2

Review of Literature

An important method of protecting metallic materials against deterioration due to corrosion is by the use of inhibitors. Large number of organic compounds are used as corrosion inhibitor in acidic medium. But the known hazardous effects of most of the synthetic corrosion inhibitors are the motivation for the use of natural products. The natural product extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds and they do not contain heavy metals **(Rani and Basu, 2011).** Due to high eco-friendliness and almost no threat to the environment, the use of plant extracts-biomass extracts-as inhibitors is becoming the subject of extensive investigation.

The present study on "**Corrosion Inhibition and Adsorption Potential of Biomass Extracts-Leaves and Flowers of *Heliconia rostrata and Canna indica* on Corrosion of Mild Steel/Aluminium 1100 in 1 M HCl**" is reviewed under the following topics.

- Biomass extracts as corrosion inhibitors for mild steel
- Biomass extracts as corrosion inhibitors for aluminium
- Phytochemical constituents as corrosion inhibitors
- Mechanism of inhibition.
- Quantum chemical studies and molecular modeling

2.1 BIOMASS EXTRACTS AS CORROSION INHIBITORS FOR MILD STEEL

The use of mild steel as construction material in industrial sectors has become a great challenge for corrosion engineers and scientists nowadays. In practice, most of the acidic industrial applications such as refining crude oil, acid pickling, industrial cleaning, acid descaling, oil–well acidization in oil recovery and petrochemical processes use mild steel as their material. Hydrochloric acid is one of the most widely used agents in the industrial sector. Due to the aggressiveness of acid solution to mild steel, the use of inhibitor to prevent the metal dissolution process will be inevitable. The use of natural products such as extracts from the leaves, flowers, seeds and roots as corrosion inhibitors have been widely reported by several authors (**Ekanem *et al*,2010** ; **Mourya *et al*, 2014**; **Okafor *et al*,2008; Obot and Obi-Egbedi,2009**). In the 21*st* century, the research in the field of ''green'' or ''eco-friendly'' corrosion inhibitors has been increased. An extensive survey of literature clearly depicts the growing use of **biomass extracts** of various plant parts as corrosion inhibitors. The study of these green inhibitors has been extended in the last decade and number of articles published during (2001-2010) compared to 1991-2000 were doubled **(Kesavan *et al*, 2012)** (Figure 2.1)

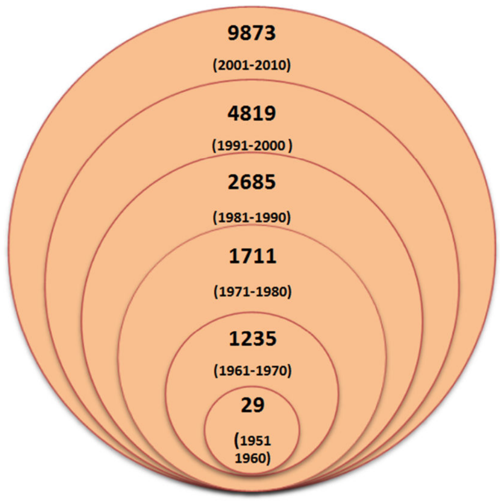

Figure 2.1 Articles published during 1950-2010 to explore green inhibitors.

Plants are sources of naturally occurring compounds, some with complex molecular structures and having different chemical, biological, and physical properties. The naturally occurring compounds are mostly used because they are environmentally acceptable, cost effective, and abundant availability. These advantages are the reason for use of extracts of plants and their products as corrosion inhibitors for metals and alloys under different environments. The use of plant extracts as corrosion inhibitor is not a recent development. The past records showed that in the Middle Ages (i.e from the 5th century to the 15th century) plant extracts (flour, bran, yeast, a mixture of molasses and vegetable oil, and starch) had been used for pickling of metal articles by master-armourers and extracts of bran among other substances used to inhibit the corrosion of iron in acids. The first patent in corrosion inhibition was awarded to Baldwin in 1895 **(Sanyal, 1981).**

The significance of plant extracts as corrosion inhibitors becomes more in the new millennium and resulted enormous data on plant extracts as corrosion inhibitors. An extensive literature survey clearly depicts the growing use of various biomass extracts as inhibitors for metal protection. The successful use of naturally occurring biomass extracts as corrosion inhibitor for mild steel in acidic environment was reported by several authors and the examples are numerous. The details of some of the investigations are tabulated in Table 2.1.

Table 2.1: Biomass extracts used as corrosion inhibitors Mild steel

S.No	Source	Medium	Techniques Utilised	References
1.	Aqueous and alcoholic extracts of seven aloe plants	5% HCl	Weight loss measurements	**Saleh *et al* 1983,**
2.	*Calotropis Procera* and *Diospyross Mesipiliformi* plant extracts	0.1N HCl	Polarization curves and weight loss measurements	**Awad 1985**
3.	Papaia, *Poinciana pulcherrima*, *Cassia occidentalis* and *Datura stramonium* seeds and Papaia, *Calotropis procera B*, *Azydracta indica* and *Auforpio turkiale* sap	HCl	Weight-loss determinations and electrochemical measurements	**Zuchhi and Omar, 1985**
4.	Acid extract of *Calotropis giganta latex*	HCl	Polarization studies	**Verma and Mehta, 1998**
5.	*Pongamia glabra* and *Annona squamosa*	HCl and H_2SO_4	Electrochemical and weight loss measurements	**Sakthivel *et al,* 1999**
6.	Juices extracted from *anacardium occidentale* (cashew)	0.1 M HCl	Weight-loss and potential measurement techniques	**Loto and Mohammed 2000**
7.	Acid extract of *Andrographis Paniculata*	HCl	Mass loss method, Tafel polarisation method and impedance studies.	**Ramesh ,2001**
8.	Bitter leaf (*Vernonia Amygdalina*) solution extract	HCl and H_2SO_4	Weight loss	**Loto, 2003**

