibitor protection is through film formation providing an unbreakable (*see SEM Fig. 75 - 86*) barrier against aggressive ions, the electrolyte and the adsorbed layer is more stable one. The values of  $\Delta G$  do not show a gradual increase or decrease with change in inhibitor concentration. This might be due to the fact that the adsorption of the phytoconstituents is dependent not only on concentration but also on other factor like presence of others constituents, electronic and steric interaction of the inhibitor constituents among themselves as well as with the others constituents present in the corrosive media, etc. The data clearly clarifies that the values of  $E_a$  increase with increasing the concentration of plant extract, while the decrease in the value of  $A$  (Arrhenius pre-exponential factor) indicates that the higher values of  $E_a$  and the lower value of  $A$  lead to a reduction in the corrosion rate. The results can be explained by this behavior that the size ratio and equals the number of adsorbed water molecules replaced by an inhibitor (adsorption) molecules.

**Table 46** Thermodynamic parameters for adsorption of ML plant (aqueous extract) on mild steel in acid solution at various Temperatures.

Adsorption isotherm	Temperature	Slope	K	R <sup>2</sup>	E <sub>a</sub>	ΔG	ΔH	ΔS
Langumir	303	0.8239	0.6049	0.9928	10.127	-8.782	7.819	-62.90
	313	0.8378	0.7827	0.9943	18.945	-10.387	6.186	-37.26
	323	0.8290	0.6638	0.9921	21.489	-11.794	16.326	-35.76

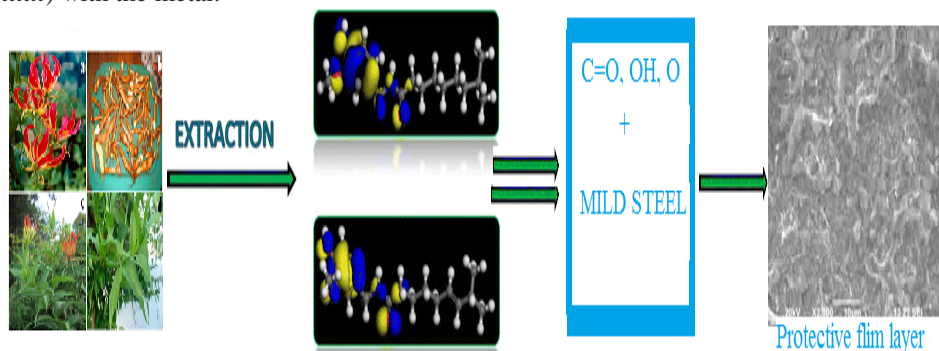
**Table 47** Thermodynamic parameters for adsorption of ML plant (alcoholic extract) on mild steel in acid solution at various Temperatures.

Adsorption isotherm	Temperature	Slope	K	R <sup>2</sup>	E <sub>a</sub>	ΔG	ΔH	ΔS
Langumir	303	0.6039	0.89	0.99	24.67	-15.77	53.38	-116.89
	313	0.8993	0.93	0.99	46.98	-15.26	60.72	-103.67
	323	0.8097	0.78	0.99	49.90	-10.79	62.43	-97.94

## 5.12 Mechanism of corrosion inhibition

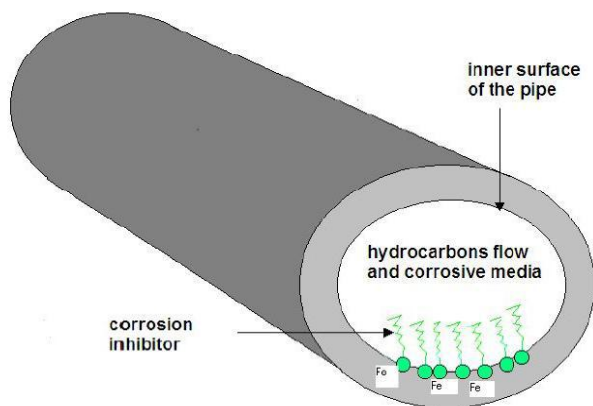
The possible mechanism of inhibition can be described on the center of adsorption method and the structure of the components present in the all plant extracts. The leading constituent of all plant extracts whose structures are given [*Figures 21-26*] having multiple bonds (*pi or double aromatic ring*) through which they get adsorbed on the metal surface. The compounds have to **block the vigorous corrosion positions** on the MS surface and hence the adsorption is occurred by the bonding of the free electron of the inhibitors (through electron transfer from the adsorbed species

to the *vacant electron orbital of low energy in the metal to form a co-ordinate type link*) with the metal.



