Chapter 2

2. REVIEW OF LITERATURE

Corrosion of mild steel in acidic solutions is a major problem and acid pickling, acid descaling, acid cleaning are industrial processes used for removal of scales. Most commonly HCl and H$_2$SO$_4$ are used for this purpose. Metal dissolution in acidic medium is a common phenomena. To overcome this problem, synthetic organic inhibitors have been used to reduce the corrosion rate. These inhibitors are hazardous for environment and human beings. The need to develop economic, nontoxic and eco friendly methods have now urged researchers to focus on the use of natural products$^{1,2}$. Increasingly, there is a need to develop sophisticated new generation coatings for improved performance, especially in view of Cr (VI) being banned and labeled as a carcinogen. Hence there is a strive to make use of environmentally friendly, non toxic / less toxic, extracts of naturally occurring plant materials as corrosion inhibitors$^3$.

2.1 Corrosion of mild steel in different acidic medium

Various researchers have recently reported the corrosion inhibitor effectiveness of metals by natural plant extracts like Swertia aungustifolia, Eugenia jambolans, Andrographis panicula, coriander, thyme, hibiscus, black cumin, anise and Garden cress, henna, Ricinus communis, Telfaria occidentalis, Prunus cerasus, Capparis deciduas, Fenugreek Leaves, Piper guinensis, Azadirachta indica, Solanum tuberosu. The corrosion inhibition efficiency of aqueous extracts of Opuntia ficus indica, Aloe (leaves) and fruit peels of Orange, Mango and Pomegranate on the corrosion of mild steel, aluminium, zinc and copper in HCl and H$_2$SO$_4$ solutions were investigated by means of weight loss and polarisation measurements$^1$.

Plant extracts of Poinciana pulcherrima, Papaia, Cassia occidentalis, Datura stramonium seeds and Papaya, Calotropis procera B, Azadirachta indica, and Auforpio turkiale sap for their corrosion inhibition potential was examined and found that all extracts except those of Auforpio turkiale and Azadirachta indica retarded the corrosion rate of steel with an efficiency of 88–96% in 1N HCl and with a lower efficiency in 2N HCl. Both the cathodic evolution of hydrogen and the anodic dissolution of steel are inhibited. They ascribed the effect to the hydrolysis of the protein content of these plants$^4$.
Tafel extrapolation and transient linear polarization resistance techniques were employed to study the inhibition efficiency of *Swertia aungustifolia* (Chirata) on mild steel in acidic solution. It was found that the corrosion rate decrease with an increase in inhibitor concentration\(^5\).

The Corrosion inhibition potential of the *Eugenia jambolans* seed extract on mild steel was investigated using polarisation resistance and tafel intercept techniques\(^6\). It was concluded that inhibition efficiency, increased with increasing the concentration of inhibitor in hydrochloric solution.

The inhibiting action of acid extracts of *Andrographis paniculata* has been studied\(^7\). The corrosion rate of the metal in aggressive solution was determined by the mass loss method, tafel polarization method and impedance studies. The results revealed that this plant extract has the potential to serve as corrosion inhibitor.

The environmental friendly compounds, namely: coriander, thyme, hibiscus, black cumin, anise and garden cress are used as corrosion inhibitor\(^8\). In this study corrosion inhibition of steel in sulfuric acid was studied by six different herb plants using AC and DC electrochemical techniques. The performance of these compounds was evaluated by electrochemical impedance spectroscopy (EIS).

The inhibiting action of natural henna on iron was also evaluated\(^9\). The inhibition efficiency and corrosion rate were studied in HCl solution by the mass loss method. The dissolution rate of metal was decreased with increase in the concentration of inhibitor. The adsorption of inhibitor on metal surface was followed the Langmuir adsorption isotherm.

Inhibition efficiency of the *Zenthoxylum alatum* plant extract on the corrosion of mild steel in aqueous orthophosphoric acidic medium is also reported\(^10\). The corrosion rate of metal was calculated by weight loss and electrochemical impedance spectroscopy (EIS). Plant extract adsorbs on the metal surface and retard the corrosion rate in acid. The mechanism of corrosion inhibition of metal in phosphoric acid medium was examined by XPS and FTIR analysis.

