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Corrosion inhibitory effect of neem leaf extract on mild steel in alkaline solution containing chloride ions

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Inhibitory effect of the neem extract (*Azadirachta indica*) for mild steel in 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution was studied by performing the gravimetric studies and Tafel study. The studies revealed that the corrosion inhibition efficiency rises with extract concentration. Inhibition efficiency increases up to 600 ppm then it stabilizes. Inhibition efficiency was found to be 86% at 600 ppm and increases with elevation in temperature. The decrease in activation energy (E_a) and enthalpy (ΔH) shows that corrosion inhibition is chemisorption and exothermic in nature respectively. Electrochemical experiments were performed with and without inhibitor and results were discussed. Result showed that neem leaf extract (*Azadirachta indica*) is a promising candidate to minimize the corrosion in alkaline medium, as it shows good inhibition efficiency.

Keywords: Mild steel, neem extract, alkaline medium, potentiodynamic polarization.

Introduction

Mild steel metal is commonly used in various industries[1]. However, these metals are exposed to aggressive environment namely alkaline, acidic medium and salt solution through many engineering developments[2].

Corrosion is a very damaging process, as it affects the act of metallic material which used in industries. Corrosion is a natural phenomenon and is defined as detoriation of metal due to adverse environmental condition. Consequences of corrosion are losses in the properties of metal like ductility, malleability and weakening of metal. It has been evidenced that, in alkaline medium, the layer forming on metal acts as a double layer model. In alkaline solution, formation of strong passivation appears on surface of metal. However, in the presence of Cl^- ions, the passivation is weakened, which leads to corrosion at higher rate[3].

Though different methods to protect metal from aggressive environment, namely corrosion preventing coating, cathodic and anodic prevention technique are available, green corrosion inhibitors is inexpensive and environmentally-benign[4].

When metal gets exposed to the aggressive environment, the extent of corrosion depends on operating condition (T, pH), time of exposure of metal in that environment, with and without inhibitor, and type of aggressive environment[5].

Green corrosion inhibitors are derived from plants and used in small quantity to combat the corrosion[6]. Inhibitors should have the ability to reduce the corrosion rate and metal protected from corrosive environment. Small quantities of inhibitor should result in higher corrosion inhibition efficiency[7]. Neem leaf extract was proposed green corrosion inhibitor for corrosion inhibition of mild steel in acidic environment (HCl, H_2SO_4 and HNO_3) due to its antioxidant property[8]. Though there are many literatures available for the acidic medium, very few works focused on the alkaline medium.

In this work, the chemical behaviour of mild steel with 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution at different temperatures and concentration with and without inhibitor (neem leaf extract) is reported with the data obtained from gravimetric method, potentiodynamic polarization technique.

Experimental

Preparation of specimen:

Mild steel specimen with 22.5 mm diameter and 10 mm thickness was used in this study. 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution was used as an alkaline medium containing chloride ion. The composition of the specimen as determined by Spectro analysis is C-0.253% Si-0.0510%, Mn-0.455%, P-0.0180%, S-0.0160%,Cr-0.0220%, Cu-0.0450% and remaining as Fe. Coupon was polished with various sand papers, subsequently washed using acetone, H_2O and then dried by passing hot air to remove moisture. The coupons were stored in a desiccator. The experiment was performed by varying different parameters such as concentration of alkaline medium and temperature. The duration of immersion of coupon in the solution was chosen as 10 min.

Plant extract preparation:

Firstly, rinse neem leaves with water and then dry it in air for two days. After drying, the neem leaves were grinded in a mixer grinder. Then take 100 g of neem leaves powder dipped into 500 ml of methanol for 24 h. The mixture was filtrated using filter paper. Reflux the filtrate at 55°C for 5 h. Liquid was concentrated in a vacuum evaporator set up and the resulting thick liquor (extract) was used in this work.

Gravimetric study:

The gravimetric study (weight loss study) was performed using various inhibitor concentration and at different range of temperatures. The cleaned coupons were dried and weighed before its use. The experiments were performed by immersing the coupon in 200 ml of alkaline medium containing with and without inhibitor for 10 min duration. Weigh coupon earlier and later the immersion was noted. Corrosion rate was intended using the difference in the weight of the sample pre- and post-immersion, density of the sample along with area and immersion time[9].

Potentiodynamic polarization measurements:

Electrochemical experiments were executed by using Parstat 2263 Potentiostat (Princeton Applied Research, USA). In this experiment, mild steel, Ag/AgCl and platinum wire were used as working electrode, reference electrode and counter electrode respectively. By using various grades of alumina powder mild steel electrode was polished, to make the surface free from scratches, wash through acetone and then water.

