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Environmental Friendly Corrosion Inhibition of Low Alloy Steel through study of Calotropis Procera (Aak) in Phosphoric Acid Medium

Parmod Kumar[1], Priti Pahuja*[1]
[1]Deenbandhu Chhotu Ram University of Science and Technology,
Murthal, Haryana, India.

Abstract
The Inhibition effect of Calotropis Procera (Aak) on the corrosion of low alloy steel has been investigated in orthophosphoric acid medium by weight loss, electrochemical linear polarization at 30°C, 40°C and 50°C.Calotropis Procera (Aak) with concentration of 1000ppm is able to minimize the corrosion of low alloy steel more effectively than its lower concentrations in phosphoric acid medium at 30°C, 40°C and 50°C. The results of corrosion rate and inhibition efficiency of electrochemical parameters are supplemented through morphological study. The Calotropis Procera (Aak) edicits as mixed type inhibitor proven by potentiodynamic polarization curves.

***Keywords**: Corrosion, Inhibitor, Low Alloy steel,Weight loss study; Polarization..*

1. Introduction

The easy availability, less cost, light weight and high mechanical strength of low alloy steel makes it useful in day today life to industries, automobile to ship building, aerospace to construction framework. The tendancy of low alloy steel to get easily affected by electrochemical environment arises issues and risks on its longevity and durability[1-2].

Phosphoric acid has many important uses in spite of this its corrosive nature stands for great loss in various industries. In order to preserve the industries loss from the corrosive nature of phosphoric acid and the like the use of corrosion inhibitors is one of the most common and economical way to achieve it[3-5]. Corrosion Inhibitors are the chemical substances that need to be added in minute quantity to prevent corrosion. The increasing risk to the environment due to the toxicity of organic and inorganic inhibitors switch the researchers to explore eco friendly corrosion inhibitors[6-8].

In the present study the Calotropis procera (Aak) has been studied as one of the eco friendly corrosion inhibitor in phosphoric acid as corrosive medium. Calotropis procera is one of the most widely distributed wild plant. Calotropis procera belongs to the family Asdepiadaceae. The flexibility of traditional spinning wheel ('Charkha') is enhanced by the use of white milky liquid of Calotropis procera. Calotropis procera use as anti-inflammatory, antitode, antidiarrhoeal, antibacterial[9]. The major constituents of the oil are oxygenated sesquiterpenes (11.84%), oxygenated heterogeneous compounds (38.11%), oxygenated monoterpenes (3.63%) and nonoxygenated sesquiterpenes (4.73%). Both phytol (33.6%), myristic acid (31.2%) contributes 60% among various constituents.

The present study investigates the efficiency of Calotropis procera fruit powder as corrosion inhibitor for mild steel in H_3PO_4 solution using weight loss method, potentiodynamic polarisation method, and scanning electron microscopy (SEM)[10-12].

2. Materials and Methods

2.1. Corrosive Solution

The experiments were performed in 1M H_3pO_4 with 88% purity which was prepared in double distilled water using AR grade phosphoric acid purchased directly by Sigma Aldrich. Each set of experiments for corrosion studies were performed by Freshly prepared 1M H_3pO_4 solution to minimize error. The volume of test solution used for weight loss measurement and electrochemical studies was 200mL and 1000mL respectively.

2.2. Low Alloy Steel sample preparation

The commercially available specimen of low alloy steel was used for the investigation of present study. The composition (wt.%) of the low alloy steel sample used for the study was with 0.14C, 0.03Si, 0.032Mn, 0.05S, 0.20P, 0.01Ni, 0.01Cr and rest Fe. The specimen low alloy metal sheets were manually cut into rectangular samples of 3cm by 1.5cm. Specimen sheet surface was uniformly polished by 600, 800, 1000, 1500 and 2000 grade silicon carbide paper till mirror shine surface was obtained.

2.3. Inhibitor preparation

The Calotropis procera fruits were dried and powdered. The extracts were prepared by refluxing the 50g Calotropis procera in ethyl alcohol.The solvent was evaporated and stock solution was prepared by adding 50ml H_3pO_4. Desired corrosive solutions were further prepared from stock solution.

2.4. Gravimetric measurements

The low alloy steel specimens were immersed in 1M H_3PO_4 for 4 hours without and with various concentrations of inhibitor at 30°C, 40°C, 50°C using a temperature control water bath. Low alloy steel samples were weighed each time before and after immersion time of 4hours. The corrosive samples were cleared , washed with double distilled water, after rinsed, dried in acetone.

