2

REVIEW OF LITERATURE

2.1 INTRODUCTION

An acquaintance with related literature of past studies is a must for formulating sound methodology which acts as a persevering force during the onset of research.

Corrosion of a metal may be due to chemical or electrochemical reactions when it comes in contact with matters present in its environment. It can be controlled by suitably modifying the environment which stifles the anodic or cathodic reactions or both. This is achieved by the use of inhibitors .Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. Inhibitors are added to many systems, e.g. cooling systems, refinery units, acids, pipelines, chemicals, oil and gas production units, boiler and process waters etc.

The toxic nature of the synthetic compounds had led to the search of alternate resources that can be utilised as inhibitors. Due to the environmental requirements that are currently imposed on the development of cleaner inhibitors, plant extracts, a source of natural, non-toxic, biodegradable organic compounds, are used as corrosion inhibitors **(Bothi Raja *et al*, 2008)**. Some authors have drawn attention to the investigations done in this area **(Bilgic *et al*, 2005, Sangeetha *et al*, 2011, Rajalakshmi *et al*, 2012)**

Historic perspective and Future directions in the field of natural corrosion inhibitors:

From antiquity till date ,in recent years, owing to increased ecological awareness and the strict environmental regulations, attention is focused on the development of green corrosion inhibitors, at low or ‘‘zero’’ environmental impact **(Znini *et al*, 2012; Li *et al*, 2012; Lecante *et al*, 2011; Lebrini *et al*, 2011; Benali *et al*, 2012; Bammou *et al*, 2011)**.

Green approaches involve the use of substances, techniques, and methodologies that reduce the use of feed stocks, products, by-products, solvents, reagents. They include the use of plant extracts, ionic liquids, bio-chemicals, and biodegradable organic and green inorganic inhibitors.

In the Middle Ages (i.e., from the 5th century to the 15^{th} century), the use of plant extracts (flour, bran, yeast, mixture of molasses and vegetable oil, and starch) for pickling of metal articles by master armourers had been reported . In one of the earliest studies, extracts of bran were used among other substances to inhibit the corrosion of iron in acidic media.

Few years later, the first patent in corrosion inhibition specified the use of natural plant product, molasses, and vegetable oils for pickling steel in acids. The first patent in corrosion inhibition was awarded to Baldwin in 1895 **(Sanyal, 1981)** who specified the use of natural plant product, molasses and vegetable oils, for pickling sheet steel in acids. In 1930, plant extracts (dried stems, leaves, and seeds) of celandine (*Chelidoniummajus*) and other plants were used in H_2SO_4 pickling baths **(Okafor *et al*, 2012)**.

Future studies will focus on modified natural compound, synthetic organic inhibitors, and the development of cheap, nontoxic, and biodegradable products. Efforts to find naturally organic substances or biodegradable organic materials to be used as corrosion inhibitors over the last years have been intensified.

The main principle of the corrosion inhibitors selection for the protection of metals is not only their inhibition efficiency but also their environmental impact . The pure plants and animals extracts had efficient performance in preventing the corrosion of different metal in acidic media. Furthermore, the use of these inhibitors decreased the negative impact of the conventional corrosion inhibitors on the environment.

There has been an upsurge in the publications regarding corrosion inhibitors **(Kesavan *et al*, 2012)** and the data available for the last half a decade (1950 – 2000) is depicted in Figure 2.1.

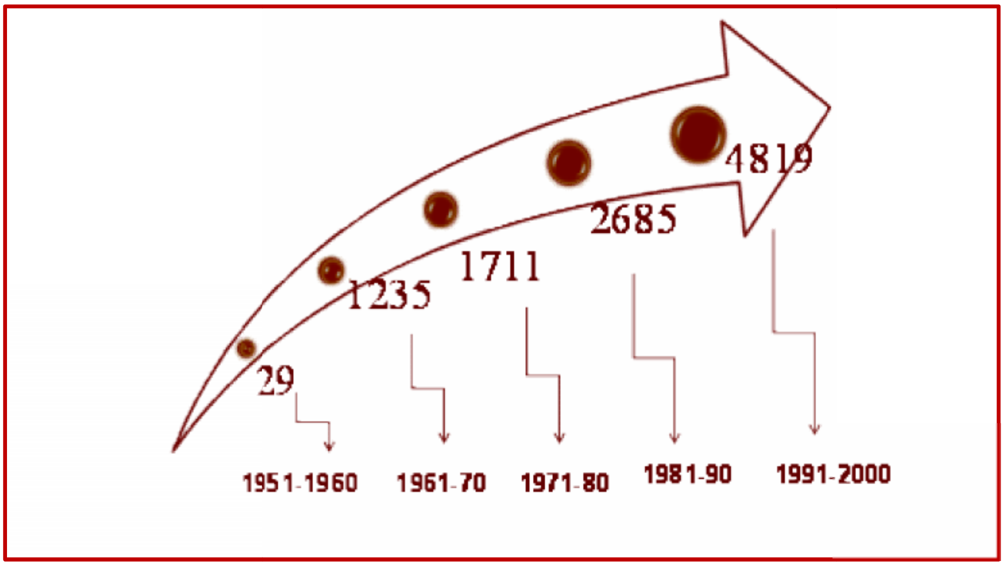

Figure 2.1 Progression of Research in the field of corrosion inhibitors

The present study on "Corrosion monitoring of metal (Mild steel, Aluminium) /1M HCl interface in the presence of *Spathodea campanulata* , *Tecoma capensis* leaf and flower extracts –Chemical , Electrochemical and Theoretical studies " is reviewed under the following topics

2.2 PLANT EXTRACTS AS CORROSION INHIBITORS FOR MILD STEEL

Mild steel, a structural material of choice due to its versatility, is a very important component of most of the objects and widely used in most of the chemical industries for fabrication of various reaction vessels, tanks, pipes etc. Since mild steel is used under different conditions in chemical and allied industries, it encounters severe attack from acids, due to their aggressive nature, resulting in awful degradation.

Several naturally occurring substances have been tried as corrosion inhibitors for mild steel in acidic media.

The inhibition of the corrosion of mild steel in hydrochloric acid solution by various parts of plant extracts were tried successfully for corrosion of mild steel in acidic media. The details of some of the investigations are tabulated in Table 2.1

Table 2.1: Corrosion inhibition efficiency of some of the investigated plant species

S.No	Name of the Plant and Parts Used	Extracts and Techniques Utilised	Phyto chemicals responsible	IE (%)	Reference
1.	*Papaia, Poinciana pulcherrima, Cassia occidentalis* and *Datura stramonium* seeds, *Calotropis procera B, Azydracta indica* and *Auforpio turkiale* sap	Acidic-Mass loss, Electrochemical	Proteins	88%–96%	**Zucchi and Omar , 1985**
2.	*Citrus paradise*	Weight loss	vitamins, pectins, flavonoids		**Olusegun *et al*, 2004**
3.	*Nypa fruticans* Wurmb – Leaves	Weight loss, hydrogen gas evolution	Nitrogenous compounds,Tannins	75.1	**Orubite and Oforka,2004**
4.	onion (*Allium cepa*) ,Garlic (*Allium sativum*) , Bitter gourd (*Momordica charantia*)	DC method-Tafel extrapolation, Resistance polarisation ,"Vicor"-computer software method; Mass loss, dissolved iron concentration		DC-82%, Mass loss-98%	**Parikh and Joshi,2004**
5.	*Ocimum viridis* –Leaves	Acidic (2 M HCl and 1M H_2SO_4) –Gasometry	Alkaloids. Terpenoids, carotenoids and aromatic oils	HCl-66.89 H_2SO_4 – 69.1	**Oguzie, 2006a**
6.	*Hibiscus sabdariffa* –Calyx	Acidic (2 M HCl and 1M H_2SO_4) –Gasometry	protonated organic species in the extract	HCl-90.4 H_2SO_4 – 93	**Oguzie, 2008**
7.	*Lawsonia inermis*	Electrochemical techniques and surface analysis (SEM/EDS)	(lawsone, gallic acid, α-D-Glucose , tannic acid		**Ostovari *et al*, 2009**