Potentiodynamic polarization study was done in the range from –250 mV to +250 mV over open circuit potential (OCP), with rate of scanning 1 mV/s was taken into consideration. I_{corr} and E_{corr} values were attained by extrapolation of Tafel plots.

Results and discussion

Gravimetric study:

Fig. 1 shows corrosion rate of mild steel immersed inside solution containing various concentration of $Ca(OH)_2$ with 0.5 wt % NaCl. Result showed that the rate of corrosion ascends with respect to increase in concentration of $Ca(OH)_2$.

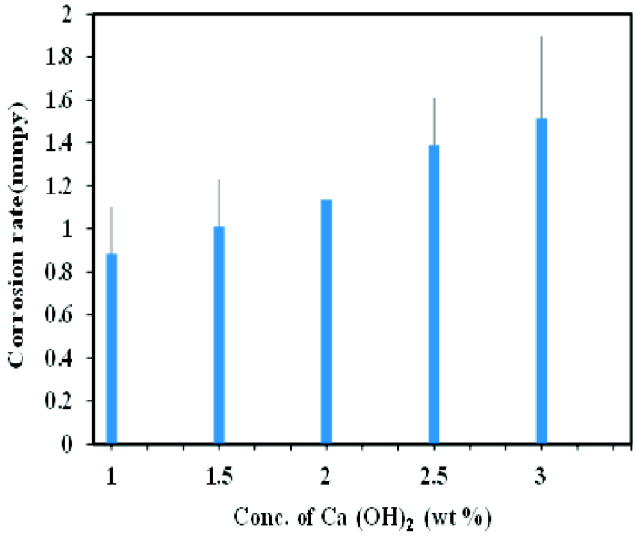

Fig. 1. Corrosion rate for mild steel with 0.5 wt% NaCl with changing concentration of solution $Ca(OH)_2$.

Rate of corrosion for mild steel submerged in a solution of 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl with and without 600 ppm of neam leaf extract maintained at various temperature is shown in Fig. 2. Corrosion rate shoots up with increase in temperature for both the cases, which is in line with the expected behavior. Temperature of the medium was sustained between 30°C and 60°C with a step size of 10°C. However, the corrosion inhibition rate is extensively reduced with plant extract.

Fig. 3 illustrates the plot of inhibition efficiency of mild steel in presence of 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl with various inhibitor concentration. Corrosion inhibition efficiency was deliberated apply the formula reported in the literature[9]. The corrosion inhibitor efficiency rises with respect to plant extract and gets stabilized. Highest inhibitor efficiency of 86% was obtained with 600 ppm plant extract concentration. This might caused to surface limitation. Plant extract molecules get adsorbed towards metal surface hence it attains stability after 600 ppm. The rise in corrosion inhibition efficiency with

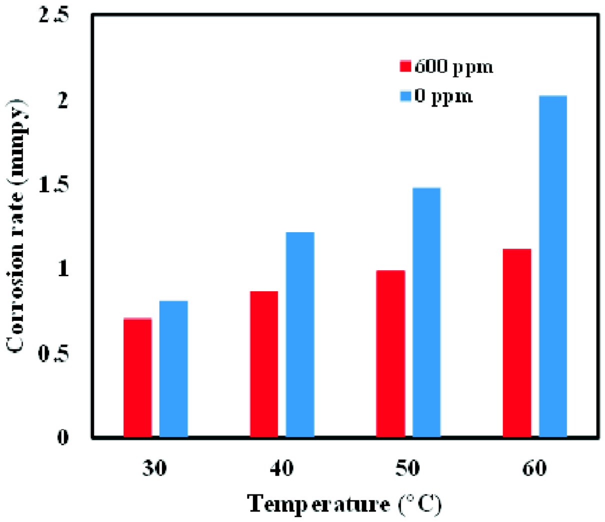

Fig. 2. Rate of corrosion for mild steel with 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl with and without 600 ppm extract concentration at different temperature.

