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Review on Corrosion inhibition of Steel in Acidic media

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Abstract: This review deals with the corrosion inhibition of steel with the emphasis on acidic media. Corrosion is process of metal deterioration when it comes in contact with the environment. One of the most practical methods to prevent corrosion is the use of plant extracts. The use of plant extracts has both economic and environmental benefits since plant extracts are low cost and biodegradable .This review provides us information about how organic molecules get adsorbed on the metal surface and form a barrier film over its surface.
Keywords: Corrosion inhibition of Steel in Acidic media.

Introduction

The steel is widely used in many applications such as desalination plants, construction materials, pharmaceutical industry, and thermal power plant, due to their stability, high strength, workability and weld ability. Ouadi[1] studied Acid solutions are widely used in industry: some of the important fields of application are acid pickling of steel, chemical cleaning and processing, ore production and oil well acidizing. Cang[2] studied acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Eddy[3] studied the use of organic inhibitors provide the best option for corrosion inhibition. The most efficient corrosion inhibitors are organic compounds containing electronegative functional groups and p electrons in their triple or conjugated double bonds. The initial mechanism in any corrosion inhibition process is the adsorption of the inhibitor on the metal surface. The inhibition of the corrosion of metals can also be viewed as a process that involves the formation of chelate on the metal surface, which involves the transfer of electrons from the organic compounds to the surface of the metal and the formation of a coordinate covalent bond. In this case, the metal acts as an electrophile while the nucleophilic centre is in the inhibitor.

An effort has been made to combine different works of authors and summarizing the literature dealing particularly with the corrosion inhibition of mildsteel, carbon steel and steel using plant extracts as corrosion inhibitors. Plant extracts used are Rhizophora mangle, Aloes, Salvia officinalis, Piper guinensis, launa nudicalis, ginger Hibiscus, Sabdariffa, juniper oxidalis, kalmegh, mentha puliguim, musa sepentum,, litchi lupine extract ,nyctanthis arbortritis,opuntia ficus indica ,Nypa fruticans, black pepper, Phyllanthus amarus ,piper guinesis ,punarvana Vernonia Amygdalina, vitex doniana and xylopia ferroginea.

Effect of concentration of Plant extracts on corrosion inhibition.

Singh[6] studied the effect of extract of Punarnava (*Boerhavia diffusa*) on corrosion of mild steel by using gravimetric, potentiodynamic polarization, and electrochemical impedance spectroscopy. The results revealed that extract acted as a mixed type of inhibitor as the maximum displacement of $-E$corr value is 46 mV as found from tafel polarization curves. The inhibition efficiency increases up to 96% at 300 ppm and decreases with increase in the temperature. The charge transfer resistance (*R*ct) value of inhibited system increased from 68 Ω cm^2 to 426 Ω cm^2 and double layer capacitance (*C*dl) value decreased from 37 Mf cm^{-2} to 17 μF cm^{-2} with increasing inhibitor concentration. Langmuir adsorption isotherm was followed by the inhibitor molecules on steel surface. The low value of energy gap (ΔE) further provided support for high efficiency of the extract.

Corrosion rate and Inhibition efficiency values for the corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of Punarnava (*Boerhavia diffusa*) extract from weight loss measurements at 308 K was determined. The efficiency found to vary from 73 % to 96 % for ro to 300 ppm of inhibitor concentration.

Oguzi[7]studied Corrosion inhibition of mild steel in 2M HCl and 1M H_2SO_4 by leaf extracts of *Occimum viridis* (OV) using the gasometric technique at temperatures of 30 and 60°C. The results indicated that inhibition efficiency varied directly with concentration and that the extracts inhibit the corrosion process in both acid media. Synergistic effects increased the inhibition efficiency in the presence of halide additives namely KCl, KBr,KI. Temperature studies revealed a decrease in efficiency with rise in temperature and corrosion activation energies increased in the presence of the extract, probably implying that physical adsorption of cationic species may be responsible for the observed inhibition behaviour. Comparative analysis of the inhibitor adsorption behaviour in 2M HCl and 1M H_2SO_4 as well as the effect halide additives suggest that cationic species may not be the only constituents responsible for the inhibiting action of the extract.

The plots between variations of inhibition efficiency with OV extract concentration showed that the extract actually inhibits the acid corrosion of mild steel and that inhibition efficiency increased with an increase in the extract concentration at temperatures 30°C and 60°C.