2.5. Electrochemical methods

Electrochemical measurements were performed out by electrochemical corrosion analyzer Potentiostat /Galvanostat (Model, PGSTAT204), AUTOLAB, Netherland using NOVA 1.11 software. Corrosion Cell comprises of system three electrode where, low alloy steel as working electrode, Ag/AgCl as reference electrode, Graphite as counter electrode. The Luggin capillary was placed near to low alloy steel specimens in order to minimize ohmic resistance. The working electrode in electrochemical set up maintained the steady state open circuit potential after 40 minutes of immersion time. The electrochemical linear polarization curves were analysed after polarizing the specimen to - 250 mV cathodically and +250 mV anodically with respect to the Calotropis procera inhibitor at a scan rate of 1mV/s.

.2.6. Scanning electron microscopy (SEM)

Surface morphological investigation of the uninhibited and inhibited low alloy steel samples were performed by Scanning electron microscopy, SEM images were recorded using Model Zeiss Ultra 55 at 3kV. The surface morphology in the presence and the absence of inhibitor was compared by recording the SEM images of the samples of low alloy steel samples immersed in 1M H_3PO_4 solution [13-14].

3. Results and Discussion

3.1. Weight loss method

The effectiveness of inhibitor measured by weight loss method[15-17] on low alloy steel at different temperatures 30°C, 40°C, 50°C in phosphoric acid as corrosive medium with immersion time of 4 h. Corrosion rate was evaluated from the following formula:

$$C \quad r \quad (m \quad) = \frac{534 \times \Delta W}{S \times T \times \rho}$$

ΔW =Weight loss in mg, S=Area in cm^2, T=Time in Hours,ρ =Density in g/cm^3

The inhibition efficiency (I.E.%) was evaluated using equation:

$$I.E.(\%) = \frac{C_{b} - C_{i\,h.}}{C_{b}} \times 100$$

Where,

CR_{blank}, is the corrosion rate of low alloy steel in absence of Calotropis procera inhibitor

CR_{inh}, is the corrosion rate of low alloy steel in presence of Calotropis procera inhibitor

The value of corrosion rate (CR), surface coverage (θ) and percentage inhibition efficiency (% IE) of low alloy steel samples exposed to 1M H_3PO_4 solution of without and with different concentration of Calotropis procera at different temperatures are summarized in Table 1. and shown graphically in Fig 1.

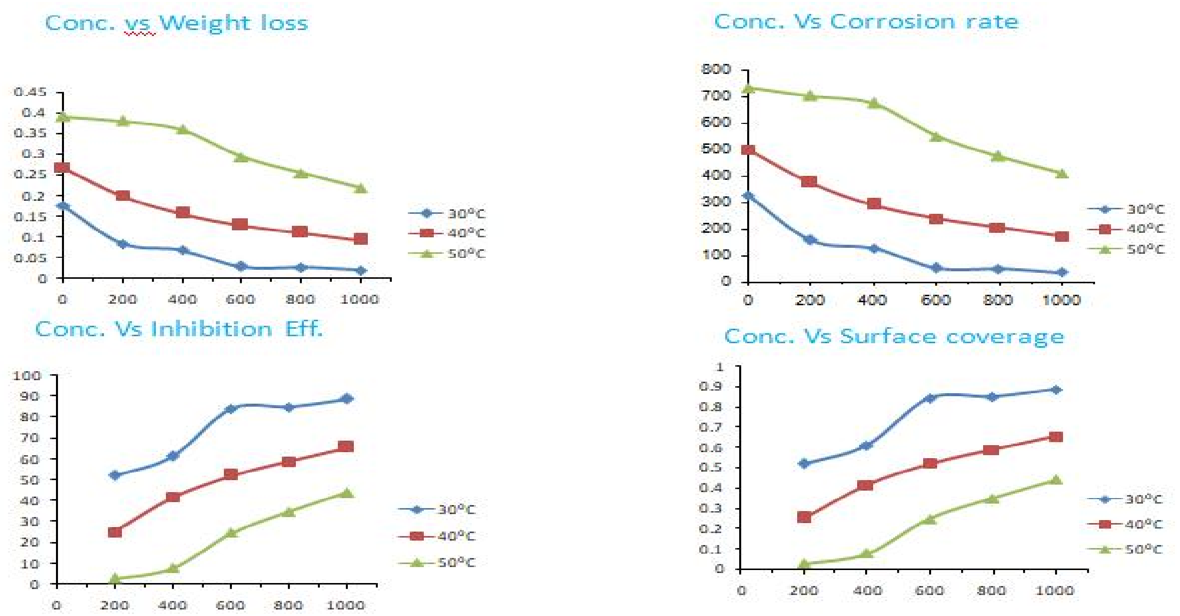


Fig 1.Graphical representation of weight loss, corrosion rate (CR), surface coverage (θ) and percentage inhibition efficiency (% IE) with various concentration of Calotropis procera inhibitor at different temperatures.