S.No	Source	Medium	Techniques Utilised	References
9.	Acid extracts *of Ficus benghalensis* bark	HCl and H_2SO_4	Weight loss and electrochemical techniques.	**Rajalakshmi *et al*, 2002**
10.	Juice extracts of *Mangifera Indica* (mango)	HCl	The weight-loss and potential measurement techniques	**Loto *et al* ,2003**
11.	*Foenum graecum*	HCl	DC electrochemical techniques.	**Kalpana and Metha, 2003**
12.	Leaves of *Nypa fruticans* Wurmb	HCl	Weight loss and hydrogen gas evolution techniques	**Orubite and Oforka 2004**
13.	*Artemisia* oil	HCl	weight loss, electrochemical and EIS polarization techniques.	**Bouyanzer and Hammouti 2004**
14.	*Citrus paradisi* (grapefruit)	HCl	Weight loss technique	**Olusegun *et al*, 2004**
15.	Jojoba oil	HCl	Weight loss and electrochemical polarization	**Chetouani *et al*, 2004**
16.	Onion (*Allium Cepa*), Garlic (*Allium Sativum*) and Bitter Gourd (*Momordica Charantia*)	HCl	DC method-Tafel extrapolation, Resistance polarisation ,"Vicor"computer software method; Mass loss, dissolved iron concentration	**Parikh and Joshi,2004**
17.	Acid extract of seeds, leaves and bark of *Prosopis Juliflora*	1N HCl , 1N H_2SO_4 and HNO_3	Weight loss method.	**Chowdhary *et al*,2004**
18.	*Ricinus communis* (castor-oil plant)	NaCl	Weight loss, electrochemical polarization and impedance measurements	**Sathiyanathan *et al*, 2005**
19.	Leaf extracts of *Occimum viridis*	HCl and H_2SO_4	Gasometric technique at temperatures	**Oguzie, 2006**

S.No	Source	Medium	Techniques Utilised	References
20.	Pennyroyal Mint (*Mentha pulegium)*	1 M HCl	weight loss measurements, electrochemical polarisation and EIS methods	**Bouyanzer *et al*,2006**
21.	*Azadirachta indica*	HCl	Gas volumetric technique	**Oguzie, 2006**
22.	Khillah (*Ammi visnaga*) seeds	HCl	Weight loss measurement as well as potentiostatic technique.	**El-Etre ,2006**
23.	Aqueous extract of Fenugreek leaves and seeds	HCl and H_2SO_4	Electrochemical impedance spectroscopy and pontentiodynamic polarization measurements	**Noor, 2007**
24.	*Zenthoxylum alatum*	5% and 15% aqueous HCl	Weight loss and electrochemical impedance spectroscopy	**Chauhan and Gunasekaran, 2007**
25.	*Datura stamonium*	HCl and H_2SO_4	Weight loss studies, electrochemical studies viz.,Tafel polarization, AC impedance, and SEM studies	**Raja *and* Sethuraman,2007**
26.	*Occimum viridis* , *Telferia occidentalis* , *Azadirachta indica* and *Hibiscus sabdariffa* leaves, *Garcinia kola* seeds	HCl and 1 M H_2SO_4	Gasometric technique at temperatures 30°C and 60 °C	**Oguzie,2008**
27.	*Hibiscus sabdariffa*	2M HCl and 1 M H_2SO_4	Gasometric technique	**Oguzie,2008**
28.	Leaves and seeds extracts of *Phyllanthus amarus*	HCl and H_2SO_4	Weight loss and gasometric techniques.	**Okafor *et al*,2008**
29.	Seed extract of *Phaseolus aureus*	HCl	Weight loss method and Potentiodynamic polarization technique	**Rajalaksmi *et al*, 2008**

S.No	Source	Medium	Techniques Utilised	References
30.	Stem, bark, leaves and fruit from *Prosopis cineraria*	HCl and H_2SO_4	Weight loss method	**Sharma *et al,* 2008**
31.	*Piper guinensis*	2.5 M H_2SO_4	gravimetric, gasometric and thermometric methods	**Ebenso *et al,* 2008**
32.	Black pepper (*Piper nigrum fem.* Piperaceae)	HCl	Weight loss measurements, Potentiodynamic polarisation, Electrochemical impedance spectroscopy	**Quraishi *et al*, 2009**
33.	*Citrus aurantiifolia* leaves	1 M HCl	Weight loss measurements and electrochemical studies.	**Saratha *et al*,2009**
34.	*Solanum Tuberosum*	HCl and H_2SO_4	Weight loss measurements, Potentiodynamic polarisation, Electrochemical impedance spectroscopy	**Raja *and* Sethuraman ,2009**
35.	*Justicia gendarussa*	HCl	Weight loss and electrochemical technique	**Satapathy *et al*,2009**
36.	*Ervantamia coronaria* leaves	HCl and H_2SO_4	Weight loss and electrochemical measurements.	**Rajalakshmi *et al,* 2010**
37.	Palmyra palm (*Borassus Flabellifer Linn*)	HCl and H_2SO_4	Weight loss and electrochemical techniques.	**Vijayalakshmi *et al*, 2010a**
38.	Coconut (*cocos nucifera*) shell extract	HCl	Weight loss and electrochemical methods	**Vijayalakshmi *et al*, 2010b**

S.No	Source	Medium	Techniques Utilised	References
39.	Leaves, fruits and twigs of *Muntingia calabura*	HCl and H_2SO_4	Weight loss method	**Santhi and Manonmani, 2010**
40.	Kalmegh (*Andrographis paniculata*) leaves.	HCl	Weight loss, electrochemical impedance spectroscopy, Potentiodynamic polarization techniques.	**Ambrish Singh *et al,* 2010.**
41.	*Adhatoda Vasica*	1 N HCl, 1 N H_2SO_4 & 1 N H_3PO_4	Weight loss and Polarization method	**Matheswaran and Ramasamy ,2010**
42.	*Artemisia pallens*	HCl	Weight loss and polarization techniques, SEM and FT-IR studies	**Kalaiselvi *et al*, 2010**
43.	*Cyamopsis tetragonoloba*	HCl	Weight loss and Potentiodynamic polarization technique	**Subhashini *et al,2010***
44.	*Spirulina platensis*	HCl and H_2SO_4	Weight loss method, potentiodynamic polarization method, electrochemical impedance spectroscopy measurements and SEM analysis	**Kamal and Sethuraman, 2012**
45.	Pineapple leaves (*Ananas comosus L.)*	HCl	Weight loss and hydrogen evolution method	**Ekanem *et al*,2010**
46.	*Pongamia pinnata* seed extract	HCl	Weight loss method, Potentiodynamic polarization method, electrochemical impedance spectroscopy	**Singh *et al*,2011**
47.	*Rauvolfia serpentina*	HCl and H_2SO_4	Weight loss ,Potentiodynamic polarization and electrochemical impedance spectroscopy	**Raja and Sethuraman,2010**

The adsorption and corrosion inhibition effect of acid extract of the seeds of *Areca catechu* on mild steel in hydrochloric acid medium was analyzed by **Kumar *et al*, 2011**. Inhibition efficiency and thermodynamic parameters such as energy of activation for corrosion reaction of mild steel, heat of adsorption of the inhibitor on the metal surface, change in entropy (ΔS), and change in free energy (ΔG) were obtained using weight-loss data. The nature of adsorption of the inhibitor on the metal surface was verified by plotting Temkin's adsorption isotherm.