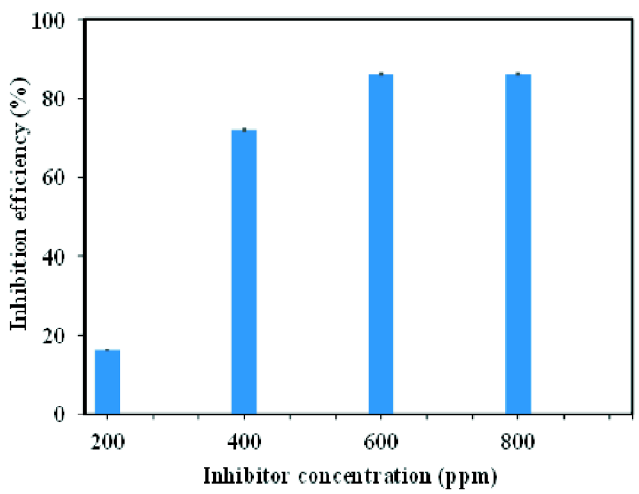

Fig. 3. Inhibitor efficiency for mild steel with 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl in various inhibitor concentration.

extract concentration can be attributed towards plant extract, which adsorbs on metal surface or solution interface.

Thermodynamic analysis:

Fig. 4 shows the corrosion inhibitor efficiency of mild steel within 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution at every instant of solution temperature. From Fig. 4, it is observe that inhibitor efficiency rises over temperature. This trend observed is consistent with the existing literatures[10].

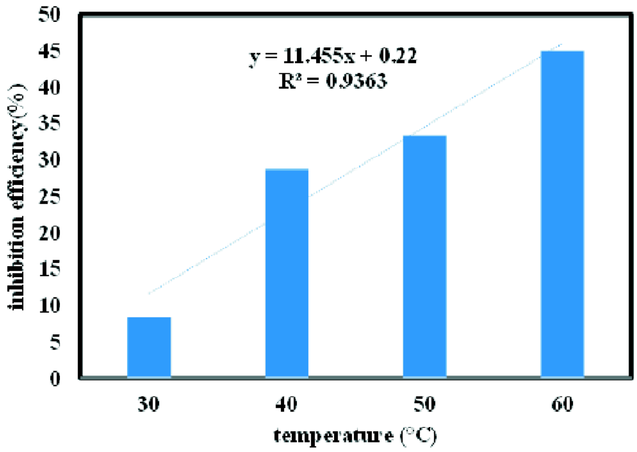

Fig. 4. Inhibitor efficiency at different temperature of mild steel in 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution.

For thermodynamic study, activation energy (E_a) was deliberated using the slope and the intercept obtained from Fig. 5. Arrhenius equation, reported in the literature[9], was used for plotting the graph. The activation energy was found to be 24.78 kJ/mol and 11.33 kJ/mol with and without plant extract respectively. The decrease in activation energy with inhibitor might be due to chemisorption[11].

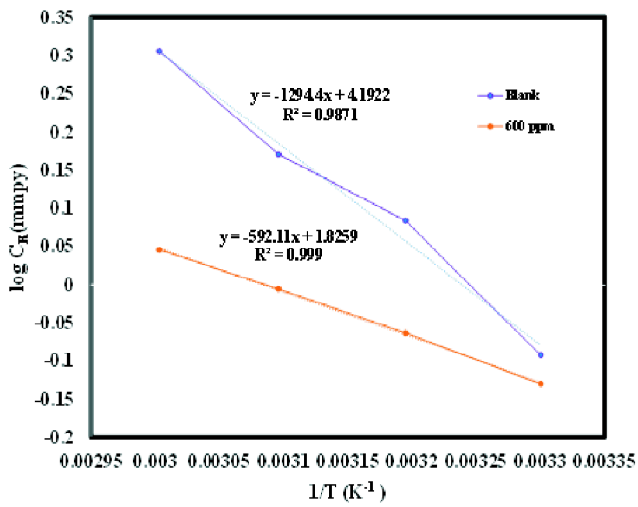

Fig. 5. Arrhenius plots onto mild steel with 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution with 600 ppm inhibitor concentration.

At higher temperature, rate of inhibitor adsorption becomes slow and closely confirms to equilibrium[12]. The higher rate of inhibition evidences decreases in activation value of corrosion attributable to the total corrosive rection situated on unexposed portion of metal surface to the exposed one[13].

To estimate the enthalpy, entropy transition state equation was used. From graph, log (CR/T) vs 1/T, shown in Fig. 6, slope and intercepts are ($-\Delta H_{act}/2.303R$) and log (R/Nh + ($\Delta S_{act}/2.303R$)). ΔS_{act} was found to be –1322.84 J/mol.K and –1783.73 J/mol.K for without and with inhibitor respectively. Higher, negative value of entropies (ΔS_{act}) specify activation complex, represents association step in rate determining step and also represents a decrease in disorderness of molecules[13].