Extracts of *Ricinus communis* leaves as a corrosion inhibitor for mild steel in 1N sodium chloride solution was also carried out\(^11\). The inhibiting action was studied by weight loss method, electrochemical polarization and impedance studies. The
maximum efficiency was found to be 84% for 300 ppm concentration of the inhibitor. The polarization study showed that the inhibitor was anodic inhibitor. Volumetric hydrogen evaluation method was employed to study the inhibition of extracts of *Telfaria occidentalis* on mild steel corrosion in HCl and H₂SO₄ solutions. Values of inhibition efficiency obtained were in good agreement and showed dependence upon the concentrations of the inhibitor.

The inhibition effect of *Prunus cerasus* juice on the corrosion of steel in hydrochloric acid (HCl) solution were carried out, using polarization and electrochemical impedance techniques. The results obtained by both methods showed that the *Prunus cerasus* juice acts as a corrosion inhibitor in HCl solution. The inhibition efficiency, increased with an increase in inhibitor concentration. The inhibition is attributed to adsorption of the phytochemical compounds in the juice.

The inhibiting properties of extracts of Chamomile (*Chamaemelum mixtum* L.), Halfabar (*Cymbopogon proximus*), Black cumin (*Nigella sativa* L.), and Kidney bean (*Phaseolus vulgaris* L.) plants on the corrosion of steel in 1M H₂SO₄ solution medium was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques and it was concluded that plant extracts behave as a mixed type inhibitors. Langmuir and Flory–Huggins adsorption isotherms were studied to clarify the nature of adsorption.

The inhibition efficiency of olive (*Olea europaea* L.) leaves aqueous extract in hydrochloric acid solution was examined by weight loss, tafel polarization and cyclic voltammetry techniques. It was observed that the inhibition efficiency, increased with the increase in concentration. The components of extract adsorb on the C-steel surface and protect the metal in 2M HCl solution. They conclude that the extract act as good corrosion inhibitor and followed Langmuir adsorption isotherm.

The protection of mild steel against corrosion in hydrochloric acid by *Zenthoxylum alatum* plant extract has been investigated through mass loss and electrochemical impedance spectroscopy (EIS) measurement. The *Zenthoxylum alatum* plant extract revealed good corrosion inhibition. The surface analysis was examined by SEM, XPS and FTIR Techniques.

Gravimetric method was used to study the temperature effects on mild steel corrosion in 2M HCl and 2M H₂SO₄ solution in the absence and presence of aqueous extract of
fenugreek leaves. Experimental results indicate that the inhibition efficiency, increased with increasing inhibitor concentration. In this investigation Langmuir and Temkin adsorption isotherms were obeyed\textsuperscript{17}.

The corrosion inhibition efficiency of mild steel by ethanol extract of \textit{Piper guinensis} (EEPG) in sulphuric acid medium has been investigated using gravimetric, thermometric and gasometric methods\textsuperscript{18}. The results revealed that the plant extract inhibit mild steel corrosion and (\%) IE of extract is found to vary with concentration, temperature and time of immersion. The inhibition efficiency depends on the concentration of plant extracts and it increases the corrosion inhibition when the concentration of extract increases. Thermodynamic consideration reveals that adsorption of plant extracts on metal surfaces is spontaneous and obey the Langmuir adsorption isotherm. A detailed review on the natural products has also been performed as corrosion inhibitor\textsuperscript{19}.

The role of seeds and leaf extract of \textit{Azadirachta indica} on corrosion of mild steel in H\textsubscript{2}SO\textsubscript{4} solution has also been investigated\textsuperscript{20}. It was found that the dissolution rate of metal decrease when inhibitor concentration increases in acidic solution due to the phytochemicals present in the extracts.