Ji *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 % corrosion inhibition was observed at around 200 mg L^{-1} inhibitor concentration and maximum of 92.5% for 500 mg L^{-1} extract concentration in 1 M HCl.

The inhibitive effect of naturally available potato peel extract towards the corrosion of mild steel in 2M HCl solution was investigated by **Ibrahim *et al*, 2011** using weight loss and electrochemical techniques. The results showed increase in the inhibition efficiency with increasing potato peels extract concentration. Corrosion inhibition efficiency of 70% was obtained at a concentration of 50 ppm of the inhibitor concentration. Impedance data showed that increasing the PPE concentration, increased the charge transfer resistance and decreased the doubled layer capacitance. The adsorption film of extract on the mild steel specimen was also found to follow Langmuir adsorption isotherm**.**

Vimala *et al*, 2011 determined the inhibition efficiency of acid extract of flowers of *Cassia auriculata* 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 %. Inhibition was found to increase with increasing concentration of the plant extract. Potentiodynamic Polarisation curves revealed the mixed nature of the inhibitor.

Rajalakshmi *et al,* 2012a studied the inhibitive properties of leaf sheath extract of *Cocos Nucifera* for the corrosion of mild steel using conventional weight loss and electrochemical measurements. The results revealed that the leaf sheath extract of *Cocos Nucifera* inhibited the corrosion of Mild steel. The adsorption of the inhibitor followed the Langmuir and Temkin type adsorption isotherm.

Several naturally occurring substances were tested as corrosion inhibitors for Mild steel in acidic media. An overview of emerging scenario in the frontiers of eco-friendly corrosion inhibitors of plant origin for mild steel was highlighted by **Rajalakshmi *et al,* 2012b**.This review listed the corrosion inhibiting properties of natural products for mild steel in aggressive media.

The influence of *Cassia alata (CALE)* leaves extract on the corrosion inhibition of Mild steel in 1 M HCl acid solution was studied by mass loss, electrochemical measurements and surface analytical techniques. *Cassia alata* leaves adsorbed on the mild steel surface following Langmuir and Temkin isotherms. Electrochemical measurements confirmed the mixed mode of inhibition. SEM investigations documented the formation of protective layer on the mild steel surface. **(Leelavathi and Rajalakshmi, 2012).**

Krishnegowda *et al*, 2013 investigated the inhibitive action of ethanol extract of *Acalypha torta* leaves on corrosion of mild steel in 1 M HCl solution by weight loss, Potentiodynamic polarization, electrochemical impedance spectroscopy, chronoamperometric measurements. Resuts obtained from polarization measurements revealed that the extract of *Acalypha torta* leaves acted as a mixed-type inhibitor.The inhibition effciencies obtained from weight loss measurements and electrochemical tests were in good agreement. The adsorption of inhibitor on mild steel followed Langmuir adsorption isotherm.

Vimala *et al*,2012 evaluated the inhibition effect of *Annona muricata* L. leaves extract on mild steel corrosion in 1 N HCl using conventional weight loss, electrochemical polarization, electrochemical impedance spectroscopy studies.The results of electrochemical impedance showed that the change in concentration of the extract changed the charge transfer resistance, and double layer capacitance which was due to the formation of a protective layer on the surface of mild steel by active molecules of the extract. Polarization data revealed the mixed mode of inhibition.

The inhibition effect of *Mundulea sericea* leaf extract (MSLE) on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 solution was carried out by mass loss, linear polarization resistance (LPR), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) methods. The results showed that *Mundulea sericea* was more efficient in 1.0 M HCl than 0.5 M H_2SO_4. The adsorption of *Mundulea sericea* on mild steel surfaces in both acid solutions was found to obey the Langmuir and Temkin adsorption isotherms. Polarization curves reveal that *Mundulea sericea* acted as a mixed-type inhibitor in both acids by simultaneously restraining anodic and cathodic reactions. **(Leelavathi and Rajalakshmi, 2013).**

Inhibition of mild steel corrosion using aqueous extract of C*ocos nucifera L.* peduncle in acidic solutions was analysed by mass loss method and electrochemical measurements.The inhibition efficiency was found to increase with increase in concentration, time of immersion and temperature. The adsorption of the inhibitor molecule onto the metal surface was found to obey El-Awady kinetic thermodynamic adsorption isotherm **(Vijayalakshmi and Rajalakshmi, 2013).**

Extract of *Clerodendrum phlomidi* plant leaves was reported as corrosion inhibitor for mild steel in 0.5M HCl using conventional weight loss method. The results showed that the inhibition efficiency was increased with increase in the concentration of *Clerodendrum phlomidis* leaves extract and reached a maximum value of 96.30 % at the highest concentration of 50 ppm at temperature of 303 K.**(Pruthviraj *et al*,2013)**

Uwah *et al*,2013 investigated the inhibition performance of the ethanol extracts of *Costus afer* stem on the corrosion of mild steel in 5M HCl solution at temperatures 303, 313 and 323 K by the weight loss and hydrogen evolution technique. The results showed that inhibition efficiency was found to increase with increase in concentration of the plant extracts but decreased with rise in temperature.Maximum inhibition efficiency of 94.8% was recorded at 5.0g/L of *Costus afer* extract. Adsorption of the extracts on the mild steel coupon was found to obey Langmuir, Temkin, Frumkin and Freundlich adsorption isotherms. The obtained thermodynamic parameters proposed the phenomenon of physical adsorption.

The inhibitive performance of Aloes leaves extract in the corrosion mitigation of mild steel in 1 M HCl was studied by **Cang *et al*, 2013** using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques.The results indicated that the inhibition efficiency increased with increase of the extract concentration. The adsorption of the extract molecules on the steel surface obeyed Langmuir adsorption isotherm.The data obtained from thermodynamic parameters showed strong interaction between inhibitor and mild steel surface.