S.No	Name of the Plant and Parts Used	Extracts and Techniques Utilised	Phyto chemicals responsible	IE (%)	Reference
8.	*Justica gendarussa*-Leaves	Methanol- Weight loss Electrochemical	alkaloids, lignans, phenolic dimmers, flavonoids , O-substituted aromatic amines	92	**Satapathy *et al*, 2009**
9.	Karanj-(*Pongamia pinnata*) – Seed	Aqueous -Mass loss Electrochemical	Karanjin,,Pongapin ,Kanjone Pongaglabrone	98	**Ambrish Singh *et al*, 2010**
10.	Kalmegh(*Andrographis panniculata*) –Leaves	Aqueous -Mass loss Electrochemical	Andrographolide	98.2	**Ambrish Singh *et al* ,2010**
11.	*Pine apple* –Leaves	Ethanol –Gasometry	ananasate, 1-O-caffeoylglycerol, 1-O-p-coumaroylglycerol, b-sitosterol, daucosterol	72	**Ekanem *et al*, 2010**
12.	*Cyamopsis tetragonaloba*-seed	Acidic extract	3-epikatonic acid,7-o-beta-(2-rhamnosyl-glucosyl) myricetin, astragalin,	92	**Subhashini *et al*, 2010**
13.	*Garcinia mangostana* -pericarp of fruit	Acidic- Mass loss	oxygenated prenylated xanthones, 8-hydroxycudraxanthone G, mangostingone		**Kumar *et al* , 2010**
14.	*Xylopia ferruginea* –Leaves	chloroform partition (CP) , *n*-hexane partition (HP), methanol extracts (ME)- Mass loss, Electrochemical, SEM,	atheroline alkaloids	ME-82 HP-88 CP-92	**Elyn Amira *et al*, 2011**

The inhibitive action of leaves (LV), seeds (SD) and a combination of leaves and seeds (LVSD) extracts of *Phyllanthus amarus* on mild steel corrosion in HCl and H_2SO_4 solutions was evaluated using weight loss and gasometric techniques **(Okafor *et al*,2008)**. The results indicated that the extracts functioned as a good inhibitor in both environments and inhibition efficiency increased with extracts concentration. Temperature studies revealed an increase in inhibition efficiency with rise in temperature and activation energies decreased in the presence of the extract. A mechanism of chemical adsorption of the plant components on the surface of the metal was proposed for the inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by Temkin isotherm.

The inhibition of the corrosion of mild steel in 1 M HCl and 1 M H_2SO_4 by *Spirulina platensis* was studied by weight loss method, potentiodynamic polarization method, electrochemical impedance spectroscopy measurements and SEM analysis **(Kamal and Sethuraman, 2010)**. The inhibition efficiency increased with increasing concentration of the inhibitor in both HCl and H_2SO_4 media. The results confirmed the mode of adsorption to be physisorption.

Matheswaran and Ramasamy, 2010 tested the inhibitive nature of *Adhatoda vasica* (AV) on the corrosion of mild steel in 1 N HCl, 1N H_2SO_4 and 1 N H_3PO_4 acid solutions by weight loss and polarization methods. From the results it was noticed that the corrosion rate decreased with increase in concentration of inhibitor in the entire investigated acid medium. Maximum inhibition efficiency of 77.77 percentage (0.1% of AV) was obtained for 1 N HCl at 1 h. In this investigation AV acted as good inhibitor in HCl than H_2SO_4 and H_3PO_4. It was suggested that the presence of alkaloids was responsible for the inhibitive nature of AV.

In a similar study , **Vijayalakshmi *et al* (2011,2010 b,2010 a)** reported the inhibitive effect of petiole extract *Cocos nucifera* , palmyra palm (*Borassus flabellifer* Linn.) shell,coconut (*Cocos nucifera*) shell extract for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl using mass loss, polarization and electrochemical impedance techniques. The results obtained indicated that the extracts behaved as good inhibitor for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl. The adsorption of the inhibitor on mild steel surface was found to be spontaneous, endothermic and consistent with the assumptions of Langmuir adsorption isotherm. The electrochemical measurements reveal that the extracts behaved like mixed type inhibitor. The maximum inhibition efficiency for Palmyra palm in 0.5 M H_2SO_4 and 1 M HCl was found to be 97.65 percentage and 98.11 percentage for a period of 24 h with 3%v/v concentration of the inhibitor respectively.

Deng *et al* , 2011 examined the inhibition effect of Ginkgo leaves extract (GLE) on the corrosion of cold rolled steel (CRS) in 1.0–5.0 M HCl and 0.5–2.5 M H_2SO_4 solutions by weight loss, potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) methods. The results showed that GLE was found to be more efficient in 1.0 M HCl than 0.5 M H_2SO_4. The adsorption of GLE on CRS surface obeyed Langmuir adsorption isotherm. GLE acted as a mixed-type inhibitor in 1.0 M HCl, while a cathodic inhibitor in 0.5 M H_2SO_4.

Rajiv Prakash *et al*, 2011 explored the effect of plant extract of Papaveraceae family *Argemone mexicana* for use as a low cost and efficient corrosion inhibitor for mild steel in acidic environment. Weight loss and electrochemical methods were used to study the corrosion. Nearly 80 percentage corrosion inhibition was observed at around 200 mg L^{-1} inhibitor concentration and maximum (92.5 percentage) for 500 mg L^{-1} extract concentration in 1 M HCl.

Bothi Raja *et al*, 2011 analysed the inhibition efficiency of acid extract of flowers of *Cassia auriculata* (CAF) plant on the corrosion of mild steel in 1 M HCl by weight loss measurements and electrochemical studies. The results obtained showed that the extract afforded a maximum efficiency of 74.7 percentage. Inhibition was found to increase with increasing concentration of the plant extract. Potentiodynamic Polarisation curves revealed the mixed nature of the inhibitor.

Solomon *et al*, 2011 examined the application of leaves and stem extracts of *Sida acuta* as corrosion inhibitors for mild steel in 1 M H_2SO_4 using chemical (weight loss and hydrogen evolution) and spectroscopic (AAS, FTIR and UV-V) techniques at 30–60 °C. They found that the inhibition efficiency increased with increase in concentration of the extracts but decreased with rise in temperature. Inhibitive effect was approximated by Freundlich adsorption isotherm.

Khalid Hasan *et al* , 2011 considered the inhibition of corrosion of mild steel using Paniala (*Flacourtia jangomas*) extract in 1M HCl and 0.5M H_2SO_4 solutions was investigated by weight loss method at 30 °C. The result showed that inhibition efficiency increased with increasing concentration of the extract. Maximum inhibition efficiency of 98 percentage in 1M HCl and 95 percentage efficiency in 0.5M $H_2SO_4$was noticed at 5% v/v inhibitor concentration. According to the authors, adsorption of *Flacourtia jangomas* depended on the presence of various compounds like flavonoids, steroids, tannins and phenolic compounds etc.

Osman *et al* , 2011 tested the influence of *Xylopia ferruginea* leaves extract and partitions in different solvents on the corrosion behavior of mild steel (MS) in 1 M HCl using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Scanning Electron Microscope (SEM) techniques. Potentiodynamic polarization studies clearly revealed that all inhibitors behaved as mixed-type inhibitors with predominant anodic effectiveness. The adsorption of inhibitors on MS surface was found to obey the Langmuir adsorption isotherm. The effectiveness as corrosion inhibitors was in the order of chloroform partition (CP) > n-hexane partition (HP) > methanol extracts (ME).