Hassan[8] studied the inhibition of corrosion of mild steel using Paniala *(Flacourtia jangomas)* extract in 1M HCl and 0.5 H_2SO_4 solutions by weight loss method at 30°C. The result showed that corrosion rate was significantly decreased in presence of the extract and inhibition efficiency increased with increasing the concentration of extract. In case of HCl maximum inhibition efficiency (98%) was noticed at 5% v/v inhibitor concentration and no considerable change in inhibition efficiency was observed after this concentration and in 0.5M H_2SO_4, it was found 95% efficiency at the same concentration of inhibitor. At lower concentration of inhibitor, better inhibition was observed in HCl medium as compared to H_2SO_4. The decreased corrosion rate was due to adsorption of plant extract which was discussed on the basis of Langmuir and Freundlich adsorption isotherm.

The decreasing corrosion rate and increasing inhibition efficiency was attributed to the fact that the adsorption of inhibitor on the metal surface. Due to adsorption the corrosion sites of metal surface get blocked and adsorbed film of inhibitor acts as physical barrier between metal surface and corrosion medium.

Ebenso[9] studied the corrosion inhibition of mild steel by ethanol extract of *Piper guinensis* (EEPG) by using gravimetric, gasometric and thermometric methods. The results of the study reveals that the different concentrations of ethanol extract of *Piper guinensis* (EEPG) inhibit mild steel corrosion.Inhibition efficiency of the extract are found to vary with concentration, temperature and period of immersion. Values of activation energy of the inhibited corrosion reaction of mild steel are greater than the value obtained for the blank. Thermodynamic consideration reveals that adsorption of *P. guinensis* extract (EEPG) on mild steel surface is spontaneous and occurs according to Langmuir adsorption isotherm.

Quraishi[5] studied the *Green Approach to Corrosion Inhibition by Black Pepper Extract in Hydrochloric acid solution. The results showed that the variation of inhibition efficiency slightly decreases (98 % - 94 %) with increase in acid concentration from 1 M to 2 M. The effect of immersion time on inhibition efficiency is shown. It has been observed that increase in immersion time from 3-9 h did not cause any significant change in inhibition efficiency, suggesting that inhibitor is effective in acid solution over this immersion range.

Prabhu[12] studied Carmine and Fast Green as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid solution. The Nyquist plots show that, the diameter of the capacitive loop and consequently the value of the charge transfer resistance, Rp increased with the concentration of inhibitors, which is an indication of the inhibitive action. The results show that RP values increased with an increase in inhibitor concentration.

Effect of temperature on rate of corrosion inhibition

Singh[6] investigated the effect of temperature on corrosion inhibition rate by studying punarnava extract as corrosion inhibitor of mild steel in acidic medium and it was seen that the inhibition efficiency of Punarnava (*Boerhavia diffusa*) extract decreases with increasing temperature.

Benabdellah[10] studied the corrosion inhibition on steel by using Artemisia oil in 2M H_3PO_4 medium using weight loss measurements, electrochemical polarization and EIS methods. The inhibition efficiency was found to increase with oil content to attain 79% at 6 g/l. Results showed that Artemisia acts as a cathodic inhibitor. The inhibition efficiency was found to be decreasing with increase in temperature. The adsorption isotherm of natural product on the steel has been determined.

The effect of temperature on the corrosion rate of steel in 2 M H_3PO_4 containing inhibitor at a maximal concentration (6 g/l) has been studied in the temperature range 298–348 K using weight loss measurements. The result shows that the increase in corrosion rate is more pronounced with the rise of temperature for the uninhibited acid solution. The presence of inhibitor leads to decrease of the corrosion rate. E% depends upon the temperature and increases with temperature.

Emeka[7] studied the nature of inhibitor adsorption with the effect of temperature (30 and 60 ◦C) on the corrosion behavior of mild steel in the presence of *O. viridis* extract. The results suggest that the extract was adsorbed on the mild steel surface at all temperatures studied. The data indicated that the rates of steel corrosion in absence and presence of the extract increased with rise in temperature in both acid media.

Ouadi[1] studied the corrosion inhibition of mildsteel by Salvia Officinalis in 1M HCl using weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS). Tafel polarization study revealed that extract of S. officinalis acts as a mixed type inhibitor. Inhibition was found to increase with increasing concentration of the essential oil and extract of S. Officinalis. Values of inhibition efficiency calculated from weight loss, Tafel polarization curves, and EIS are in good agreement. The effect of temperature on the corrosion behavior of mild steel in 1M HCl with addition of essential oil and extract was also studied and thermodynamic parameters were determined and discussed.