Assessment of the corrosion inhibition effect of *Artemisia halodendron* leaves extract on mild steel in 1 M HCl medium was done by electrochemical potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS) techniques. The polarization studies showed that *Artemisia Halodendron* acted as mixed-type inhibitor. The Nyquist plots showed that increase of inhibitor concentration increased the charge transfer resistance and decrease double layer capacitance.Adsorption of the inhibitor on mild steel surface obeyed Langmuir adsorption isotherm **(Huang *et al*, 2013)**

The extract from the seeds of *Aframomum melegueta* (AM) was examined as corrosion inhibitor for mild steel in aerated 1 M HCl and 0.5 M H_2SO_4 solutions using gravimetric and electrochemical techniques. AM extract was found to inhibit both the cathodic and anodic reaction by adsorption of the organic matter on the metal/solution interface.Increasing the temperature of the system enhanced inhibition efficiency of AM extract in 1 M HCl, but decreased efficiency in 0.5M H_2SO_4. Molecular dynamics simulations were performed to theoretically illustrate the electronic structure and adsorption behaviour of the active constituents of the seeds of *Aframomum melegueta* to evaluate their contributions to the corrosion inhibiting action of the extract **(Oguzie *et al,* 2013)**

The anti corrosion behaviour of *Aquilaria Crassna* leaves (agarwood) extracts in 1 M HCl solution on mild steel was studied using gravimetric method and electrochemical methods. EIS analysis revealed that increase in concentration increased the charge transfer resistance which increased the inhibition efficiency. The potentiodynamic polarisation measurements showed that the inhibitor acted as mixed-type with predominantly cathodic effectiveness. The adsorption mechanisms was found to follow physisorption **(Helen *et al*, 2014)**

Elmsellem *et al*, 2014 reported the inhibition effect of *curcumin* on the corrosion of mild steel in 1 M HCl solution using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results suggested that the inhibition efficiency increased with increase in inhibitor concentration. Adsorption of this compound on mild steel surface obeyed Langmuir isotherm. The structural parameters E_{HOMO} and E_{LUMO}, energy gap ΔE, the frontier molecular orbital energies and electronic parameters such as mulliken atomic populations were calculated using Density Functional Theory method (DFT).

Owate *et al*, 2014 investigated the inhibitive effect of *Aspilia africana* leaves extract on mild steel corrosion in 1 M hydrochloric acid (HCl) at room temperature and at 60 ºC. The leaves extract showed good inhibition efficiency on the corrosion of mild steel with optimum values of 88.1% at room temperature and 91% at 60 °C.Langmuir and Temkin isotherms were used to analyse the adsorption mechanism of the inhibitor-metal interaction.Gibb's free energy of adsorption showed a spontaneous and mixed adsorption-physisorption and chemisorption.

The inhibitive effect of the aqueous extract of *Rothmannia longiflora* on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions was investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy measurements. The extract was found to inhibit the corrosion process in both environments and inhibition efficiency increased with increasing extract concentration as well as rise in temperature. Data from electrochemical measurements suggested that the extract functioned by adsorption of the organic matter on the metal/corrodent interface, inhibiting both the anodic and cathodic half reactions of the corrosion process. Adsorption of the inhibitor on the mild steel surface obeyed Langmuir adsorption isotherm **(Akalezi *et al*, 2015)**

Inhibition effect of pomegranate peel extract on the corrosion of mild steel in hydrochloric acid (HCl) solution was assessed by mass loss and electrochemical impendence techniques. The results revealed that pomegranate peel extract acted as a corrosion inhibitor in HCl solution. The inhibition efficiency increased with the increase in concentration of pomegranate peel extract.The inhibition action was attributed to the adsorption of the chemical compounds present in the extract on mild steel surface **(Ashassi Sorkhabi *et al,* 2015)**

Karthik *et al,* 2015 determined the anticorrosion activity of *Tiliacora acuminata* leaf extract as a corrosion inhibitor in 1 M HCl using mass loss, potentiodynamic polarization, and electrochemical impedance spectroscopy. The mass loss results showed a maximum value of 93.02 % at a concentration of 320 ppm at 333 K.Polarization measurements demonstrated that the inhibitor acted as a mixed type. Nyquist plot illustrated that on increasing concentration the inhibitor influenced the charge transfer resistance and the double layer capacitance.The adsorption of *Tiliacora acuminata* leaf extract on mild steel obeyed Langmuir adsorption isotherm.

The corrosion inhibition effect of red apple (*Malus domestica*) fruit extract on mild steel surface in hydrochloric acid was investigated by gravimetric and electrochemical methods at 30 °C-60 °C. Inhibition efficiency increased with increase in concentration of the inhibitor and temperature. Polarization curves indicated that the extract functioned as mixed-type inhibitor. The adsorption of the extract onto mild steel surface followed Langmuir adsorption isotherm. Quantum chemical calculations and molecular dynamics simulations were used to provide the mechanism of interaction of the major components present in the inhibitor with mild steel surface (**Umoren *et al*, 2015**)

Verma and Khan, 2016 explored the corrosion inhibitive property of fresh water green algae *Spirogyra* on mild steel corrosion. The study was carried out in 0.5 M HCl solution using weight loss measurements, scanning electron microscopy, energy-dispersive

X-ray spectroscopy, X-ray diffraction and FT-IR techniques. The maximum inhibition efficiency was found to be 93.03% at 2 g L^{-1}. The adsorption of extract of *Spirogyra* on mild steel surface obeyed the Langmuir adsorption isotherm. Corrosion inhibition mechanisms were inferred from the temperature dependence of the inhibition efficiency and from thermodynamic and kinetic parameters.FT-IR analysis of green algae *Spirogyra* revealed that the presence of hydroxyl, amino and carbonyl groups present in the algae were responsible for the adsorption on the mild steel surface.

The inhibitive action of leaves, latex and fruit extracts of *Calotrpis procera* and *Calotropis gigantea* on mild steel corrosion in HCl and H_2SO_4 and mixture of solutions was studied using mass loss and thermometric technique at different temperatures. The results indicated inhibition efficiency increased with extracts concentration and maximum of up to 86.37% was obtained. Chemical adsorption mechanism was proposed for the adsorption plant components on the surface of the metal for the inhibition behaviour (**Kumar, 2016)**

Akalezi *et al,* 2016 investigated the corrosion inhibition of mild steel in 1 M HCl by *Mucuna pruriens* seed extract was investigated by weight-loss and electrochemical techniques. Potentiodynamic polarization data indicated that inhibitor acted as mixed type, but the anodic effect was more pronounced. Nyquist plots showed that on increasing the concentration of the inhibitor, the charge transfer resistance increased and double layer capacitance decreased. The strong interaction between the constituents of the inhibitor and the corroding metal surface was evidenced from the thermodynamic parameter data. Corrosion inhibition was attributed due to blocking of the mild steel surface through chemical adsorption.