Aisha *et al*, 2012 reported the impact of *Plectranthus tenuiflorus* (Shara) plant on the corrosion of mild steel in 2.0 M H_2SO_4 solution using weight loss and hydrogen gas evolution technique. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with rising temperature. The inhibition was attributed to adsorption of the inhibitor molecules on mild steel surface. Adsorption characteristics of the aqueous extract of Shara plant were approximated by Langmuir adsorption isotherm.

Hui Cang *et al*, 2012 investigated the corrosion inhibition of mild steel in sulphuric acid solution by the extract of *Stevia rebaudiana* leaves using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. Thermodynamic parameters (Ea, ΔH and ΔS) for the inhibition process reflected strong interaction between inhibitor and mild steel surface.

Ethanolic extract of the leaves of *Chromolaena odorata* L. (LECO) **Obot *et al*, 2012** was explored as a possible source of green inhibitor for corrosion of mild steel in 0.5 M H_2SO_4 using mass loss experiments. Results obtained reflected that LECO functioned as a corrosion inhibitor for mild steel in the acidic environment. Inhibition efficiency increased with extract concentration and decreased with temperature. LECO afforded a maximum efficiency of 95 percentage at 303 K and 89 percentage at 333 K at 5 %v/v of the extract.

Ramananda Singh , 2013 analysed the inhibition effect of extract of *Adhatoda vasica* in aqueous 0.5 M H_2SO_4 on corrosion of mild steel and its mechanism of the inhibition by weight loss method, potentiodynamic polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency of *Adhatoda vasica* on corrosion of mild steel in 0.5 M H_2SO_4 solution increased on increasing in its concentration and decreased with rise in temperature. The results of the Potentiodynamic Polarization measurement revealed that the extract acted as mixed type inhibitor. The adsorption of the extract on mild steel surface was found to follow Langmuir isotherm.

Assessment of the inhibitive action of *Petersianthus macrocarpus* leaves extract on corrosion of mild steel in 1M HCl and 0.5M H_2SO_4 solutions was done using gravimetric, electrochemical impedance and potentiodynamic methods. The inhibition efficiency of the inhibitor increased with increasing extract concentration. Temperature studies in the range 313-333K revealed increase in inhibition efficiency of the extract with rise in temperature. The authors proposed a mechanism of chemical adsorption. The adsorption characteristic of the inhibitor was found to obey Langmuir adsorption isotherm. **(Akalezi *et al*, 2013).**

Benali *et al* 2013 tested the corrosion and inhibition behaviour of mild steel in sulfuric acid + 5% EtOH in the presence of tannin extract of *Chamaerops humilis* plant (LF-Ch) and potassium iodide (KI) using electrochemical methods. It was found that the inhibition efficiency increased with LF-Ch extract concentration. According to the authors, the adsorption of LF-Ch extract on the mild steel in aggressive medium led to the formation of a protective film that increased in thickness with increasing exposure time.

Nwosu *et al*, 2013, stated that leaf extract of *Achyranthes aspera* L. afforded a maximum efficiency of 92.3 percentage against the corrosion of mild steel in 0.5 M H_2SO_4 medium. The authors inferred that *A. aspera* L. extract was adsorbed on the mild steel surface in accordance with Langmuir, Frumkin, and Flory-Huggins adsorption isotherm models. The thermodynamic data inferred that the adsorption of the inhibitor onto the surface of mild steel was spontaneous in nature.

Eupatorium odoratum (E.O) was utilised as a corrosion inhibitor for mild steel in 1.0M H_2SO_4 acid medium. The weight losses of the mild steel were taken for complete four days, for two temperatures namely 30 and 60 °C. The rates of corrosion of the mild steel was found to increase with increase in concentration of the acid and also decrease with increase in concentration of the *Eupatorium odoratum* extract. The extract afforded a maximum efficiency of 71 percentage at a concentration of 0.5g/L. **(Onuegbu *et al*, 2013).**

According to **Bothi Raja *et al*, 2013**, *Neolamarckia cadamba* crude extract (bark, leaves) and its pure alkaloid (3b-isodihydrocadambine) exhibited excellent inhibition properties against corrosion at all studied concentration of the inhibitors. Potentiodynamic polarization, electrochemical impedance, scanning electron microscopy, FTIR spectroscopy and molecular modeling were employed for this study. Polarization measurements indicated that these green inhibitors acted through mixed type inhibition. SEM studies evidenced the formation of a protective film over metal surface .According to the authors, FTIR, supported by molecular modeling proved that this shielding effect was caused by alkaloids, particularly 3b isodihydrocadambine.

Corrosion inhibition effect of *Piper longum* fruit extract on mild steel in 1M HCl medium was scrutinized by weight loss and electrochemical techniques **(Ambrish singh *et al*, 2013)**. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. Values of inhibition efficiency calculated from different techniques are in good agreement. Polarization curves reflect the mixed nature of inhibitor in hydrochloric acid. The results obtained show that the *Piper longum* fruit extract could serve as an effective inhibitor of corrosion of mild steel in HCl.

Hui *et al*, 2013 reported the corrosion inhibition of mild steel in 1.0 M HCl by the Aloes leaves extract .The investigation was carried out using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results reflected that the inhibition efficiency increased with the increase of the extract concentration. The adsorption of the extract molecules on the steel surface was found to obey Langmuir adsorption isotherm.

A study on the effectiveness of acid extract of *Nicotiana tabacum* leaves on mild steel in 1M HCl was carried out using weight loss method **(Olasehinde, 2013)**. Experiments were performed for varying immersion period, concentration of the inhibitor and temperature. The inhibition efficiency was found to increase with increase in concentration of *Nicotiana tabacum* leaves extract but decreased with rise in temperature and exposure time. Thermodynamic studies revealed that corrosion inhibition may be due to the spontaneous physical adsorption of the plant constituents on the surface of mild steel.

2.3 Plant extracts as corrosion inhibitors for ALUMINIUM

Aluminium and its alloys are widely used for many applications in food industry due to their low density, favourable mechanical properties, good surface finishing and relatively good corrosion resistance. Many industries use mineral acids especially HCl for pickling and chemical/electrochemical etching of Al. **(Umoren, 2012)**. The stable protective layer of oxide film tend to dissolve at a pH less than 4 or greater than 8 the necessity of protection of the metal arises. The importance of application of aluminium–magnesium alloys in chemical-processing industry and food handling equipment elucidates the need for examining the possibility of corrosion inhibition of Aluminium using natural plant extracts.

The inhibitive action of the mucilage extracted from the modified stems of prickly pears, toward acid corrosion of aluminium, was effectuated by **El-Etre, 2003**, using weight loss, thermometry, hydrogen evolution and polarization techniques. It was found that the adsorption of the extract on aluminium surface is a spontaneous process. The inhibition efficiency (IE) increased as the extract concentration was increased. It was found that the presence of extract increased the activation energy of the corrosion reaction.

Berković *et al*, 2004 evaluated the influence of rutin and quercetin on corrosion processes of aluminium. All the investigations were performed in 3% solution of sodium chloride, in aqueous rutin and quercetin solutions as well as in rutin and quercetin solutions in 3% sodium chloride solution using electrochemical methods. The results obtained showed that rutin and quercetin at concentrations of 10^{-4} and 10^{-5} mol dm^{-3} acted as aluminium corrosion inhibitors, while at higher concentrations (10^{-2} and 10^{-3} mol dm^{-3}) their effects were opposite. The efficiency of the corrosion inhibition of aluminium by rutin and quercetin solutions was due to the formation of protective film on the metal surface.