The inhibitory effect of the \textit{Solanum tuberosum} extract on the corrosion of mild steel in H\textsubscript{2}SO\textsubscript{4} and HCl solution was also investigated using different techniques when temperature ranges between 303-323K. The polarization curve showed that the plant extract behaves as a mixed mode inhibitor\textsuperscript{21}. The adsorbed layer acts as a barrier between the mild steel surface and acidic solutions which follow Temkin adsorption isotherm.

The inhibiting effects of leaves root and seeds extracts of \textit{Azadirachta indica} on mild steel corrosion in sulphuric acid solutions was reported\textsuperscript{22}. The experiment was performed using gravimetric and gasometric techniques. The results revealed that the extract was a very good inhibitor and inhibition increased with increase in concentration and temperature. The inhibition was attributed to the adsorption of the major component of the extracts onto the metal surface. The experimental data obeyed the Freundlich adsorption isotherm.

The inhibitive and adsorption potential of ethanolic extract of \textit{Ocimum gratissimum} for the mild steel corrosion in sulphuric acid medium was evaluated using
gravimetric, thermometric and gasometric techniques\textsuperscript{23}. The (%) IE of the inhibitor was found to increase with increase in the inhibitor concentration. Thermodynamic parameters indicated that the adsorption of the extract was spontaneous and can be described by Langmuir adsorption isotherm.

The efficacy of methanolic extract of \textit{Euphorbia falcata} L. as corrosion inhibitor for mild steel in hydrochloric acid medium\textsuperscript{24}. Gravimetric measurement results clearly revealed that the inhibition efficiency increases with increase in the inhibitor concentration and reached 96\% at 323K at 3g/L. The thermodynamic studies concluded that the adsorption of plant extracts on mild steel surface was spontaneous and obeyed Langmuir adsorption isotherm at all temperatures.

The corrosion inhibition efficiency of an acid extract of the flowers of \textit{Cassia auriculata} plant mild steel in hydrochloric acid medium was studied\textsuperscript{25}. The corrosion rate was calculated by weight loss measurements and electrochemical studies. The extract adsorbs on the metal surface and formed a protective layer for inhibiting the corrosion. Maximum inhibition efficiency of \textit{Phaseolus aureus} in 1 M HCl was found to be 74.7\%. The adsorption of flower extract was found to obey Temkin, Freundlich and Langmuir adsorption isotherms. Polarization results showed that the extract is a mixed type inhibitor.

The detailed mechanisms of the adsorption process of plant extract as corrosion inhibitors and identification of the active components was also reported\textsuperscript{26}. This review listed the development of computational modeling, experimental results, plant species, mechanism of inhibitory action, their adsorption patterns and the inhibitor metal surface interface.

The inhibition efficiency of \textit{Capsicum annuum} fruit extract on mild steel in acidic media was examined\textsuperscript{27}. Results obtained by different methods showed higher inhibition efficiency at the inhibitor concentration of 1400 mg/L. The adsorption of components of the fruit extracts on the metal surface obeyed Langmuir adsorption isotherm. Surface morphology was investigated through micro photograph obtained by optical microscopes.

The corrosion inhibition of mild steel in sulphuric acid medium by \textit{Ficus glumosa} gum was also evaluated\textsuperscript{28}. The gravimetric, gasometric and thermometric methods were used for determination of inhibition efficiency. The results obtained revealed
that FG gum was a good corrosion inhibitor for mild steel in acidic medium. The value of the free energy of adsorption, $\Delta G_{\text{ads}}$, indicated that adsorption of the inhibitor for mild steel is exothermic and negative value of the free energy showed that the adsorption of inhibitor molecules was typical of chemisorptions. The adsorption of inhibitor on the metal surface followed the Langmuir adsorption model.

The acid corrosion of mild steel and its inhibition by apricot juice was studied at a temperature range of 30°-60°C. It was observed that the Apricot juice acts as a corrosion inhibitor for mild steel with maximum inhibition efficiency of 75% at 30°C and higher level of inhibitor concentration. The thermodynamic model explained that the inhibitor adsorbs on the mild steel surface and obey Langmuir adsorption isotherm. The low value of free energy indicate physical adsorption. This analysis showed that the corrosion rate is influenced by temperature and inhibitor concentration.