The inhibitive effect of the rice straw extract on the corrosion inhibition of mild steel in 1 M HCl was reported using electrochemical techniques. The results revealed that the rice straw extract inhibited the anodic and cathodic reactions.The inhibitor acted as a mixed type. Thermodynamic calculations revealed adsorption of the inhibitor obeyed Langmuir isotherm ***(*Mahross *et al*, 2016*).***

Sharma and Sharma,2016 assessed the corrosion inhibition effect of acid extract of *Heliotropium Indicum* on mild steel in Hydrochloric acid using weight loss method. Inhibition efficiency of the extract was studied with iodide additive with different concentrations of the extracts.Thermodynamic parameter such as energy of activation (Ea), change in free energy (ΔG) and heat of adsorption (ΔS) were calculated. Inhibition efficiency increased with increase in concentration of the inhibitor and decreased with rise in temperature. Addition of KI enhanced the inhibition efficiency of the extract.

2.2 Biomass extracts as corrosion inhibitors for ALUMINIUM

Aluminium is the third most abundant element in the Earth's crust. It makes up about 8% by weight of the earth's solid surface. It is the most widely used non-ferrous metal. Aluminium lends itself too many engineering applications because of the combination of light weight, good appearance, and mechanical strength, high thermal and electrical conductivity. Aluminium relies on the formation of a compact, adherent passive oxide film for its corrosion immunity in various environments. However, when it is exposed to acid medium (pH < 5), this surface film dissolved substantially. HCl is usually used as industrial acid cleaning, chemical or electrochemical etching, and acid pickling of aluminium. It is necessary to add inhibitors to retard the corrosion of aluminium in HCl.

Details of some of the biomass extracts used to mitigate corrosion of aluminium in acidic environment are tabulated in Table 2.2.

Table: 2.2 Biomass extracts used as corrosion inhibitors for aluminium

S.No	Inhibitor	Metal	Medium	Method	Ref
1.	*Hibiscus subdariffa* (karkade)	Al and Zn	HCl and NaOH	Weight-loss and the galvanostatic polarization techniques	**El-Hosary *et al* ,1972**
2.	The mucilage extracted from the modified stems of prickly pears (*opuntia*)	Al	2M HCl	Weight loss, thermometry, hydrogen evolution and polarization techniques	**El-Etre ,2003**
3.	Leaves of date palm, *phoenix dactylifera*, henna, *Lawsonia inermis*, and corn	Al, Cu and brass	Acid chloride and NaOH	Weight loss, solution analysis and potential measurements	**Rehan,2003**
4.	*V. amygdalina*	Al	HNO_3 and HCl	Weight loss method	**Avwiri and Igho ,2003**
5.	*Azadirachta indica*	Al	HCl	Weight loss and thermometric methods	**Ebenso *et al*,2004**
6.	Peepal (*Ficus religiosa*).	Al	HCl	Mass loss and thermometric methods	**Jain *et al*, 2005.**
7.	*Delonix Regia*	Al	HCl	Hydrogen evolution technique at 30°C	**Abiola *et al*,2007**
8.	*Capparis deciduas*	Al	HCl	Mass loss and thermometric methods	**Arora *et al*, 2007**
9.	Leaf extract of *Sansevieria trifasciata*	Al	HCl and KOH	Gasometric technique.	**Oguzie, 2007**
10.	*Pachylobus edulis* with halides ions	Al	HCl	Weight loss method	**Umoren *et al*, 2008**

S.No	Inhibitor	Metal	Medium	Method	Ref
11.	*Azadirachta indica* (AZI) with iodide additive	Al	0.5M HCl	Potentiodynamic polarization and impedance techniques	**Arab *et al* 2008**.
12.	*Zenthoxylum alatum*	Cu and Al	0.1 M HCl	Weight loss measurement and potentiometry polarization technique	**Chaühan,2009**
13.	Root of *ginseng*	Al	1 M HCl	Weight loss techniques	**Obot and Obi-Egbedi, 2009**.
14.	Aqueous extract of *Hibiscus rosa-sinensis*	Al	pH 12	Weight loss method	**Rajendran *et al* ,2009**
15.	*Raphia hookeri*	Al	HCl	Weight loss and thermometric method	**Umoren *et al*,2009**
16.	*Chromolaena odorata* L.	Al	2M HCl	Gasometric and thermometric techniques (30–60∘C)	**Obot and Obi-Egbedi, 2010**
17.	*Ananas sativum*	Al	HCl	Weight loss and hydrogen evolution methods	**Ating *et al*, 2010**
18.	*Ipomoea invulcrata*	Al	1 M HCl	Weight loss technique, kinetic and thermodynamic techniques. Temp 30°C-60°C , KI and KSCN	**Obot *et al*, 2010**
19.	*Cocos nucifera* L. water	Al	HCl	Chemical technique	**Abiola and Tobun, 2010**
20.	*Euphorbia hirta* and *Dialum guineense*	Al alloy (AA3003)	HCl	Gravimetric technique at 30 and 60°C	**Nnanna *et al*,2010**

The inhibitive effect of leaf extracts of *Euphorbia hirta* and *Dialum guineense* on aluminium alloy (AA8011) in 0.5M HCl solution was studied by **Anozie *et al*,2011** using gravimetric technique at 30° and 60°C. The results indicated that both extracts functioned as good inhibitors and inhibition efficiency improved with concentration of the extracts..

The corrosion inhibitive effect of *Aningeria robusta* extract for aluminium in 2 M HCl solution and the influence of potassium iodide additives on the inhibition efficiency was assessed by hydrogen evolution method at 30° and 60°C. It was found that the inhibition efficiency of *Aningeria robusta* extract increased with increase in concentration and temperature. On the other hand, the inhibition efficiency synergistically increased on addition of potassium iodide but decreased with increase in temperature **(Obot *et al*,2011)**

Abiola *et al*, 2011 reported the Inhibitive effect of *Gossipium hirsutum* L. leaves extract on the acid corrosion of aluminum in 1 M HCl solution by weight loss technique. The results obtained revealed that the inhibition efficiency increased with increasing concentration of the extract at 30°C at optimum concentration maximum of 92% inhibition efficiency was obtained.The adsorption of the inhibitor molecule onto metal surface was found to obey Lanqmuir adsorption isotherm**.**

The corrosion inhibition efficiencies of holy basil on aluminium in HCl solution were evaluated by **Kumpawat *et al*,2012** by weight loss and thermometric methods in presence and in absence of stem extract of three different varieties of holy basil viz. *ocimum basilicum , ocimum canum and ocimum sanctum*. Inhibition efficiency increased with increased concentration of stem extract but decreased with increased acid strength. Results showed that all varieties under study are good corrosion inhibitors, among which, ocimum basilicum is the most effective. Maximum inhibition efficiency was found to be 97.09% in 0.5 N HCl solution with 0.6% stem extract.