Table 1 weight loss study of Calotropis procera at different temperatures

Temperature / °C	Concentration /ppm	Weight loss mg	Corrosion rate / mmpy	Inhibition efficiency I E %	Surface coverage / θ
Blank	0	0.1750	329	0	0
30°C	200	0.0840	157.9	52.00	0.520
30°C	400	0.0681	127.8	61.08	0.611
30°C	600	0.0278	50.76	84.11	0.841
30°C	800	0.0264	48.88	84.91	0.849
30°C	1000	0.0199	35.72	88.60	0.886
Blank	0	0.2668	500	0	0
40°C	200	0.1998	374.12	25.11	0.251
40°C	400	0.1556	291.4	41.68	0.416
40°C	600	0.1279	238.76	52.06	0.521
40°C	800	0.1096	204.92	58.92	0.589
40°C	1000	0.0925	172.96	65.32	0.653
Blank	0	0.3902	733.20	0	0
50°C	200	0.3794	703.12	2.76	0.027
50°C	400	0.3594	674.92	7.89	0.078
50°C	600	0.2933	550.84	24.83	0.248
50°C	800	0.2537	475.64	34.98	0.349
50°C	1000	0.2180	409.84	44.13.	0.441

3.2. Electrochemical methods

Linear Polarization measurements have been carried out and analyzed through extrapolation of tafel plots in order to assemble the electrochemical parameters with summarizing the anodic and cathodic reactions [19-22].The percentage inhibition efficiency (I.E.%), was calculated using the equation:

$$I.E.(\%) = \frac{i_{c} - i_{c\,(i;\,h.)}}{i_{c}} \times 100$$

where, i_{c} and $i_{c\,(i;\,h.)}$ are the values of corrosion current density in absence and presence of Calotropis procera inhibitor

Potentiodynamic polarization curves for low alloy steel in H_3PO_4 solution without and with various concentration of calotropis procera at 30ºC. Table 2 showed that the presence of calotropis procera causes a prominent decrease in the corrosion rate at 30ºC The interpretation of curves indicates calotropis procera as mixed type inhibitior. The Tafel regions further indicates that the electrochemical reactions are activation controlled. It is also shown that corrosion current (i_{corr}) decreases noticeably in the presence of extract [23-27].