For most chemical reactions, the reaction rate increases with increasing temperature. Temperature affects the corrosion rate of metals in electrolytes primary through its effect on factors which control the diffusion rate of oxygen. The corrosion of iron and steel is an example of this because temperature affects the corrosion rate by virtue of its effect on the oxygen solubility and oxygen diffusion coefficient. As temperature increases the diffusion coefficient of oxygen also increases which tends to increase the corrosion rate. However as temperature is increased oxygen solubility in aqueous solutions decreases until at the boiling point all oxygen is removed; this factor tends to decrease the corrosion rate. The net affect of mild steel, is that the corrosion rate approximately doubles for a temperature rise of 30°C up to a maximum temperature at about 80°C, the rate then falls off in an open system because the decrease in oxygen solubility becomes the most important factor. In a closed system, where oxygen cannot escape the corrosion rate continues to increase indefinitely with temperature until all the oxygen is consumed.

Sorkhabi[13] studied Corrosion inhibition of mild steel in hydrochloric acid by betanin as a green inhibitor .The results indicate that the corrosion current density increases more rapidly with temperature in the absence of the inhibitor. In the presence of betanin, surface coverage θ, defined by $\eta p/100$, decreases slightly with increasing temperature, which could be caused by desorption of the inhibitor from the steel surface. The slight decrease of θ suggests that the inhibition efficiency of betanin is independent of temperature. Therefore, betanin acts as an efficient inhibitor in the range of temperatures.

Raja[14] studied Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel. Results suggested that the increase of temperature increases the IE also. This suggests that phytoconstituents of the black pepper adsorb strongly on the mild steel surface to form a protective layer and shield the metal from corrosion.

Adsorption studies

Singh[6] investigated that efficiency of Punarnava (*Boerhavia diffusa*) extract molecules as a successful corrosion inhibitor mainly depends on their adsorption ability on the metal surface. To emphasize the nature of adsorption, the adsorption of an organic adsorbate at metal/solution interface can be presented as a substitution adsorption process between the organic molecules in aqueous solution, and the water molecules on metallic surface.

Attempts were made to fit surface coverage values determined from weight loss measurements into different adsorption isotherm models. The linear regression coefficient values (R2) determined from the plotted curve was found to be in the range of 0.9993 for Langmuir.

Langmuir adsorption isotherm can be expressed by following equation:

$$\frac{C_{(\mathrm{inh})}}{\theta} = \frac{1}{K_{(\mathrm{ads})}} + C_{(\mathrm{inh})}$$

Where, Cinh is inhibitor concentration and Kads is equilibrium constant for adsorption-desorption process.

Hassan[7] studied the corrosion inhibition of mildsteel by Flacourtia Jagonmas in acidic medium. The surface coverage (θ) values for different concentrations of the inhibitor in 1M HCl and 0.5M H_2SO_4 have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of C/ θ) against C showed a straight line indicating that adsorption follows the Langmuir adsorption isotherm and a straight line was also found in the plot between Log θ & log C, this showed that the adsorption obeys a Freundlich adsorption isotherm.

Ebenso[9] used *Piper guinensis* as corrosion inhibitor for steel in acidic medium. Results indicated that calculated values of Gads were negative and ranged from -5.8193 to -14.5648 KJ/mol indicating that the adsorption of the extract is spontaneous and that the mechanism of adsorption is physical adsorption. The degree of surface coverage was evaluated from the weight loss measurements.

In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristic of this inhibitor. Assumptions of Langmuir adsorption isotherm is expressed in equation below:

$$C/\theta = 1/k + C$$

Hui cang[2] studied the corrosion inhibition of mild steel in 1.0 M HCl by the *Aloes* leaves extract using weight loss methods, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results show that the inhibition efficiency increases with the increase of the extract concentration. The effect of temperature on the corrosion behavior of mild steel in 1M HCl with addition of the extract was also studied. The adsorption of the extract molecules on the steel surface obeys Langmuir adsorption isotherm and occurs spontaneously.