The corrosion inhibition in 1M HCl solution of mild steel surface by Curcuma longa extract has been studied at different temperatures. In the gravimetric measurement they found that the dissolution rate of metal is increasing with increasing temperature. The inhibition was physisorption in nature with an endothermic reaction. The adsorption process on the mild steel surface obeys the Langmuir adsorption isotherm. SEM studies reveal that the corrosion of mild steel in 1M HCl was diminished by the addition of the extract and observed smoother surface.

The properties, mechanism of corrosion inhibiting and efficiencies of green inhibitors were reviewed in acidic media.

Aqueous extracts of the henna leaves on carbon steel was also studied for its corrosion inhibiting action on mild steel in 1M HCl solution by mass loss and potentiodynamic polarization techniques. The dissolution rate of metal increases with increasing temperature, but decreases with increasing inhibitor concentration. The results show that the adsorption of plant extracts on metal surface is endothermic, spontaneous and consistent with the Langmuir adsorption isotherm. The adsorption of phytoconstituents on mild steel was analysed by SEM, FTIR, X-ray diffraction analysis.

Corrosion inhibition of mild steel in hydrochloric acid by eight different plant extracts namely: Lycium shawii, Teucrium oliverianum, Ochradenus baccatus, Anvillea
gue, Cassia italica, Artemisia sieberi, Carthamus tinctorius, and Tripenrospermum auriculatum were investigated and the open circuit potential (OCP), Tafel plots and A. C. impedance were performed which suggest that the plant extracts act as mixed type inhibitors and protect the metal in aggressive medium. The inhibition of the corrosion of mild steel in hydrochloric acid solution by Aquilaria crassna leaves extracts was also carried out. The authors studied the surface coverage and inhibition efficiency by mass loss and electrochemical methods. The protective film formed on the metal surface was analyzed by SEM techniques. The effect of the extract of rice husk ash on the corrosion of mild steel in HCl and H2SO4 solutions was carried by using weight loss, atomic adsorption spectroscopy (AAS) and FTIR spectroscopy. They reported that inhibition efficiency of extract of rice husk ash in HCl is greater than H2SO4. The inhibition efficiency increases with increase in concentration of inhibitor. The FTIR spectrum showed that the inhibition is due to the formation of a film on the metal/solution interface through adsorption of extract molecules. The surface morphology was determined by scanning electron microscope technique. Gravimetric and potentiodynamic polarization and impedance spectroscopy (EIS) techniques were used to characterize the mechanism of corrosion inhibition of mild steel in HCl using Capparis spinosa extracts. Inhibition efficiency, increased with extra concentration, but decreased with temperature. Polarization curves clearly revealed that extract act as a cathodic inhibitor. The adsorption of inhibitor molecule on carbon steel followed the Langmuir adsorption isotherm. The inhibition effect of Black tea extract on the corrosion of mild steel in H3PO4 solution was analyzed by mass loss method. Surface analysis was examined by Scanning electron microscope, FTIR Spectroscopy. The negative values of Gibbs free energy strongly support the physical adsorption of inhibitor molecules on the metal surface. The corrosion inhibitor effect of Rosmarinus officinalis extract on corrosion of mild steel in 0.5M and 1M H2SO4 was studied using potentiodynamic polarization test, weight loss and optical microscopy techniques. The results revealed that adsorption of plant extract on mild steel surface was found to be a spontaneous process which obeyed Langmuir adsorption isotherm and the inhibitor compound have been found to
obey physical adsorption mechanism. Surface morphology was observed by Optical microscopy micrographs.