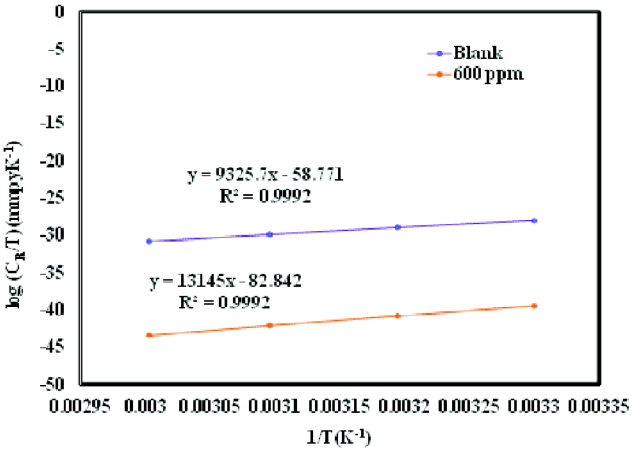

Fig. 6. Plots of log (CR/T) vs 1/T on mild steel with and without inhibitor.

ΔH_{act} was found to be –178.571 kJ/mol, –251.70 kJ/mol for without and with plant extract respectively. Process is exothermic in nature as the enthalpy values are negative value. This is in congruence with the existing literature[11].

Potentiodynamic polarization:

Mild steel was used as working electrode in NaCl solution with different concentration of $Ca(OH)_2$. The measurement was recorded and analyzed and the results are shown in Fig. 7. I_{corr} and E_{corr} values were obtained by linear extrapolation of Tafel plots.

Inhibitor efficiency to be estimated against I_{corr} value employ the formula reported in the literature[8]. I_{corr} and E_{corr} values are reported in the Table 1 along with the inhibition efficiency. It is clear that I_{corr} value declines with rise in inhibitor concentration. This decline in corrosion current density (I_{corr}) value indicates confirms the decrease in corrosion of metal[11]. The corrosion potential value (E_{corr}) becomes more negative value with increase in extract concentration[9]. A similar trend was reported in *Aquilaria crassna* leaves extract in 1 *M* HCl_4. This is matching with the gravimetric trend, which is reported earlier.

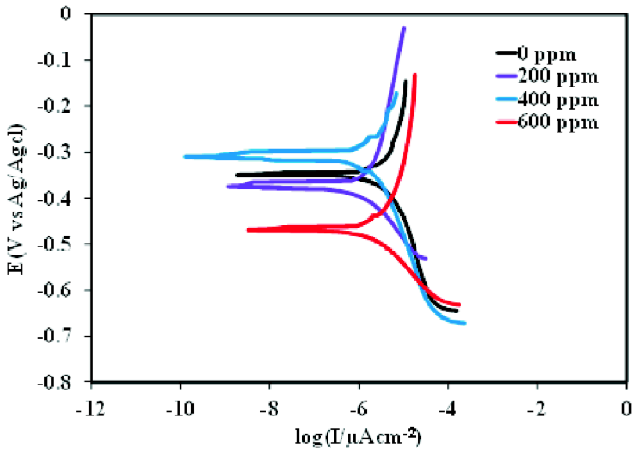

Fig. 7. Potentiodynamic plots for mild steel with 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution at various inhibitor concentrations.

Table 1. Potentiodynamic (Tafel) parameters and inhibition efficiency of mild steel with 1 wt% $Ca(OH)_2$ + 0.5 wt.% NaCl solution in presence and absence of inhibitor concentration

Inhibitor concentration	E_{corr} (mV vs Ag/AgCl)	I_{corr} (µA cm^{-2})	Inhibition efficiency (%)
0	–348.236	1.881	0
200	–371.296	1.081	42.90
400	–407.89	0.591	68.58
600	–510.07	0.440	76.60

Conclusion

Neem leaf extract (*Azadirachta indica*) act as an effective corrosion inhibitor in 1 wt% $Ca(OH)_2$ + 0.5 wt% NaCl solution. From gravimetric studies, it's confirmed, inhibitor efficiency rises along extract concentration and temperature. Highest inhibition efficiency of 86% was attained at 600 ppm extract concentration and then stabilizes. The behavior of *Azadirachta indica* extract on mild steel follows chemisorption and it is exothermic in nature. From potentiodynamic studies, I_{corr} value decline with rise in extract concentration, which matches with gravimetric data. Result showed that neem leaf extract (*Azadirachta indica*) is a potential substitute to minimize corrosion in alkaline medium, as it shows good inhibition efficiency.

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