The inhibition effect of *Newbouldia laevis* leaves extract reported as a good inhibitor on the corrosion of aluminum in HCl and H_2SO_4 solutions by the use of gravimetric technique.The Obtained results showed that inhibition effect of *Newbouldia laevis* extract was more efficient in HCl than H_2SO_4.**(Nnanna *et al*, 2012)**

The corrosion inhibition of aluminium in 1 M HCl solution by leaf extract of *Irvingia gabonensis* was investigated by **Babatund *et al*, 2012** using chemical method at 30°, 35° and 40°C. It was found that the inhibition efficiency of the extract increased with increasing concentration but decreased with increase in temperature. The adsorption of the inhibitor molecules on aluminium surface was found to obey Langmuir adsorption isotherm.

The infuence of different extracts of *Ocimum gratissimum* on the corrosion of aluminium surface in 1 M HCl was examined by weight loss method. The result of the analysis showed that inhibition efficiency increase with increase in inhibitor concentrations. Adsorption behaviour was approximated by Langmuir and Flory – Huggins isotherms. The trend of inhibition efficiency of different extracts was in the order: distilled H_2O > C_2H_5OH>1 M HCl (**Alinnor and Ejikeme, 2012)**

Sharma *et al*, 2012 tested the plant extract of *Solanum surrattence* in acetone, petroleum ether, and methanol on corrosion inhibition of aluminium using mass loss and thermometric measurements in acid solution.The results revealed that the inhibition effciency plant extract *Solanum surrattence* depends upon the concentration of inhibitor and inhibition efficiency was found to be 97.60% at 25◦C and at higher temperature the inhibition efficiency decreased.

Ejikeme *et al*,2012 inspected the the inhibitive effect of *Treculia Africana* leaves extract in the corrosion of aluminium in HCl solution using weight loss and thermometric methods at 30° - 60 ºC. The results showed that inhibition efficiency of *Treculia Africana* extract increased with increase in concentration, but decreased with increase in temperature and the interaction of inhibitor with the metal surface was found to obey Freundlich and El-Awady adsorption isotherms.

The effect of some ion-additives on the inhibitive effect of extract of *Trigonella foenum graceums* seeds on acid corrosion of aluminium alloy (AA6063) in 0.5 N HCl was studied by weight loss method. The investigation was carried out for different immersion periods at room temperature. An optimum concentration (1.056 g/L) of the inhibitor was used for the 0.05 g/L of various ion-additives (halide and Zn^{2+} ions). The inhibition efficiency was observed to increase synergistically on adding the additives. The extract of *Trigonella foenum* acted as a potential inhibitor for acid-induced corrosion of AA6063 **(Sharma *et al*, 2012).**

Satar *et al*, 2012 explored the effectiveness of *Nipah* extract on corrosion inhibition of aluminium surface in hydrochloric acid by weight lost technique. The aluminium concentration in the inhibitor solution was detected by inductively coupled plasma (ICP-OES). It was found that the weight loss of aluminium was decreased with increased concentration of the inhibitor and the inhibition efficiency was found to be 51.43 %.

Assessment of the corrosion inhibitive effect of *Vernonia amygdalina* extract on aluminium in 0.5 M HCl solution was studied by **Ajanaku *et al*, 2012** using gravimetric method at 40°C temperature. The results revealed that corrosion inhibition efficiency of the extract increased with extract concentrations in the corrosion media.

Different extracts of *Vernonia amygdalina* (1 M HCl, ethanol and distilled water) on the corrosion inhibition of aluminium was explored by **Alinnor and Ukiwe, 2012** using gravimetric method. The result of the study revealed that inhibition efficiency of different extracts of *vernonia amygdalina* increased with increase in concentration of the studied extracts. This study revealed that inhibition efficiency decreased with increased temperature. The experimental data were corroborated with Langmuir as well as Flory – Huggins adsorption isotherms. The inhibition efficiency of extracts was in the order: C_2H_5OH>distilled H_2O>1 M HCl at 303K and C_2H_5OH> IM HCl> distilled H_2O at 333 K.

A study on the effectiveness of Coconut coir dust extract as a efficient inhibitor for aluminum corrosion in 1 M HCl medium was carried out using weight loss and hydrogen evolution method. It was reported that % IE efficiency increased with increasing temperature and concentration. Obtained results were found to follow Langmuir adsorption isotherm **(Umoren *et al*,2012).**

Inhibitory efficacy of ethanolic extract of *Azadirachta indica* fruit was evaluated in HCl medium at room temperature as well as elevated temperature using weight loss measurement. Efficiency of the inhibitor increased with the increasing concentration of the inhibitor. Observed IE % was high (92.37 %) at room temperature at concentration 1.052 g/L. High inhibitive effect may be attributed to phytochemical present in the extract **(Sharma *et al,*2013)**

Yadav *et al*, 2013 estimated the corrosion behaviour of Aluminium and copper exposed to HCl solution containing 0.0644 – 1.288 g/L of *Ziziphus mauritiana* fruit extract at room temperature using weight loss method. It was observed that the inhibition efficiency increased with increase in concentration of the inhibitor and reached a maximum of 76.8% for aluminium and 88.58% for copper at 1.288 g/L concentration of *Ziziphus mauritiana* fruit extract at room temperature. The obtained results indicated that the extract acted as better corrosion inhibitor for copper than aluminium. The inhibitor was found to obey Langmuir adsorption isotherm for both the metals.

The effective performance of *Mentha pulegium* extract on the acid corrosion of aluminium in 1 M HCl solution was assessed by **Khadraoui *et al*, 2013** using gravimetric, gasometric and EIS techniques. It was observed that the inhibition efficiency of the extract depended on the concentration of the plant extract as well as on the time of exposure of the aluminium samples in HCl solutions containing the extract. The corrosion behavior of aluminium in 1 M HCl was also studied in the range 298 K and 318 K. The adsorption of *Mentha pulegium* extract on the aluminium surface was found to follow Temkin adsorption model.

Halambek *et al*, 2013 reported the inhibitive action of ethanol solution of *Ocimum basilicum* L. oil on aluminium corrosion in 0.5 M HCl using weight loss, potentiodynamic polarization and EIS methods. Results of potentiodynamic polarization measurements revealed that presence of basil oil in HCl solution reduced the current densities. The formation of protective layer of the investigated compound on aluminium surface of was confirmed by EIS method. Thermodynamic adsorption parameters showed that compounds present in basil oil were adsorbed on aluminium surface by an exothermic process.