2.2 Essential oils as corrosion inhibitor
The inhibition efficiency of jojoba oil, on the corrosion of iron in acidic solution was studied by using weight loss measurement and electrochemical polarisation methods. Studies revealed that jojoba oil was an excellent corrosion inhibitor and showed 100 per cent inhibition at 0.515 g/l concentrations of jojoba oil, indicating that jojoba oil was inhibited. The adsorption on the metal of jojoba oil, obeyed the Frumkin isotherm.39

*Mentha pulegium* (Pennyroyal Mint) oil was tested as a corrosion inhibitor of steel in 1M HCl solution using weight loss measurements, electrochemical polarisation and EIS methods. Results showed that the inhibition efficiency was found to increase with oil content to attain 80% at 2.76 g/L and oil acts as a cathodic inhibitor40. The corrosion inhibiting nature of Artemisia oil as steel in 2M H₃PO₄ was reported using gravimetric, electrochemical polarisation and electron impedance spectroscopy methods41. The oil reduces the corrosion rate with increasing the concentration and maximum inhibition efficiency attains 79% at 6 g/l. at the different temperature. They found that the inhibition efficiency of the oil decreases with the rise of temperature. The adsorption isotherm of natural product on the steel has also been determined.

The inhibiting effect of Artemisia herb Alba oil for steel in 0.5 M H₂SO₄ acid medium was studied using gravimetric and electrochemical techniques. It was found that the corrosion inhibition efficiency increased with the concentration and attains the maximum (74%) at 1g/L. The results showed that this natural oil reduced the corrosion rate by the cathodic action42.

Essential oil of fennel (*Foeniculum vulgare*) as a corrosion inhibitor was tested on carbon steel in 1M HCl using weight loss measurements, Tafel polarization and electrochemical impedance spectroscopy (EIS) methods43. The results showed that the molecules are present in oil adsorbed on the carbon steel surface. The polarization curve revealed that the oil acts as a mixed-type inhibitor. The corrosion rate estimated by weight loss measurements confirmed the above results. The inhibition efficiency attains a maximum of 76% at 3mL/L, but decreases with the rise of temperature.
The efficacy of essential oil of *Warionia saharea* as a corrosion inhibitor for mild steel in H$_2$SO$_4$ acidic solution was studied by using mass loss measurements$^{44}$. It was suggested that the corrosion inhibition may be due to the adsorption of inhibitor molecules on the metal surface and inhibitor efficiency increase with increasing concentration of the oil to attain 74% at 3g/L. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface and obeyed the Langmuir adsorption isotherm. The results obtained showed that the *Warionia saharea* essential oil act as an effective inhibitor for the corrosion of mild steel in sulfuric acid media.

The inhibiting action of *Pulicaria mauritanica* oil on the corrosion of mild steel in sulphuric acid solution was also evaluated$^{45}$. The qualitative and quantitative analysis was performed by GC/MS and NMR Spectroscopy. The inhibition efficiency was calculated using weight loss measurements, electrochemical polarization and EIS technique. It was found that, the inhibition efficiency increases with oil concentration to attain 91.5% at 2g/L. Polarisation curves revealed that this oil act as a mixed type inhibitor. The oil adsorbs spontaneously on the metal surface and followed the Langmuir adsorption isotherm.

An essential oil from *Eucalyptus globulus* (Myrtaceae) was hydrodistilled and tested as a corrosion inhibitor on C38 steel in sulphuric acid medium$^{46}$. The mass loss measurements, electrochemical impedance spectroscopy, potentiodynamic polarization methods were used at different temperature. The results obtained show that this natural oil reduced the corrosion rate and inhibition efficiency attained a maximum of (76%) at 298K. Values of inhibition efficiency calculated by different methods are in good agreement. The essential oil behaves as a mixed-type inhibitor in sulfuric acid. The adsorption of the essential oil of *Eucalyptus globulus* on the C38 steel surface followed the Langmuir adsorption isotherm. The activation energy values showed that the essential oil was physically adsorbed on the metal surface.