Umoren, 2008 estimated the corrosion behaviour of mild steel and aluminium exposed to H_2SO_4 solution and their inhibition in H_2SO_4 containing 0.1–0.5 g/L Gum Arabic (GA) at a temperature range of 30–60 °C using weight loss and thermometric techniques. Inhibition efficiency increased with increase in concentration of the inhibitor reaching a maximum of 37.88% at 60 °C for mild steel and 79.69 percentage at 30 °C for aluminium at 0.5 g/L concentration of GA. The inhibitor, GA was found to obey Temkin and El-Awady adsorption isotherm for mild steel and aluminium respectively from the fit of the experimental data at all concentrations and temperatures studied. The phenomenon of chemical adsorption was proposed for mild steel corrosion, while physical adsorption mechanism was proposed for aluminium corrosion.

The anti-corrosive effect of *Pachylobus edulis* exudate gum in combination with halides ions (Cl^-, Br^- and I^-) for aluminium corrosion in HCl was studied by **Umoren, 2008** at temperature range of 30-60˚C using weight loss method. Results obtained showed that the naturally occurring exudate gum act as an inhibitor for aluminium corrosion in acidic environment. Inhibition efficiency (%IE) increased with increase in concentration of the exudate gum and synergistically increased to a considerable extent on the addition of the halide ions. *Pachylobus edulis* exudate gum obeyed Temkin adsorption isotherm.

Obot *et al*, 2009 reported the inhibitive action of the root of ginseng on aluminium corrosion in HCl solution using weight loss method at 30-60 °C. Results obtained showed that ginseng root functioned as an effective and excellent inhibitor in the acid medium. Inhibition efficiency increased with increase in concentration of the inhibitor but decreased with increase in temperature reaching a maximum of 93.1 percentage at 30°C at 50 % v/v concentration of ginseng. The adsorption of extract components onto the aluminium surface was found to be a spontaneous process and to follow the Freundlich adsorption isotherm.

Asuke *et al*, 2010 inspected the corrosion inhibition property of Palm exudate (palm wine) in 0.5M sodium hydroxide solution (caustic soda) for Al-5%Si/15%SiC composite using gravimetric and potential measurements. Results obtained revealed that palm wine was a moderate corrosion inhibitor for the composite with optimum concentration of 1.0% v/v, a maximum inhibition efficiency of 47.6 percentage was obtained at 30°C at the optimum inhibitor concentration. The inhibitor was chemically absorbed onto the surface of the composite.

The inhibition of corrosion of aluminum in hydrochloric acid solutions by the ethanolic extract of the leaves of *Ananas sativum* was studied by **Atinga *et al*, 2010** using weight loss and hydrogen evolution methods. It was found that the plant extract retarded the acid induced corrosion of aluminum. Inhibition efficiency was found to vary with concentration of the extract and temperature.

The inhibition of aluminium in 0.5 M H_2SO_4 by extracts of *Spondias mombin* L. was carried out by **Obi-Egbedi *et al*,2010 b** using mass loss technique at 30–60 °C. It was found that the S. mombin L. extract acted as an inhibitor for acid-induced corrosion of aluminium. Inhibition efficiency (%IE) of the extract increased with an increase in concentration of the S. mombin L. extract but decreased with temperature. Furthermore, inhibition efficiency (%IE) synergistically increased on addition of potassium iodide. Inhibitor adsorption characteristics were approximated by Langmuir adsorption isotherm at all the studied concentrations and temperatures.

The effect of *Solanum melongena* L. leaf extract on the corrosion of aluminium in 0.5 M H_2SO_4 was examined using the gravimetric technique. It was shown that the presence of S. melongena L. leaf extract inhibited the corrosion of aluminium in the test solutions and that the inhibition efficiency depended on the concentration of the plant extract as well as on the time of exposure of the aluminium samples in 0.5 M H_2SO_4 solutions containing the extract. The experimental data complied with a modified form of the Langmuir adsorption isotherm. **(Ihebrodike Maurice Mejeha *et al*, 2010)**

The ability of *Cocos nucifera* L. water (CW) as non-toxic corrosion inhibitor for acid corrosion of aluminium in 0.5 mol/L HCl was studied using chemical technique.

CW showed significant inhibition as corrosion inhibitor, with 93 percentage efficiency at the highest concentration of the inhibitor. The inhibitive action was attributed to the adsorption of the inhibitor molecules on metal surface following Langmuir adsorption isotherm. **(Olusegun *et al*, 2010)**

Chromolaena odorata L. Leaf extract (LECO) was explored as a possible source of green inhibitor for corrosion of aluminium in 2M HCl by **Obot *et al*, 2010** using gasometric and thermometric techniques at 30 and 60 °C. Inhibition efficiency increased with extract concentration but decreased with temperature. The adsorption of LECO on Al surface was in accord with Langmuir adsorption isotherm.

Nnanna *et al* ,2010 tested the corrosion inhibition of aluminium alloy (AA3003) in 0.5 M HCl by extracts of *Euphorbia hirta* and *Dialum guineense* using gravimetric technique at 30 and 60°C.The results indicated that all the extracts inhibited the corrosion process in the medium by virtue of adsorption and inhibition efficiency improved with concentration. Adsorption of both plant extracts on the aluminium alloy was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption was proposed from the obtained thermodynamic parameters.

2.4 PHYTOCHEMICAL CONSTITUENTS AS CORROSION INHIBITORS

The corrosion inhibiting activity of the plant extract could be due to the presence of heterocyclic constituents like alkaloids, flavonoids, etc., even the presence of tannins, cellulose and polycyclic compounds normally enhanced the film formation over the metal surface, thus affording corrosion inhibition. **(Bothi Raja *et al,* 2008)**.

Isolated compounds from plants as corrosion inhibitor

Berberine extracted from *Coptis chinensis* was tested for its corrosion inhibitive nature of mild steel in 1M H_2SO_4 using weight loss, electrochemical and SEM techniques by **Yan Li *et al,* 2005** and a good fit to Flory – Huggins isotherm was observed from the experimental results.

Arbutin, an active principle from *A. pallens* and the crude methanolic extract exhibited inhibition efficiency of 93 percentage and 98 percentage in 400 mg L^{-1} concentration at 30 °C respectively. The results indicated that arbutin in acidic medium acted as good anti-corrosive agent synergistically with its hydrolyzed products hydroquinone and d-glucose. Adsorption of both the inhibitors on mild steel surface conformed to the Langmuir isotherm with standard adsorption free energy of −33.07 kJ mol^{-1} for arbutin**. (Subhadra Garai *et al*, 2012)**

Ervatinine, the alkaloid present in the leaves of the plant *Ervatamia coronaria* was isolated and its anti-corrosive potential was investigated using weight loss, electrochemical impedance, Tafel polarization, scanning electron microscope and X-ray diffraction techniques. The results suggested the effectiveness of ervatinine as a good corrosion inhibitor **(Sethuraman *et al,* 2013).**

Essential oils as corrosion inhibitor

Essential oil of various natural products obtained by hydrodistillation using clevenger type apparatus were tested as corrosion inhibitors in acidic media especially hydrochloric and sulphuric acid. The inhibitors were evaluated using electrochemical polarisation and weight loss measurements. The corrosion rate of steel decreased in the presence of natural oils. While *Eucalyptus* natural oil and *Artemisia herba alba* oil acted as a cathodic inhibitor, the rest of them acted as mixed inhibitors. *S.aucheri mesatlantica* revealed that the oil acted as mixed type inhibitor with a strong predominance of anodic character. An elaborate description on the efficiency and components responsible for the inhibitive nature these tested inhibitors were recorded (Table 2.2).