The inhibitive nature of alcoholic extract of *Cassia alata* leaves towards the corrosion of aluminum in 1N HCl was evaluated by **Petchiammal and Selvaraj, 2013a** using mass loss measurement.The observed results suggested that the % of inhibition efficiency was enhanced with increase of inhibitor concentration and temperature. The calculated values of ΔH_{ads}, ΔG_{ads} showed that the adsorption process is endothermic and spontaneous. The protective film formed on the metal surface was confirmed by UV, FT-IR and EDX spectral studies**.**

Petchiammal and Selvaraj, 2013b analysed the inhibitive behaviour of alcoholic extract of *Albizia lebbeck* seed on Aluminum in 1N Hydrochloric acid by mass loss measurement with various immersion periods and temperature ranging from 303 to 333K. The observed results revealed that the % of inhibition efficiency enhanced with increase of inhibitor concentration and decreased with increased immersion period. However, in temperature variation, the inhibition efficiency decreased with increase of temperature. The adsorption of the inhibitor on aluminium surface was found to be physisorption process**.**

The inhibition and adsorption properties of *Commiphora africana* gum for the corrosion of aluminium in hydrochloric acid was examined by **Eddy *et al*, 2014.**The gum was found to be a good adsorption inhibitor for the corrosion of aluminium in HCl solution. The adsorption of the inhibitor was spontaneous, exothermic and best fitted the Langmuir adsorption model. The temperature studies revealed that values of the activation and free energies were lower than their respective threshold values.

The effect of *Commiphora pedunculata* gum on the inhibition of the corrosion of aluminium alloy AA 3001) in 0.1 M HCl was investigated by **Ameh and Eddy, 2014** using gravimetric and thermometric methods. The inhibition efficiency of *Commiphora pedunculata* gum was found to increase with increase of inhibitor concentration but decreased with increasing temperature. The results obtained indicated that the gum acted as a good adsorption inhibitor for the corrosion of aluminium in 0.1 M HCl.

The corrosion behaviour of commercial aluminium in HCl was analysed by gravimetric method in absence and presence of date palm leaf extract as inhibitor.It was found that the corrosion rate decreased in presence of the inhibitor in the temperature range 20°C-50ºC. IE was found to increase with increasing inhibitor concentration from 0.2 to 0.6 g/L and decreased with rise of temperature. Hot-water extract of date palm leaves showed 40- 88% inhibition efficiency at the tested conditions. Adsorption of the inhibitor on aluminium surface followed Langmuir adsorption isotherm **(Al-Haj-Ali *et al*,2014)**

The inhibition efficiency of extract of Garlic on aluminium in hydrochloric acid solutions was evaluated by **Al- Mhyawi, 2014** using weight loss technique. Values of inhibition efficiency obtained are dependent upon the concentration of inhibitor and temperature. Results revealed that the inhibition was found to increase with inhibitor concentration, half-life, and activation energy but decreased with rise of temperature. The phenomenon of physical adsorption was proposed from the obtained thermodynamic parameters. A good fit to Langmuir and Temkin adsorption isotherms were obtained from the experimental results.Thermodynamic data revealed that corrosion inhibition process is spontaneous and exothermic.

Shalabi *et al*,2014 examined the inhibition efficiency of alcoholic extract of *Phoenix dactylifera* plant on aluminium and aluminium silicon in 0.5 M hydrochloric acid by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM). Values of inhibition efficiency obtained are dependent upon the plant extract concentration and temperature.Inhibition efficiency was found to increase with increased concentration of the inhibitor and decreased with rise of temperature. The adsorption of the extract on Al and Al–Si alloy was found to follow Temkin adsorption isotherm.

Assessment of the inhibitive behaviour of *Piper guineense* seed extract on Al alloy in acidic environment was carried out by **Nwosu *et al*, 2014** using gravimetric technique. The investigation showed optimal inhibition efficiency of 95.34% on Al alloy surface. The seed extract of *Piper guineense* was adsorbed in accordance with Langmuir adsorption isotherm. The negative adsorption energy $\Delta Gads$ obtained inferred that the adsorption rates were spontaneous.

The inhibition of the corrosion of aluminium in 1.0 M HCl solution by Xanthan gum was studied using weight loss and polarization measurements techniques.The results revealed that inhibition was found to increase with increasing concentration of the xanthan gum. The effect of temperature and immersion time was also studied. The inhibitive action was attributed to the adsorption of the inhibitor molecules on metal surface following Temkin and El-Awady adsorption isotherms. The apparent activation energy as well as free energy of adsorption, ΔG_{ads} for the inhibition process was calculated. Polarization measurements indicated that the inhibitor is of mixed-type, with predominant inhibitive effect on cathodic partial reaction **(Arukalam *et al*,2014)**

The adsorption and inhibition potentials of the *Ficus sycomorus* gum on aluminium corrosion in HCl was performed at different temperatures at 303K and 333K using gravimetric method.It was found that the inhibition efficiencies of the gum increased with increase in concentration and decreased with increase in temperature and period of immersion. The calcullated values of activation energy of the inhibited corrosion reaction of aluminium were greater than the value obtained for the blank. Thermodynamic consideration revealed that adsorption of the inhibitor on aluminium surface was first order, exothermic, spontaneous and followed physical adsorption. The adsorption characteristic of the inhibitor was best described by the Langmuir adsorption isotherm **(Aliyu *et al*,2015)**

Ability of different concentrations of bitter kola water-extract on the corrosion of aluminium in 0.5 M hydrochloric acid was analysed by **James and Odey, 2015** using weight loss technique from 30°C to 50°C. The % inhibition efficiency increased with the concentration of the inhibitor and temperature. The inhibition was due to the adsorption of the active component kola flavonone present in bitter kola extract on aluminum surface. The adsorption of the inhibitor molecule on aluminium surface was in accordance with Langmuir adsorption isotherm.