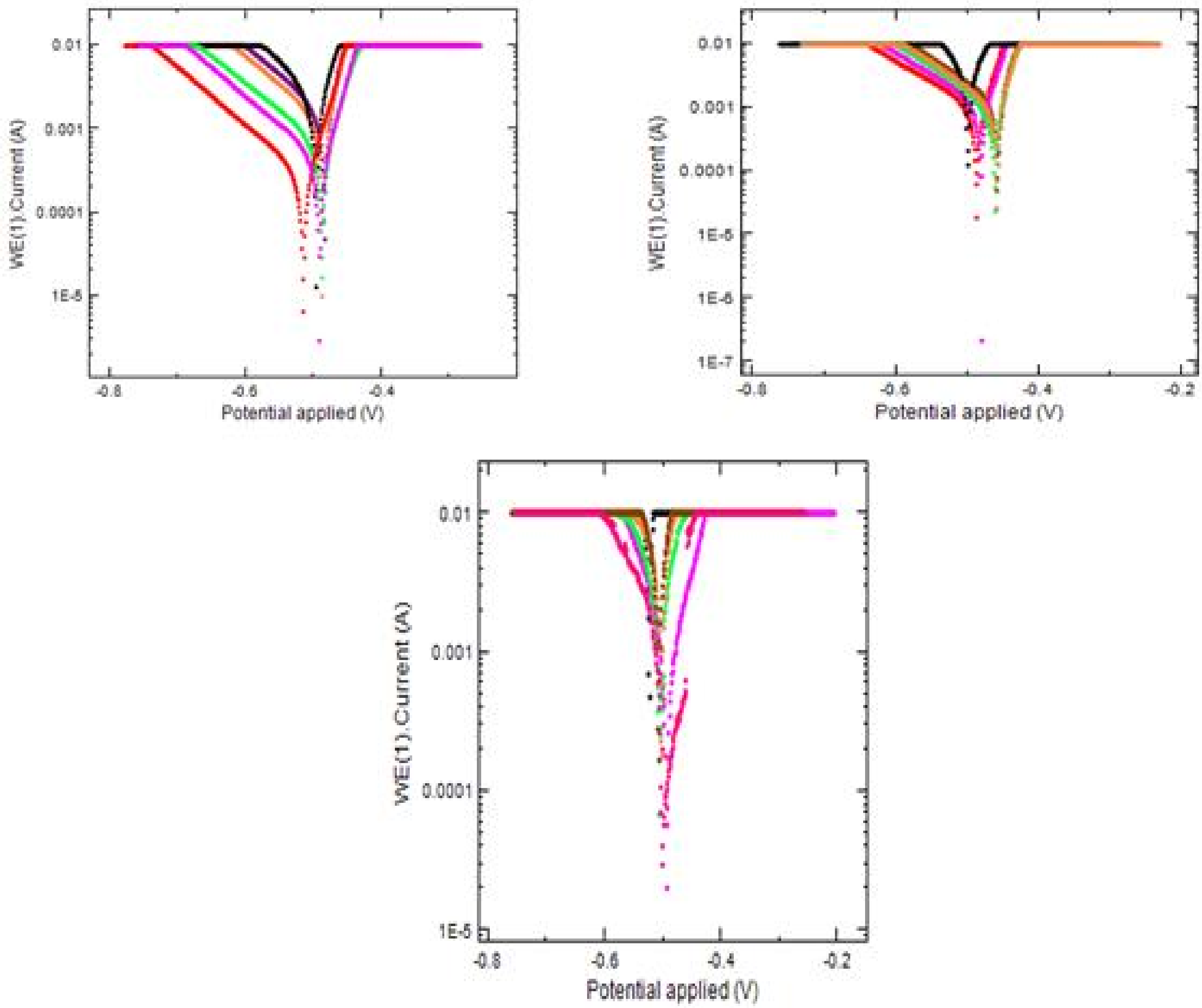


Fig 2. Potentiodynamic polarization curves for low alloy steel in H_3PO_4 in the presence of Calotropis procera with concentration from 100 ppm to 1000ppm.

Table2. Potentiodynamic polarization parameters for low alloy steel in H_3PO_4 in the presence of Calotropis procera

Concentration (ppm)	**E_{corr} (mV)**	**i_{corr} (μA/cm^2)**	**Inhibition Efficiency (%)**	**Surface coverage θ**
Blank	497.060	2282.60	- - - - -	- - - - -
200	485.030	680.430	72.28	72.28
400	489.950	301.640	75.41	75.41
600	487.740	574.420	76.59	76.59
800	492.040	480.330	80.43	80.43
1000	515.910	365.580	85.10	85.10

Langmuir Adsorption isotherm

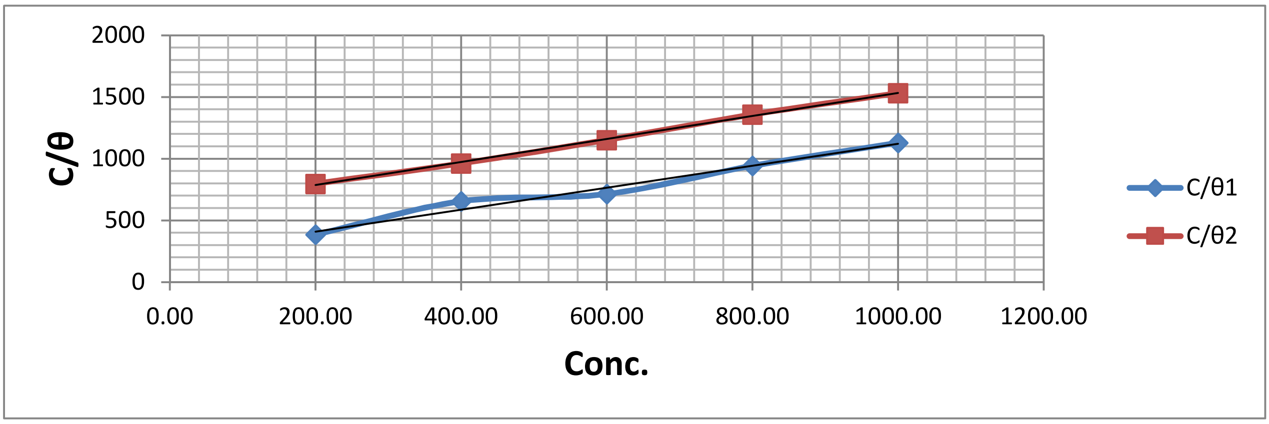
The Langmuir adsorption isotherm was used to illicit gas-solid-phase adsorption onto activated low alloy and has been used to quantify and complement the performance of various adsorbents. The maximum adsorption occurs in Langmuir adsorption isotherm when a saturated monolayer of solute molecules is present on the metallic surface, no migration of adsorbate molecules and the energy of adsorption is constant.