Table 2.2 Insight into the components and efficiency of the tested Natural oils

S.No	Plant name / Parts /Medium	Major Components	% Efficiency	Reference
1.	Eucalyptus / Natural oil/1M HCl		72% at 3 mL/L	**Bouyanzer *et al*, 2006 b**
2.	Artemisia herba alba/Essential oil/0.5M H_2SO_4	chrysanthenone (30.6%) and camphor (24.4%).	74% at 1 g/L.	**Ouachikh *et al*, 2009**
3.	*Argan oil/* Kernel (AKE) & Cosmetic argan oil (CAO)/ 1M HCl	Palmitic acid (13.8 %), Oleic acid (46.3 %), Linoleic acid (32.3 %), Schottenol (48.4%); Spinasterol (39.1 %) and α - tocopherol (86.9 %).	97% at 1g/L of AKE and 91% at 6g/L of CAO	**Afia *et al*, 2011**
4.	*Mentha spicata L/* Aerial parts /1M HCl	Carvone (29.00%) and Trans carveol (14.00%)	97% at 2.00 g/l	**Znini *et al*, 2011**

S.No	Plant name / Parts /Medium	Major Components	% Efficiency	Reference
5.	*Eucalyptus globules/*Essential oil/0.5M H_2SO_4	Pentadecanoic acid (01.90%) Palmitic acid (36.00 %) Palmitoleic acid (07.30%) Margaric acid (00.70%) Heptadecenoic acid (01.00%) Stearic acid (03.30%) Oleic acid (27.20 %) Linoleic acid (19.30%)	81% at 6g/L	**Rekkab *et al*, 2012**
6.	*Salvia aucheri mesatlantica /* Essential oil of aerial parts/0.5M H_2SO_4	camphor (49.59%)	86.12% at 2 g/L	**Znini *et al*, 2010**
7.	Carob / seed oil/1M HCl	linoleic acid (45.05%), oleic acid (33.66%), palmitic acid (14.84%), and stearic acid (3.50%).	86.7% at 0.5 g/L	**Hmamou *et al*, 2012**

The inhibition efficiency of the tested inhibitors was found to increase with oil content. The adsorption of the tested essential oils on the steel surface followed Langmuir adsorption isotherm. The inhibitors formed a thick film on the surface of the metal that acted as a barrier layer on the iron surface to minimize corrosion.

Alkaloids as corrosion inhibitor

A largest group of secondary metabolites, the alkaloids comprise basically of nitrogen bases and oxygen. Alkaloids are found to have numerous pharmacological applications. Till date more than 12,000-alkaloids are known to exist in about 20% of plant species and only a few were exploited for medicinal purposes.

Lakhan Jha *et al,* 1991 investigated the inhibitive action of pomegranate alkaloids on acid corrosion of mild steel in sulphuric acid at different temperatures. According to the authors the active constituent pelletierine had been instrumental in the corrosion inhibition mainly due to amine chemisorption on the surface of mild steel which resulted in the metal – additive complex formation.

Hammouti *et al,* 1995 tested the effectiveness of alkaloids as corrosion inhibitor for mild steel in acid medium by weight loss and polarization measurements. Effect of temperature on the corrosion behaviour of iron in 1M HCl in the absence and presence of bgugaine at 2 x 10^{-4} M was studied. The value of the inhibitor efficiency was found to exceed 97 percentage at different temperatures.

The alkaloid extract of *Rauvolfia serpentina* was studied as corrosion inhibitor for mild steel in 1M HCl and H_2SO_4 using weight loss, potentiodynamic polarization, EIS and SEM techniques and reported that the inhibition efficiency increased with increase in inhibitor concentration and temperature. The studies reflect that the plant extract acted as a good inhibitor in both acid media and found that chemisorption takes place and the inhibition followed Temkin adsorption isotherm. The results showed that the extract acted as mixed type inhibitor **(Bothi Raja and Sethuraman, 2010)**.

The corrosion mitigating nature of alkaloids extracted from *Annona squamosa* **(Lebrini *et al*,2010)**, *Palicourea guianensis* (AEPG) **(Lebrini *et al*,2011)** *Isertia coccinea* (AEIC) **(Lebrini *et al*, 2011)** *Oxandra asbeckii* (OAPE) **(Lebrini *et al*,2011)** and *Aspidosperma album* **(Faustin *et al*, 2011)** plants on C38 steel in 1 M HCl medium were analysed by Potentiodynamic polarization and AC impedance methods. The corrosion inhibition efficiency increased on increasing plant extract concentration for all the investigated inhibitors. Polarisation studies indicated that the extracts behaved as mixed-type inhibitors in 1 M HCl. The adsorption of the extracts followed Langmuir's adsorption isotherm.

The effect of alkaloid extracts from two Amazonian trees (*Guatteria ouregou* and *Simira tinctoria*) on low carbon steel corrosion was carried out in acidic solutions by **Lecante *et al,* 2011)** using electrochemical techniques. All of these plant extracts were found to inhibit the corrosion of low carbon steel in 0.1 M HCl solutions. As their concentration increased to 250 mg/L, the inhibition efficiencies of *S. tinctoria* and *G. ouregou* alkaloid extracts reached approximately 92 percentage in 0.1M HCl solution.

The inhibition effect of mild steel corrosion in 1 M HCl was studied by the addition of indole alkaloids (crude) isolated from *Alstonia angustifolia* var. *latifolia* (*A. latifolia*) leaves at 303 K by **Bothi Raja *et al,* 2013.** Results inferred that the isolated alkaloid extract of *A. latifolia* exhibited maximum inhibition efficiency (above 80 percentage) at concentrations between 3 and 5 mg/L.

Lignin as corrosion inhibitor

The inhibition potentials of lignin extract of sun flower was effectuated by evaluating the corrosion behaviour of medium carbon low alloy steel immersed in 1M H_2SO_4 solution containing varied concentration of the extract. The results revealed that the lignin extract was an efficient inhibitor of corrosion in mild steel immersed in 1M H_2SO_4. The corrosion rates were found to decrease with increase in concentration of lignin extract but increase with temperature. The activation energies and the negative free energy of adsorption obtained from the adsorption studies indicated physical adsorption of the lignin on to the surface of the steel, and fitted excellently with the assumptions of the Langmuir adsorption isotherm **(Alaneme and Olusegun, 2012)**.

Tannins as corrosion inhibitor

The inhibitive action of mangrove tannins, extracted from mangrove barks and phosphoric acid, on pre rusted steel in a 3.5% NaCl solution was evaluated and the inhibitive efficiency was compared with that of mimosa tannins. From the electrochemical studies, the inhibition efficiency of solutions containing 3 g/L tannins depended upon the concentration of phosphoric acid added and the pH of the solution. At pH 0.5 and pH 2.0, inhibition was greatest with mangrove and mimosa tannins alone, while at pH 5.5 the addition of phosphoric acid alone gave the highest inhibition. **(Rahim *et al,* 2008)**

Flavonoids as corrosion inhibitor

Rahim *et al,* 2007 noticed that flavonoid monomers that constitute mangrove tannins namely catechin, epicatechin, epigallocatechin and epicatechingallate afforded excellent protection to steel in an aerated HCl solution. The authors, through electrochemical investigations, found out that the monomers acted as cathodic inhibitors and the inhibition efficiency was dependent on concentration of the inhibitors.

The inhibition of corrosion of mild steel using Paniala (*Flacourtia jangomas*) extract in 1M HCl and 0.5M H_2SO_4 solutions was analysed by **Khalid Hasan *et al,* 2011a** using weight loss method at 30°C. The results indicated that inhibition efficiency increased with increasing concentration of the extract. At lower concentration of inhibitor, better inhibition was observed in HCl medium as compared to H_2SO_4.

2.5 THEORY BEHIND INHIBITION

According to **Mann, 1936**, an inhibitor formed an ionisable salt with the corroding acid and the inhibitor cations thus formed may replace the positive metal ions of the double layer formed on the surface of the immersed metal. The adsorbed ions were attracted to the cathodic area of the metal and are held there tenaciously as a continuous covering layer. This layer being not penetrable by hydrogen ions protected the metal against corrosion.