The potency of African Black Velvet Tamarind (VT) as an environmentally safe inhibitor for aluminium dissolution in 0.5 M hydrochloric acid was evaluated by weight loss method. The evaluation was carried at three different temperatures 30,40 and 50°C.Results indicated that maximum of 96% efficiency was obtained at the highest concentration (0.25 g/500 ml) at 50°C. The phenomenon of chemical adsorption was proposed from the obtained thermodynamic parameter. The inhibition action was attributed to the adsorption and surface chelation of some electron rich chemical compounds in

VT on metal surface. A perfect fit of Langmuir adsorption isotherm was observed at all studied temperatures **(James and Osarolube, 2015)**

Njoku *et al*, 2016 investigated the ethanol extract of *Kola nitida* seed (KN extract) on the corrosion mitigation of aluminium alloy AA3003 in acidic environment using joint experimental and computational approach. The obtained results revealed that KN extract hindered the corrosion reaction. The effectiveness of protection became more pronounced with increasing extract concentration and decreased with prolonged exposure time. Electrochemical data showed that organic constituents of the extract adsorbed on the aluminium surface reduced the anodic and cathodic current densities.Computational simulations were adopted to visualize the adsorption of various constituents of KN extract on aluminium.

2.3 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 **(Raja and Sethuraman, 2008).**

Isolated compounds from plants as corrosion inhibitor

Berberine extracted from *Coptis chinensis* was tested for its corrosion inhibitive nature of mild steel in 1 M H_2SO_4 using weight loss, electrochemical and SEM techniques by **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 % and 98 % 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 −33.07kJ mol^{-1} for arbutin. **(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 2.3).

Table 2.3 Insight into the components and efficiency of the tested Natural oils

S.No	Plant name / Parts /Medium	Major Components	% Efficiency	References
1	Eucalyptus / Natural oil/1 M HCl		72% at 3 mL/L	**Bouyanzer *et al*, 2006 b**
2	Artemisia herba alba/Essential oil/0.5 M 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)/ 1 M 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 / 1 M HCl	Carvone (29.00%) and Trans carveol (14.00%)	97% at 2.00 g/l	**Znini *et al*, 2011**
5	Eucalyptus globules/Essential oil/0.5 M 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 6 g/L	**Rekkab *et al*, 2012**
6	*Salvia aucheri mesatlantica* / Essential oil of aerial parts/ 0.5 M H_2SO_4	Camphor (49.59%)	86.12% at 2 g/L	**Znini *et al*, 2010**
7	Carob / seed oil/ 1 M 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 was 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, 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 1 M HCl in the absence and presence of bgugaine at 2×10^{-4} M was studied. The value of the inhibitor efficiency was found to exceed 97 % at different temperatures.

The alkaloid extract of *Rauvolfia serpentina* was studied as corrosion inhibitor for mild steel in 1 M HCl and H_2SO_4 using weight loss, potentiodynamic polarization, EIS and SEM techniques.It was 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 % in 0.1 M HCl solution.

The inhibition effect of mild steel corrosion in 1 M HCl was tested by the addition of indole alkaloids (crude) isolated from *Alstonia angustifolia var. latifolia* (A. latifolia) leaves at 303 K by **Raja *et al*, 2013.** Results inferred that the isolated alkaloid extract of A. latifolia exhibited maximum inhibition efficiency (above 80 %) 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 1 M 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 1 M 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 1 M HCl and 0.5 M H2SO4 solutions was analysed by **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.

2.4 THEORY BEHIND INHIBITION

According to **Mann *et al*,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,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 Namboothiri, 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 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 1 M HCl and 0.5 M 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 % in acid medium.

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).**

$$Al + Cl^{-} \leftrightarrow [AlCl^{-}]_{ads}$$

$$[AlCl^{-}]_{ads} + Cl^{-} \rightarrow AlCl^{2+} + 3e^{-}$$

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 and Ozcan, 2006, Keles *et al*, 2009**

According to **Li and Deng, 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.

2.5 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).**

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

Singh 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 Venkatakrishna 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.

2.6 PHYTOCHEMICAL INVESTIGATION OF SELECTED INHIBITORS

The exploration of natural products origin as corrosion inhibitors is becoming the subject of extensive investigation due rich source of natural chemical compounds present in them. The most effective inhibitors are those compounds containing heteroatoms like nitrogen, oxygen, sulfur and phosphorus, as well as aromatic rings.Plant extracts constitute several organic compounds like amino acids, alkaloids, steroids, flavonoids, proteins and tannins which have corrosion inhibiting abilities. These compounds are rich in *π*-electrons and donor atoms with which they get adsorbed on the metal surface and form a compact barrier film.

In the present investigation ***Heliconia rostrata and Canna indica*** have been selected to study the inhibitive effect on mild steel and aluminium corrosion.

The plant *Canna indica was* reported to possess the phytochemical constituents such as Betulinic acid, Oleonolic acid and Traraxer-14-en-3-one (***Bachheti et al, 2013***). It was found to contain terpenes, paraffin hydrocarbons and a toxic red oil termed cannabinol as the major chemical constituent **(Chopra *et al*, 1982).** The flowers of Canna indica are brightly red.The appearance of red color is due to presence of flavonoids, phenols and anthocyanins **(Vankar *et al*, 2008)**

Qualitative phytochemical analysis of *Canna indica* L. flower confirm the presence o farious phytochemicals such as alkaloids, carbohydrates, proteins, flavonoids, terpenoids, cardiac glycosides, steroids, tannins, saponins, Phlobatinins **(Lamaeswari and Ananthi,2012)**. The essential oil isolated from rhizome of *Canna indica* L. was found to contain terpene/terpenoid constituents **(Indrayan *et al*, 2011)**

Studies about the exact phytochemical constituent present in ***Heliconia rostrata*** was not found in literature. The preliminary assessment of phytochemical evaluation of ***Heliconia rostrata*** extracts showed the presence of primary metabolites such as glucids and proteins, the secondary metabolites phenolics compounds, terpenoides and cumarins **(Quintana *et al*, 2009).**

It was reported that the ethanol extracts of stem part of ***Heliconia rostrata*** contains tannin and saponin in its composition and the flower extract contains saponin, the leaf extracts contain flavonoid and tannin, the rhizone extracts contains flavonoids.(**Chavasco *et al*,2014).**

2.7 Molecular modeling

Recently theoretical prediction of the efficiency of corrosion inhibitors became very popular as it not only support experimental results but also find the efficient 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, 1997)**

Martinez and Stagljar, 2003 calculated molecular properties of chestnut and mimosa tannins namely, the geometrical structure of the molecule, the dipole moment (l), 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 Flavonoid 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 adsorbed as neutral molecules by means of electrostatic forces that act between the molecular dipoles and the charged metal surface.

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 adsorption sites in one berberine molecule which favoured strong adsorption and high inhibition efficiency.

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).**

Gece and 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 DMol3 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*, 2012a).**

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).

Thorough literature survey reveals that the leaves and flowers of *Heliconia rostrata* and *Canna indica* have not yet been reported as corrosion inhibitors for mild steel and aluminium in acid media.