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds, and the adsorption depends on the compounds' chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the water molecules could also adsorb on metal/solution interface. Thus, the so-called adsorption can be regarded as a quasi-substitution process between the plant extract in the aqueous phase [PE(sol)] and water molecules at the electrode surface [H_2O(ads)].

According to Langmuir adsorption isotherm, surface coverage is related to equilibrium adsorption constant (Kads) and C(inh) by the equation

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

These results show that all the linear correlation coefficients (*R*2) are almost equal to 1 and the slopes are close to 1, which confirmed that the adsorption of the plant extract on mild steel surface good obeyed Langmuir adsorption isotherm.

Quraishi[5] studied the corrosion inhibition of mild steel in hydrochloric solution by Black pepper extract (*Piper nigrum* fem. *Piperaceae*). The techniques employed for study were mass loss measurements, potentiodynamic polarisation, linear polarization resistance and electrochemical impedance spectroscopy (EIS). The results obtained revealed that Black pepper extract was a good corrosion inhibitor for mild steel in hydrochloric acid medium and maximum inhibition efficiency (98%) was found at 120 ppm at 35 ºC. black pepper acted as a mixed type of inhibitor as shown by Potentiodynamic polarization. EIS showed that the charge transfer controls the corrosion process in inhibited solutions. Adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm. The value of the free energy of adsorption, that the adsorption of inhibitor molecules was typical of chemisorption.

The degree of surface coverage for 120 ppm of extract in 1M HCl at 35-55°C for 3 hour immersion time were evaluated from mass loss values. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plot log versus log C as shown in Fig. This indicates that the extract as inhibitor found to obey Langmuir adsorption isotherm.

Oguzie[7]studied the inhibiting action of the calyx extract of *Hibiscus sabdariffa* on mild steel corrosion in 2 M HCl and 1 M H2SO4 solutions using a gasometric technique. The results demonstrate that *Hibiscus sabdariffa* extract suppressed the corrosion reaction in both acid media and inhibition efficiency increased with extract concentration with slightly higher values obtained in 1 M H_2SO_4. Synergistic effects increased the efficiency of the extract in the presence of halide additives. Adsorption characteristics of the extract were approximated by the Langmuir isotherm. Adsorption of the extract is further substantiated by the fit of the experimental data to the Langmuir adsorption isotherms

Rahim [15]studied Aquilaria Crassna Leaves Extracts as a Green Corrosion Inhibitor for Mild Steel in 1 M HCl Medium **.**The mechanism of the adsorption is further understood by fitting the weight loss method, EIS analysis and potentiodynamic polarisation measurements into adsorption isotherm models. The fit of the adsorption isotherm models are determined by the closeness of linear correlation coefficient (R2) value to unity. The best fitted models with R2 closest to unity were then picked to describe the mechanism of adsorption.

Yan li[16] studied Berberine as a natural source inhibitor for mild steel in 1 M H2SO4. The surface coverage degree u were calculated using the data obtained from potentiodynamic and electrochemical impendence measurement. The result showed both potentiodynamic polarization and electrochemical impendence data giving similar result and indicating a good reproducibility. Then the u values from electrochemical impedance and inhibitor concentration C were fitted with some common adsorption isotherm and a good linear chemical adsorption of the berberine and it was spontaneous in the thermodynamics.

In discussing corrosion inhibition by surface-active organic compounds various factors are taken into consideration including the number and types of adsorbing groups and their electron structure. The calyx extract under investigation contains different organic substances with proven corrosion inhibiting capabilities such as ascorbic acid, amino acids, flavonoids, pigments and carotene. This makes it difficult to assign the observed inhibiting effect to a particular constituent. The net adsorption of the organic matter on the corroding steel surface creates a barrier that isolates the metal from the corrodent. Inhibition efficiency increases with an increase in the metal surface fraction occupied by the organic matter

Conclusion:

The review research involving the summary of various articles on the green corrosion inhibitors has been done. In this review an attempt has been made to study the effect of green corrosion inhibitors on the rate of corrosion. Other factors such as effect of concentration of inhibitor the rate of corrosion, effect of temperature, and the adsorption mechanism of some plant inhibitors has been discussed.

It has been seen that the corrosion inhibition generally increases with increase in the concentration of inhibitor. The temperature has been shown to effect the corrosion inhibition directly in some cases while in others it affects inversely. The adsorption mechanism has been seen to generally follow Langmuir adsorption while in some cases Freundlich adsorption is also seen.

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