Compounds containing nitrogen, oxygen and sulphur atoms proved to be very effective in inhibiting the rate of corrosion of metals by forming a typical chemical bond with the metal atoms through the lone pair of electrons which these atoms possess **(Hackerman *et al*,1962)**

Frankenthal ,1967 demonstrated that adsorbed oxygen films stop corrosion only at more positive potentials than the passivation potential. Frankenthal considered that the adsorption film doesn't interfere with the system reversibly, whereas a phase film would result in additional breaking down.

According to **Hausler, 1985** and **Putilova *et al*, 1960** effective protection of metals by inhibitors was mainly due to the formation of a layer of insoluble or slightly soluble corrosion products on the metal surface.

Agrawal and Namboothii, 1997 attributed electron density on the functional group as the causative factor for the adsorption of the organic molecules on the metal surface.

Extract of *Bauhinia purpurea* leaves was investigated as a corrosion inhibitor for mild steel in 1 N H_2SO_4 using conventional weight loss, electrochemical polarization, electrochemical impedance spectroscopy, and scanning electron microscopic studies **(Patel *et al*, 2009)**. The weight loss results showed that the extract of *Bauhinia purpurea* leaves acted as excellent corrosion inhibitor. Electrochemical polarization data revealed the mixed mode of inhibition. Scanning electron microscope studies provided the confirmatory evidence of an improved surface condition, due to the adsorption of the inhibitor, for the corrosion protection.

Eddy *et al*, 2009 d determined the inhibitive and adsorption properties of ethanol extract of *Lasianthera africana* for inhibition of corrosion of mild steel in H_2SO_4 using gravimetric, thermometric, gasometric, and infrared (IR) methods. The extract was found to be a good inhibitor of corrosion of mild steel in H_2SO_4. Inhibitive properties of the extract were attributed to enhancement in adsorption of the inhibitor on mild-steel surface.

Bothi Raja and Sethuraman,2009 on the effectiveness of acid extract of *Solanum tuberosum* as corrosion inhibitor for mild steel , ascribed the adsorption of the inhibitor on the surface of MS to the adsorption of alkaloids and other phyto chemical constituents present in the plant extracts. The authors proposed the following mode of mechanism (Figure 2.1).

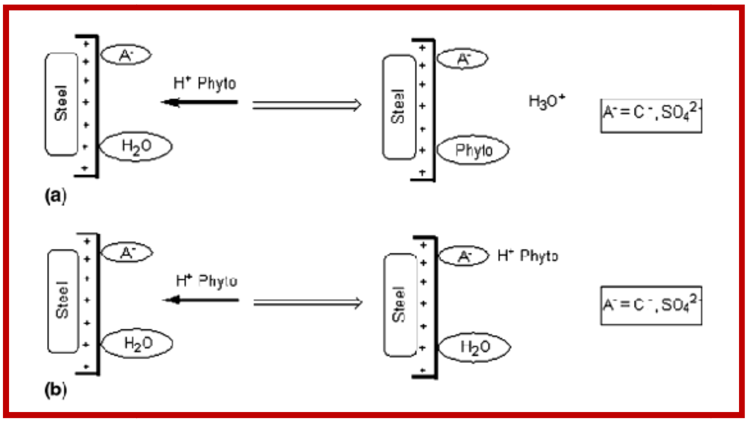

Figure 2.2 a) Competitive and b) Cooperative adsorption of green inhibitor in acid solutions

The leaves extract of *Murraya koenigii* was evaluated as an inhibitor for the corrosion of mild steel in hydrochloric acid and sulphuric acid by **Quraishi *et al*, 2010** using weight loss, electrochemical impedance spectroscopy (EIS), linear polarization and potentiodynamic polarization techniques. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface.

An evaluation of the effective performance of extract of *Ervatamia coronaria* leaves on the corrosion inhibition of mild steel in 1M HCl and 0.5M H_2SO_4 at ambient temperatures were carried out by **Rajalakshmi *et al*, 2010**. Conventional weight loss and electrochemical measurements were used for the evaluation. Electrochemical studies reveal that both the tested extracts acted as mixed type inhibitors. *Ervatamia coronaria* leaves extract yielded a maximum of 98 percentage in acid medium. The authors proposed the following model of inhibition

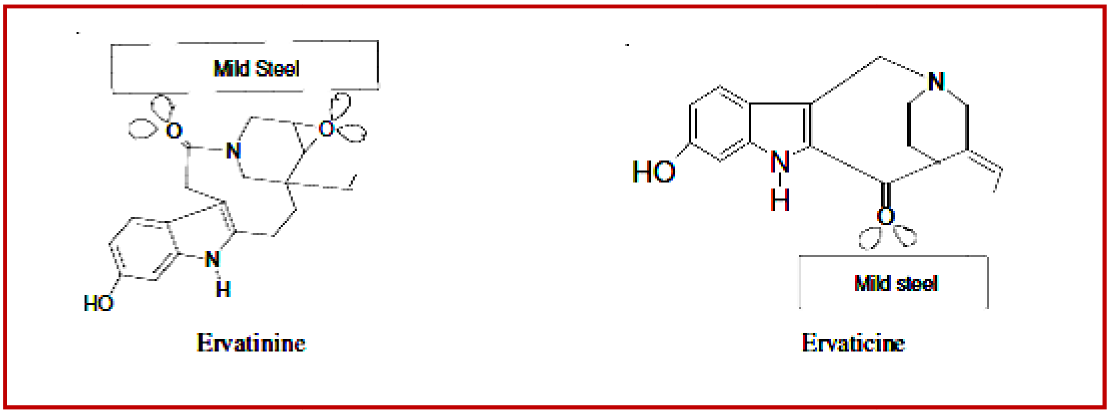

Figure 2.3 Proposed skeletal model of mode of adsorption of inhibitor on mild steel surface

Adsorption of xanthan gum on the aluminum surface was followed by replacement of pre-adsorbed water molecules and modification of the low stable aluminium surface in the acid medium to a more stable aluminium-inhibitor complex. According to the authors, a more stable complex was formed due to the donor – acceptor interactions between pi electrons, oxygen atoms and the carboxylic functions of the neutral species as well as the pi electrons of cationic species and the vacant d orbitals of aluminium. The mechanism of adsorption of protonated xanthan gum on aluminium followed the proposed reaction sequence of aluminium corrosion in hydrochloric acid **(Arukalam *et al*, 2014).**

$$Al + Cl^- \leftrightarrow \lfloor AlCl^- \rfloor_{ads}$$

$$\lfloor AlCl^- \rfloor_{ads} + Cl^- \rightarrow AlCl_2^{\ +} + 3e^-$$

Obot *et al*, 2009 inferred that the adsorption of CTM and FLC onto the aluminium surface was physical in nature due to the electrostatic attraction between charged species in the bulk of the solution. According to the authors, CTM and FLC were adsorbed onto aluminium surface in two different ways:

(i) The protonated inhibitors electrostatically adsorb onto the anion covered aluminium surface, through their protonated form.

(ii) The inhibitors compete with acid anions for sites at the water covered surface and adsorbed by donating electrons to the aluminium. Similar observations were also documented by **Dehri *et al*, 2006, Keles *et al*, 2009**

According to **Li *et al*, 2012**, *Dendrocalamus brandisii* leaf extract could be protonated in the acid media due to the interaction between O atom and H^+. In HCl solution, Cl^- ions get accumulated closely to the aluminum/solution interface thereby creating an excess negative charge towards the solution and favor more adsorption of the cations. Thus, the protonated inhibitor was adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface due to synergism between Cl^- and protonated inhibitor.