The fraction of the surface (θ) which is covered by inhibitor molecules is given by the equation

$$\theta = \frac{I_c^{\circ} - I_c}{I_c^{\circ}}$$

blank corrosion rate (I^{o}_{corr}) and inhibited corrosion rate (I_c) represents the total number of 'active sites' on the surface of corroding metal minus the inhibited sites.

θ = The fractional coverage of the surface with inhibitor indicates protection percentage. The surface coverage (θ) depends on the concentration of the inhibitor and explain with adsorption isotherms. In the present study adsorption isotherm was analysed by Langmuir



where, C is inhibitor concentration, θ is the degree of surface coverage, and K_{ads} is the equilibrium constant for adsorption–desorption process. the Langmuir isotherm refers to homogeneous adsorption, all active sites possess equal affinity for the adsorbate with constant enthalpies and sorption activation energies.

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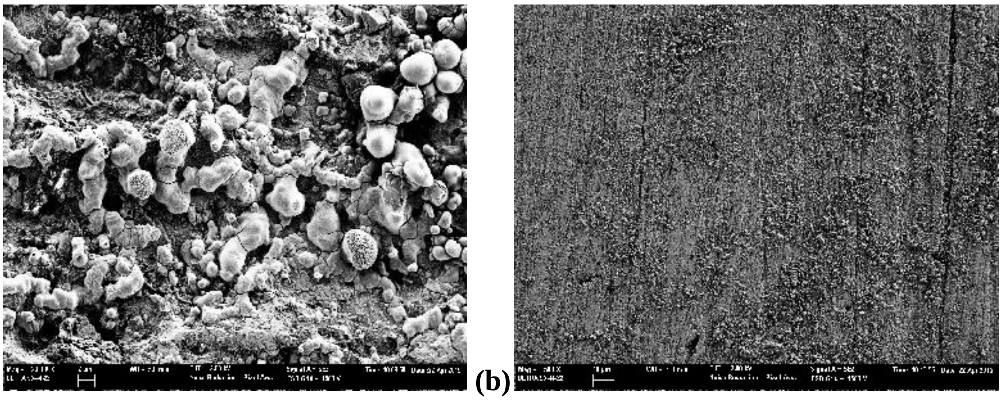
Regression co-efficient values greater than 0.99, indicating that the adsorption of the Calotropis procera follows the Langmuir adsorption isotherm $\frac{C}{\theta} = \frac{1}{K_a} + C$

where, C is inhibitor concentration, θ is the degree of surface coverage, and K_{ads} is the equilibrium constant for adsorption–desorption process.

3.4. Scanning electron microscopy

The surface morphology of the low alloy steel specimen immersed in 1M H_3PO_4 solution in the presence and the absence of inhibitor was compared by recording the SEM images of the samples. The immersion time of the low alloy steel coupon for the SEM analysis was 4 hours through weight loss measurement.



(a) **(b)**

Fig. 1: SEM image of the surface of low alloy steel after immersion for 4 h in 1 M H_3PO_4 at 30°C in absence and presence of inhibitor Calotropis procera

(a) blank and (b) 1000ppm of Calotropis procera

Conclusions

The inhibiting effect of CALOTROPIS PROCERA on low alloy steel in H_3PO_4 solution at the temperature range of 30°C, 40°C and 50°C through gravimetric method proved it as effective and good corrosion inhibitor . The inhibition efficiency increases with the increase of inhibitor concentration.

calotropis procera acting as mixed-type inhibitor on the analysis of electrochemical linear polarization.

The inhibition efficiencies obtained by weight loss measurements, polarization and EIS showed good agreement. calotropis procera considered as effective, good and eco friendly corrosion inhibitor as shows good adsorption on the surface of the low alloy steel .

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