**Fig. 131** Phytochemical constituent involve in corrosion mechanism

Phytochemical analysis showed the presence of [Table 4-9] *glycosides, flavonoids, saponins, steroids, phenols, tannins, and alkaloids* with the heteroatoms like *N, S, O* etc. Above organic fragments grows adsorbed (iron has co-ordinate affinity towards heteroatom) on the metal surface developing a protecting film and difference in inhibitory properties of inhibitor is closely related to the difference in molecular structure. The inhibitive effect of the natural plants extract were attributed by FTIR spectra [see Figures 27-38] that the functional *hydroxyl groups, carbonyl groups and oxygen* within the inhibitor macromolecules could make bridge between the mild steel, as a results the corrosion rate was decreased. Moreover, the presence of lone-pair of electrons on the oxygen atoms of the hydroxyl groups of the inhibitor may enhance the interaction between the inhibitor and positives sites formed on mild steel surface.



**Fig. 132** Representation of a corrosion inhibitor adsorbed into metal surface

The inhibition efficiency depends on many factors including the *number of adsorption centers, mode of interactions with metal surfaces, molecular size and*

**structure.** From all the above facts, it is confirmed that the investigated selected plants (i) electrostatic interaction between the charged molecules and the charged metal (ii) interaction of unshared electron pairs in the molecules with the metal (iii) interaction of pi electron with the metal (iv) combination of type) obey a **combination type** mechanism [1]. Adsorption of negatively charged species is facilitated if the metal surface is positively charged. Positively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate, such as acid anion adsorbed on the mild steel surface. Better corrosion inhibition properties exhibited by the plant extracts give new alternative way for the sustainability of green or eco-friendly material applications.

## 5.13 Conclusion

The effect of various concentrations of green extracts, namely, *Gloriosa Superba* Linn (GSL), *Madhuca longifolia* (ML), *Alangium lamarckii* (AL), *Holoptelea integrifolia* (HI), *Pithecellobium dulce* (PD) and *Schreabera swietenoides* (SS) plant's extracts on the corrosion of mild steel in 1N HCl has been studied. The

following conclusions can be made based on the results obtained.

- ❖ Based on the literature survey, during the corrosion reaction the metal loses its useful properties. As a result, chemical or electrochemical reaction takes place with the environment.
- ❖ The studies on various extracts of six different plants showed promising corrosion inhibition properties for mild steel in 1N HCl media.
- ❖ The weight loss data showed that the inhibition efficiency of all these green inhibitors increase with the increase in the concentration of the extract and inhibit the corrosion of mild steel.
- ❖ Corrosion rate reduced with increase in concentration of inhibitor and increased with raise in acid concentration.
- ❖ Potentiodynamic polarization studies revealed that the extracts act through mixed mode of inhibition.
- ❖ The Nyquist diagrams obtained in impedance method revealed that charge-transfer process mainly controls the corrosion of mild steel.
- ❖ The mechanism involved in this study is the phytochemical constituents present in both (aqueous and alcoholic) the plant extracts that have adsorbed on the mild steel surface forming a protective thin film layer and hence the anti-corrosive behavior.
- ❖ Phytochemical constituents in both the extracts play a very vital role in the inhibiting action.
- ❖ The SEM morphology of the adsorbed protective film on the mild steel has confirmed the high performance of inhibitive effect of the plant extracts.
- ❖ Organic molecules present in the extract were also found responsible for the performance of the inhibitor which was well supported by FTIR studies.
- ❖ The Temperature studies showed that when the temperature increases,

the inhibition efficiency decreases. Therefore, the isotherm observed is the Temkin, Langumir, Hasley adsorption isotherm.

- ❖ The reduction of corrosion inhibition efficiencies by increasing the temperature, may be due to thermal degradation of its organic content especially degradation of plant extracts.
- ❖ The adsorption study results revealed that the nature of all the studied inhibitors showed that the adsorption is of physisorption and no chemisorption occur between the inhibitor molecules and the metal surface.
- ❖ The natural of plant extracts were identified as very good inhibitors because of the presence of heteroatoms and unsaturated bond that cause effective adsorption process leading to the formation of an insoluble protective surface film which suppresses the metal dissolution reaction.
- ❖ Results obtained in weight loss method were very much in good agreement with the electrochemical methods (Potentiodynamic polarization and impedance method).
- ❖ All the studied plant extracts exhibit various biological and pharmacological activities approximately such as 97 % antiviral, antibacterial, antifungal etc., but 98 % serve as anticorrosion activity.
- ❖ Comparing the inhibition efficiency of the plant extract, the aqueous extract showed higher inhibition than that of the alcoholic extract in 1N HCl medium.
- ❖ Among the six plant extracts studied, the maximum inhibition efficiency was found in *Alangium lamarckii* leaves which showed 99.79 % inhibition efficiency at 15 v/v concentration of the extract.

This investigation gave an overview on material science in relation with a background of physical and chemical science and the nature of the metal have been studied. For further conclusion of corrosion rate the same work can be carried out in microorganism mediated corrosion.

## References

- [1] M. Lebrini, F. Robert and C. Roos, *Int. J. Electrochem. Sci.*, 6 , 847-859, 2011.