2.6 Correlation between molecular structure and corrosion inhibition

When a corrosion inhibitor was added to a system, adsorption of inhibitor molecules at the metal-solution interface occurs and this was accompanied by a change in potential difference between the metal electrode and the solution due to the non-uniform distribution of electric charges at the interface **(Sastri, 1998)**.

An inhibitor's efficiency depended on many factors. From a macroscopic view, it depended on flow patterns, solution chemistry, temperature, pressure, etc. At a molecular level, it depended on the number of adsorption sites, inhibitors' charge density, molecular size, mode of interaction with the metal surface, electronic structure of the molecules etc. Hetero atoms, such as sulfur, phosphorus, nitrogen, and oxygen, together with aromatic rings in inhibitor structure, acted as adsorption centers that could adsorb on the metal surface and form barrier film. The planarity and the lone electron pairs in the hetero atoms were also important features that determined the adsorption behavior of molecules on the metallic surface **(Ebenso *et al*, 2010; John *et al*, 2011)**

A new and potential class of corrosion inhibitors, the Macrocyclic compounds were found to act as excellent corrosion inhibitors .Their inhibitive nature was attributed to their fascinating molecular structure, presence of pi- electrons or non bonding electrons. In addition to these structural features, planarities of these molecules further facilitated the formation of strong bond between the metal and these compounds. **(Zemer *et al*, 1966)**

Mehta and Sastry, 1981 correlated the inhibition efficiency of the investigated alkaloids to the macro molecular structure and high molecule weight of the inhibitor where in, the inhibition was mainly contributed by the methoxy groups present in the compounds.

The studies of **Mansfeld, 1985** pointed out that interface inhibition presumed a strong interaction between the corroding substrate and the inhibitor

Sing and Chaudhary, 1996 attributed the inhibition of corrosion of stainless steel in acidic media to the molecular structure of dithiazone and thio semi carbazide. The dithiazone molecule was adsorbed through "sulphur atom "in the molecule because the electron density of the sulphur atom was higher than that of β nitrogen atom in the phenyl hydroazo group and the inhibition was mainly due to chemisorption. In sulphuric acid solution, the nitrogen atom in the amino group in the thio semi carbazide molecule acquired a positive charge and acted as an active centre for its adsorption on the surface of 304 stainless steel.

Imidazole and benzimidazole were found to inhibit the corrosion of mild steel in hydrochloric and sulphuric acid media at low concentrations whereas methyl imidazole was found to accelerate the corrosion at low concentration. The inhibition of corrosion caused by imidazole was due to the interaction between π electrons of the imidazole ring with positively charged metal surface in the adsorption of the compound on the metal surface. The enhanced inhibition of benzimidazole was mainly due to availability of mobile

π electrons in the benzene ring that interacted with vacant d-orbitals of iron atoms of the metal that led to efficient surface coverage. **(Muralidharan and Venkata Krishan Iyer, 1997)**.

The studies of **Wang *et al*, 1999** provided further information on the electron configuration of several imidazoline inhibitors by the quantum chemical calculation and the correlation between molecular structure and behavior of corrosion inhibition. It was concluded that electron donor group introduced, particularly, the substituent group with conjugated system, to imidazoline ring will improve corrosion inhibition efficiency of imidazoline derivatives.

Inhibition of corrosion of mild steel in acidic solutions by the oxadazoles was mainly due to the adsorption of these compounds onto the metal surface, through the lone pair of electrons of sulphur, Nitrogen, Oxygen atoms and delocalized π –electrons of hetero cyclic ring and a protonated species **(Ajmal *et al*, 2000)**.

Abdallah, 2004 tested the effect of guar gum on carbon steel corrosion and showed that the inhibiting action of guar gum on carbon steel corrosion reaction was due to its adsorption at the electrode/solution interface. The presence of oxygen atom in the guar gum structure eased its adsorption by coordinate type linkage through the transfer of lone pairs of electron of oxygen atoms to the steel surface that gave a stable chelate five member ring with ferrous ions as follows

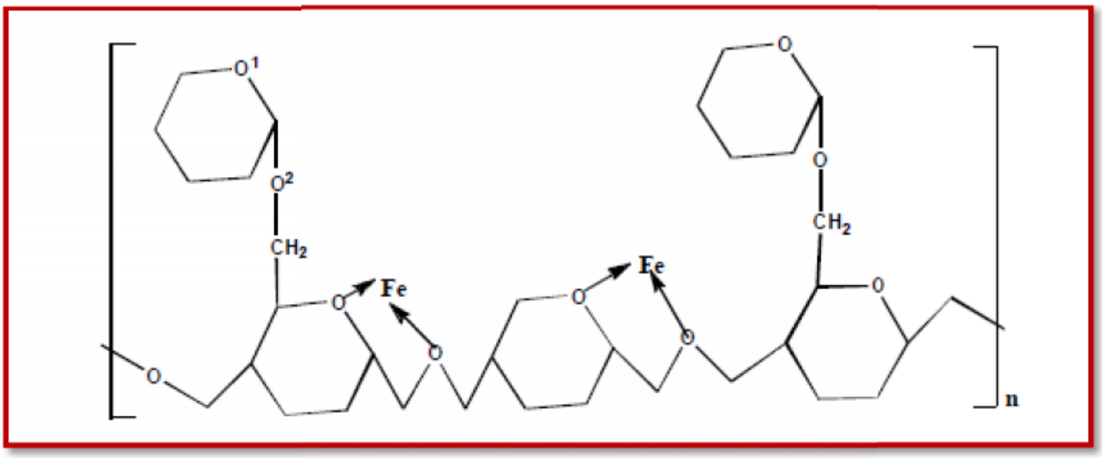

Figure 2.4 Stable chelate model of Iron with Guar gum inhibitor

2.7 PHYTOCHEMICAL INVESTIGATION OF SELECTED INHIBITORS

The plant extracts were selected based on the review which supply information about the phytochemical analysis of the plant extracts. Bignoniaceae is characterized by the presence of terpenoids, flavonoids, alkaloids, and special aromatic derivatives of the shikimic acid pathway **(Cipriani *et al*, 2007)**. Phytochemical investigations reveal the chemical constituents of the plant materials. There are some criteria that help us to choose the inhibitor. The predominant among them is that the plant material should contain hetero atoms in the phytochemical component of the plant.

Spathodol, a new dihydroxylated sterol, was isolated from the leaves of *Spathodea campanulata,* along with the previously reported triterpenoids 3 p-acetoxyoleanolic acid, siaresinolic acid, 3p-acetoxy- 12-hydroxyoleanan-28,13-olide,oleanolic acid, and ~ sitosterol-3-O-~-~-glucopyranoside **(Ngouela *et al*, 1991).**

The antioxidant principles isolated from the various parts of the plant were verminoside (leaf, stem bark and flowers), Specioside (flowers), Kampeferol diglucoside (leaf) and Caffeic acid (leaf and fruits). The non anti-oxidant components isolated in the study included ajugol (stem bark and fruits) and phytol (leaf). **(Elusiyan *et al*, 2011)** while **Banerjee and De (1993)** showed the presence of anthocyanins in the flowers of *Spathodea campanulata.*

Ethanolic extracts of the leaves of *Tecoma capensis* revealed the presence of tecomoside and its four 7-O-acyl derivatives [cinnamoyl, (p-methoxy) cinnamoyl, (p-hydroxy) cinnamoyl and (p-hydroxy) benzoyl], a novel iridoid glucoside, 7-O-(p-methoxy)benzoyl tecomoside .The glucosidic fraction of these extracts showed the presence of cornoside and of its 2,3,5,6-tetrahydroderivative, rengioside B. The nonglycosidic fraction contained the non-natural, rearranged aglucone of 7, halleridone **(Guiso *et al*, 1997).**

2.8 Molecular modelling

Recently theoretical prediction of the efficiency of corrosion inhibitors became very popular as it not only support experimental results and but also find the efficiency way to minimize the chemical expenditure. Many researchers focus on the molecular modeling of phytochemicals present in the plant extract to highlight the correlation between theoretical and experimental results.