The influence of *Asteriscus graveolens* leaves oil on mild steel corrosion in 0.5M H$_2$SO$_4$ was studied using Mass loss and electrochemical polarization technique. The oil was obtained by hydrodistillation and analyzed by GC/MS and $^{13}$C NMR technique. It was found that the inhibition efficiency increase with increasing concentration of the essential oil to attain 82.89% at 3g/L. Polarisation curves showed
that the oil acts as a mixed type inhibitor. The associated activation energy has been determined. The inhibitor spontaneously adsorbed on metal surfaces via physical adsorption process and obeys the Langmuir adsorption isotherm\textsuperscript{47}.

The corrosion inhibition efficiency of carob seed oil as inhibitor on C38 steel in hydrochloric acid was reported and the results showed that the inhibition efficiency depends on the concentration of inhibitor attains approximately 86.7\% at 0.5 g/L. Polarization curves reveal that the oil is a mixed-type inhibitor\textsuperscript{48}.

The corrosion inhibition of mild steel in 2M Sulphuric acid containing \textit{Glycine max} oil was studied by using weight loss measurement at 293K and 303K temperature. The inhibition efficiency (\%) IE of oil depends on its concentration and attains approximately 47.98\% for 20g/L at 298K and 40.21\% for 20g/L at 303K. The results showed that increase in temperature decreases inhibition efficiency (\%) IE and degree of surface coverage (\theta). An adsorbed film of inhibitor is formed on the metal surface which protects the metal against corrosion. The adsorption of inhibitor on the metal surface was found to obey Langmuir’s adsorption isotherm and negative value of free energy indicated that the adsorption of inhibitor molecule was typical of physical adsorption\textsuperscript{49}.

The effect of Argan oil on the corrosion of C38 steel in 1M HC1 was studied using weight loss, electrochemical polarization and EIS techniques\textsuperscript{50}. It was found that the inhibition efficiency increased with increase in inhibitor concentration, but decreased with an increase in temperature. The inhibition was attributed to the adsorption of the oil on the surface of mild steel which followed the Langmuir isotherm model. The values of activation energy showed the inhibitor was physically adsorbed on the steel surface.

Corrosion inhibition efficiency of garlic essential oil was also investigated\textsuperscript{51}. The oil was examined the oil as an effective inhibitor for carbon steel in acidic medium. Weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization methods were used for determination of corrosion rate. The oil formed a protective layer on the metal surface and retarded the corrosion. The result showed that the corrosion rate decreases as the concentration of the inhibitor increases. Polarization curves indicated that oil behaves as a mixed-type inhibitor.
The influence of Pistachio essential oils on the corrosion of carbon steel in 0.5M H₂SO₄ was studied using mass loss, EIS spectroscopy and potentiodynamic polarization technique. It was found that the corrosion inhibition efficiency increased with the concentration of the Pistachio essential oil. The studies of the Potentiodynamic polarization curve suggested that this inhibitor is a mixed type inhibitor. The adsorption of oil on the carbon steel surface obeyed the Langmuir adsorption isotherm.

Natural oil extracted from *Athenanta sicula* was evaluated as a corrosion inhibitor of mild steel in molar hydrochloric acid. The corrosion rate and inhibition efficiency were determined by using Gravimetric, Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization curve methods. The oil was a mixed type inhibitor and retards the corrosion rate of mild steel in aggressive medium.

### 2.3 Compounds isolated from plants as corrosion inhibitor

The inhibition efficiencies of two Amazonian trees (*Guatteria ouregou* and *Simira tinctoria*) alkaloid extracts on the corrosion of low carbon steel in 0.1M HCl solution was investigated by using electrochemical techniques. The results obtained show that both extracts provide adequate inhibition of corrosion of low carbon steel in acidic media. Authors found that harmane was an active component of *S. tinctoria* extract and the anti corrosion activity in low carbon steel is in aggressive environment.

Lawsone, an active principle was isolated from Henna (*Lawsonia inermis*) plant and was used as corrosion inhibitor. The inhibition efficiency of active molecule was studied in 1M HCl solution on mild steel surface by weight loss method. Results revealed that the corrosion rate decreased with increase in the concentration of Lawsone. Adsorption of the inhibitor obeyed Langmuir adsorption isotherm.

Piperanline was isolated from black pepper (BP) extract and studied as corrosion inhibitor. The inhibition efficiency of C38 steel in 1 M HCl solution was studied by weight loss method at temperature range of 298K to 353K. NMR technique was used for identification of Piperanline. Results inferred that 97.5% corrosion inhibition was observed at 10⁻³M inhibitor concentration. Piperanline adsorbs on the metal surface according to Langmuir isotherm.

Inhibition of Q235A steel corrosion was analysed using *Ginkgo biloba* leaves extract by the mass loss method and potentiodynamic polarization techniques. The inhibition
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efficiency was found to vary with inhibitor concentration. Potentiodynamic polarisation curves showed that extract were mixed type inhibitors. The antibacterial activity of the extracts was also investigated.

Ervatinine, isolated from the leaves of *Ervatamia coronaria* plant was tested as corrosion inhibitor on the mild steel in acidic medium. The corrosion inhibition efficiency was examined by gravimetric, electrochemical impedance, Tafel polarization, SEM, XRD techniques. Results showed that the Ervatinine alkaloid present in the plant extract acts as a good corrosion inhibitor. The adsorption of inhibitor on metal surface followed Langmuir adsorption isotherm and ervatinine physically adsorb on it. The surface morphological examination via SEM techniques indicated that the Ervatinine retard the corrosion on the specimen surfaces by forming a protective layer. The results suggest that ervatinine act as a good corrosion inhibitor.

The corrosion inhibition potential of vasicine molecule isolated from *Adhatoda vasica* plant extract was studied on mild steel in acidic medium. The characterization of vasicine compound was done by of $^{13}$C NMR and LC/MS. The corrosion rate of metal was carried out by the mass loss method, electrochemical impedance method and polarisation technique. Results showed that the inhibition efficiency of vasicine in acidic medium increases with increase in inhibitor concentration and decreases with rise in temperature. Polarization measurement showed that vasicine acts as a mixed type inhibitor. The AC impedance study revealed that the charge-transfer process controls the corrosion of mild steel. Through SEM analysis it was examined that a protective film was formed over the surface by adsorption of compound and followed Langmuir adsorption isotherm.

2.4 Corrosion inhibition studies by quantum chemical calculations

The effect of *Spondias mombin* L. extract was studied on aluminium corrosion in 0.5 M $\text{H}_2\text{SO}_4$ solution. The standard weight loss method was used for the determination of inhibition efficiency of inhibitor at 30$^\circ$-60$^\circ$C temperature. It was found that the corrosion rate decreases with increase in the concentration of inhibitor. Quantum chemical descriptors such as the total energy, energy of highest occupied molecular orbital ($E_{\text{HOMO}}$), energy of lowest unoccupied molecular orbital ($E_{\text{LUMO}}$), energy gap ($\Delta E$) and the dipole moment were obtained by (B3LYP/6-31G (d) level of theory
using Spartan'06 V112 program package. Quantum chemical descriptor values revealed that theoretically obtained results were in accordance with the experimental data reported.

The corrosion inhibition potential of the seed extract of Jeera (*Cuminum cyminum*) was investigated on mild steel in acidic solution by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy\textsuperscript{61}. Polarization results showed that the extract acted as a mixed type inhibitor and obeyed the Langmuir adsorption isotherm. Molecular modeling calculations were carried out by means of the Gaussian 03 for windows Package. The low value of energy difference showed high efficiency of the extract.

The corrosion inhibition of mild steel in Hydrochloric acid solution was investigated by extracts of Punarnava (*Boerhavia diffusa*) using different techniques\textsuperscript{62}. The quantum chemical calculations were performed by means of the DFT electronic structure program, Gaussian 03W package for investigating the metal-inhibitor interaction. The values obtained by DFT calculations were supporting the experimental results.