Computer modeling techniques were successfully applied to corrosion problems **(Zamani *et al,* 1986)**.The necessary criteria for the selection of inhibitor was hydrophobicity, molecular structure, and electron density at the donor atom of the inhibitor and solubility of the inhibitor **(Sastri and Perumareddi, 1991)**

Martinez *et al,* 2002 calculated molecular properties of chestnut and mimosa tannins namely, the geometrical structure of the molecule, the dipole moment (I), HOMO and LUMO energies .The results obtained by the above analysis imply the possibility of soft–soft interaction between metal acting as a soft acid and inhibitor acting as a soft base.

The molecular spatial structure, atomic charges, dipole moment, HOMO–LUMO energy gap and HOMO density of four types of flavanoid units that constituted mimosa tannin, was theoretically investigated by **Martinez and Stern, 2002** using HyperChem 5.11 computer package. Optimization of the molecular geometry yielded a non-planar structure with the electron charge density distributed non-uniformly. The highest values of the HOMO density was found in the vicinity of the functional groups indicating them as most probable adsorption centers.

Martinez and Stagljar, 2003 investigated the frontier orbital theory and the inhibitor adsorption theory was applied to the results of the quantum calculations and corrosion rate measurements. Nine major constituents of chestnut tannin—vescalagin, castalagin, vescalin, castalin, gallic acid, ellagic acid, mono-, di- and trigalloylglucose—were modeled by molecular mechanics, molecular dynamics and semiempirical quantum NDDO method with PM3 parametrization. The quantum calculations results reflected that tannin constituents probably adsorb as neutral molecules by means of electrostatic forces that act between the molecular dipoles and the charged metal surface.

Yan Li *et al,* 2005 applied experimental and quantum chemical methods to discuss the correlation of the inhibition effect and molecular structure of berberine. The authors predicted that the adsorption of berberine on the mild steel surface in sulfuric acid may be achieved by the interaction between iron atoms and cyclic molecular p orbital and calculated HOMO and LUMO energies. The density distribution of HOMO/LUMO indicated that there were several feasible absorption sites in one berberine molecule which favoured strong adsorption and high inhibition efficiency.

Gokhan Gece, 2008 highlighted the general reference pertaining to quantum chemical methods in corrosion inhibitor studies. He also summarized the most used quantum chemical parameters, semi empirical methods and the results of research articles in corrosion science over the past 20 years.

The description of frontier orbital theory indicated that L-tryptophan had high value of E_{HOMO} and low value of E_{LUMO} with low-energy band gap. Adsorption energy calculated for the adsorption of L-tryptophan on Fe surface in the presence of water molecules equaled −29.5 $kJmol^{-1}$, which implied that the interaction between L-tryptophan molecule and Fe surface was strong **(Khaled, 2008)**.

Gokhan Gece and Semra Bilgic, 2010 evaluated the inhibition efficiencies of a total of 12 amino acids for the corrosion of nickel in acidic medium with the help of a density functional theory (DFT) study using the B3LYP/LANL2DZ method. Quantum chemical descriptors such as the energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), and the energy gap (ΔE) values revealed that theoretically obtained results were consistent with the experimental data reported.

A molecular dynamics study for the adsorption of three benzimidazole derivatives and their inhibition characteristics was studied using chemical (weight loss) and electrochemical measurements. The molecular dynamics study revealed that the benzimidazole ring as well as the side chain acted as the active sites in these inhibitors and they can adsorb on Fe surface by donating electrons to iron d-orbital **Khaled *et al,* 2010.**

Oguzie *et al*, 2010 investigated the inhibition of low-carbon-steel corrosion in 1 M HCl and 0.5 M H_2SO_4 by extracts of *Dacryodis edulis* (DE) using different techniques. The calculations were performed by means of DFT electronic structure program $DMol^3$ using Mulliken population Analysis. The authors stated that the HOMO orbital for Cryophyllene was saturated around the C=C double bond while that of amino acid was mainly around the lactone nucleus.

The adsorption and corrosion inhibition of *Osmanthus fragran* leaves extract (OFLE) on C-steel in hydrochloric acid was investigated by electrochemical and quantum chemical calculations which provided reasonable theoretical explanation for the adsorption and inhibition behaviour of OFLE on C-steel. The values of Mulliken charge distributions showed that the oxygen atoms had high charge densities, implying that the most probable reactive site for the adsorption on C-steel was located on the oxygen atoms.**(Li *et al,* 2012**).

Bothi Raja *et al,* 2013a studied the effect of *Neolamarckia cadamba* crude extract (bark, leaves) and pure alkaloid (3β-isodihydrocadambine on mild steel corrosion in 1 M HCl medium. SEM studies evidenced the formation of a protective film over metal surface while FT-IR, supported by molecular modelling proved that this shielding effect was caused by alkaloids, particularly 3β-isodihydrocadambine. From the quantum chemical studies, it was evident that electron density (HOMO) was located within the vicinity of the aromatic indole moiety while that of LUMO was located on carbonyl group (C=O).

Some of the recent investigations in the field of green corrosion inhibitors were noted from perusal of literature and tabulated in Table 2.3

Table 2.3 Recent research activity on MS and Aluminium corrosion

S.No	Plant name & Reference	Metal / Medium	Techniques Utilised				Adsorption Isotherm	% Efficiency
			Mass Loss	Electro chemical	Surface analysis	Quantum Chemical		
1	Strawberry fruit/ **Umoren *et al*, 2014**	Mild Steel /HCl/ H_2SO_4	✓	✓	✓	✓	Langmuir	95 (HCl) 86 (H_2SO_4)
2	Xanthan gum/ **Arukalam et al, 2014**	Aluminium /1M HCl	✓	✓			Temkin and El-Awady	69.1
3	*Commiphora africana*/**Eddy *et al*, 2014**	Aluminium /1M HCl	✓	✓	✓	✓	Langmuir	84.1
4	*Commiphora kestingii* gum/ **Paul Ocheje Ameh, 2014**	Aluminium /0.1M H_2SO_4	✓	✓	✓		Flory Huggins, Temkin	83
5	Catechin from *Nypa fruticans Wurmb* /**Olubunmi *et al*, 2014**	Steel/0.1M H_2SO_4	✓					74.5
6	Coconut coir dust /**Umoren *et al*, 2014**	Mild Steel/0.5M H_2SO_4	✓	✓	✓		Freundlich	
7	*Litchi Chinensis* / **Singh *et al*, 2015**	Mild Steel/ 0.5M H_2SO_4	✓	✓	✓		Langmuir	97.8
8	*Ilex paraguariensis*/ **Souza *et al*, 2015**	C- Steel /1M HCl	✓	✓	✓		Langmuir	91
9	*Musa paradisica* peel/**Ji *et al*, 2015**	Mild Steel/ 1M HCl	✓	✓	✓		Langmuir	92

Selection of an appropriate corrosion inhibitor is an arduous task for any industry. This chapter focussed on up-to-date developments of corrosion inhibitors utilised successfully on mild steel and aluminium .As the current environmental legislation reinforces the need for non toxic, biodegradable, zero cost corrosion inhibitors, focus on natural compounds tagged as green inhibitors are gaining momentum in recent years for the development of a better tomorrow. Careful perusal of literature clearly reveals that the study of green inhibitors is of recent trend. Hence an attempt has been made out to analyse the effectiveness of two invasive plant species namely *Spathodea campanulata* and *Tecoma capensis* on corrosion of mild steel (MS) and aluminium (AA1100).

The methodology adopted for the present research work is dealt in Chapter III.