The inhibition and the adsorption potential of the aqueous extract of Coffee senna on the corrosion of mild steel in acidic solutions was studied by mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements\textsuperscript{63}. The results reveal that the extract adsorb on the metal surface and retard corrosion rate. The adsorption behavior of selected organic constituents of the extract on the metal surface was evaluated at the molecular level, in the model of the density functional theory. The simulations were performed by means of the DFT electronic structure program DMol\textsuperscript{3} available in Material Studio 4.0. The quantum chemical parameters of specific components of the extract confirmed their inhibition potential.

The inhibition and adsorption potentials of active constituents present in different plant extract was studied by quantum chemical approach. The values of descriptors such as Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), Dipole Moment, Mulliken charges on heteroatoms and Molecular volume were calculated by Density functional theory (DFT) formalism with electron basis set 6-31G (*,\ast). The observations confirmed strong interaction of
extract molecules with the metal surface and thereby forming protective adsorption layer in acid solution\textsuperscript{64}.

The GC/MS analysis was performed for identification of active phytochemical constituents present in the ethanolic extracts of the fruits of \textit{Cucumis trigonus} Roxb. and \textit{Cucumis sativus} Linn\textsuperscript{65}. The quantum chemical parameters such as geometry optimization, energy of HOMO, LUMO, total energy, electron affinity, ionization potential, electrophilicity, and dipole moment of these molecules were recorded by Density Functional Theory methods using B3LYP/6-311++G(d,p) basic set using Gaussian 09W program package. The results proved that the DFT calculation is a valuable tool for predicting biological activity of phytochemical constituents. The HOMO-LUMO energy gap showed the stability index of compounds.

The adsorption and corrosion inhibition of \textit{Tagetes erecta} (Marigold flower) extract in sulphuric acid medium on mild steel was investigated by gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopic measurements and quantum chemical calculations which provided a reasonable theoretical explanation for the adsorption and the inhibition behaviour of \textit{Tagetes erecta} mild steel. Tafel polarization studies reveal that the extract acts as an efficient mixed inhibitor, which adsorb on the metal surface followed the Langmuir adsorption isotherm. The surface morphology was studied by SEM and AFM technique. The quantum chemical parameters were calculated by Gaussian 03 program for Lutien molecule, a major component present in \textit{Tagetes erecta} extract. The density distribution of HOMO/LUMO indicated strong adsorption of components and high inhibition efficiency\textsuperscript{66}.

The corrosion inhibition effect of red apple (\textit{Malus domestica}) fruit extract for mild steel in hydrochloric acid was investigated by weight loss and electrochemical methods\textsuperscript{67}. Quantum chemical descriptors, molecular spatial structure, dipole moment, HOMO-LUMO energy, energy difference and atomic charges were calculated by DFT method. The HOMO-LUMO energy gap was used to determine the electron donating ability of the major extract components. The highest values of the HOMO density were found in the vicinity of the functional groups, indicating them as most probable adsorption centers.
The adsorption and corrosion inhibition of *Nicotiana tabacum* leaves extract on mild steel in sulphuric acid was investigated by using weight loss and quantum chemical calculations which provided a reasonable theoretical explanation for the adsorption and the inhibition behaviour of plant extracts on mild steel. The Quantum chemical calculations were performed by means of Gaussian 03 program DFT-B3LYP level using 6-31G (d) basis set to optimized structure. The quantum chemical parameters, total energy, $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, energy gap ($\Delta E$), dipole moment ($\mu$) and Mulliken charges were studied. The values of Mulliken charge distributions showed that the nitrogen atoms have higher charge densities, implying that the most probable reactive site for the adsorption on mild steel is located on the nitrogen atoms. The gravimetric experimental results were supported by the theoretical data.

Thorough analysis of literature survey reveals that *Mentha spicata* extract have not yet been reported as corrosion inhibitors for mild steel in acid media. To explore this possibility, an attempt has been made to ascertain its corrosion inhibition properties on mild steel in acidic solution.
REFERENCES


