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Research Article

JATROPHA GOSSYFOLIA- A GREEN INHIBITOR ACT AS ANTICORROSIVE AGENT ON CARBON STEEL

Sangeetha C*¹, Chinnakani C¹, DeepaRani P², Selvaraj S¹

¹PG and Research Department of Chemistry, Sri Paramakalyani College, Alwarkurichi ²Aditanar College of Arts and Science, Thiruchendur *Corresponding author: geetharaja.np@gmail.com

ABSTRACT

A new and eco friendly alternative green inhibitor is proposed for anticorrosion in carbon steel instead of commonly adopted Synthetic counterpart. Adsorption behaviour and Inhibition efficiency of the inhibitor on Carbon steel surface investigated by Weight loss method. Observed result reveals that the percentage of inhibition efficiency (95.99%) increased with increase of concentration (0-1000ppm) and the efficiency decreased (88%) when the temperature rose from 303k to 333k. Adsorption of the inhibitor on the carbon steel surface follows Langmuir isotherm (R^2 = 0.9973) and the values of activation energy suggested that the adsorption of inhibitor is physisorption. The image of Scanning electron microscope and the characterization studies of corrosion products revealed the adsorption behavior of active organic compounds of the extract on the interface metal/solution. Thus may concluded that the applicability of the proposed green inhibitor on carbon steel behave more efficient anticorrosion agent.

Keywords: Jatropha gossyfolia leaf, 1.0 NHCl, Carbon steel, Non electrochemical, Characterization studies

1. INTRODUCTION

Materials are precious resources of a country such as aluminium, copper, chromium, manganese, iron, titanium, etc., are dwindling fast. An impending metal crisis does not seem anywhere to be a remote possibility but it will be a reality. To preserve these valuable materials, we need to understand how these resources are destroyed by corrosion and how they must be preserved by applying corrosion protection technologies. Among these, carbon steel is widely used material in many industries because of economically cost-effective and easy fabrication, but it is prone to undergo corrosion in aggressive conditions. The environment may be a liquid, gas or mixture of solid and liquid. Mostly hydrochloric acid is used as pickling, descaling solution in industry, when Carbon steel exposed to this medium gets corroded. So, metal has to be protected to avoid such kind of serious problems. Most of the researches have conducted their investigation with funding agenesis mainly in large areas such as development of construction of plants, new pipelines for natural gas and oil transportations etc. [1-4]. The focus of these research areas towards the inhibitor applications in environment and concrete steps has to be taken for the protection of metals. But now a days, some industrial corrosion inhibitors are being not used due to high toxicity of chromate, phosphate and arsenic compounds, related to various environmental and health problems, strict international laws were imposed [5-10]. In order to reduce the use of this kind of inhibitors, need for the development of other inhibitor is increasing. Thus our scientific community and researchers began searching for friendly, environmentally inhibitors, like naturally occurring organic inhibitors. This type of inhibitors can minimize the dissolution rate of corrosion due to the adsorption of main phytochemical constituents in such plant extract. The presence of large molecules with functional groups containing of heteroatoms (such as oxygen, nitrogen, sulphur, and phosphorus and π bonding) [11] forms a passivating layer that prevents access of corrosive agent onto the metal surface, either by inhibiting the reduction or oxidation part of the redox reaction.

Thus in our present study, Non electrochemical studies were used to evaluate the inhibition properties of *Jatropha gossyfolia* leaf (JGL) extract on carbon steel. The alcoholic base of *Jatropha gossyfolia* leaf extract has an excellent characteristic as a corrosion inhibitor owning to the fact that it may contains inhibitive components such as d-Mannitol, 1-decylsulfonyl-($C_{16}H_{34}O_7S$), Lanosterol ($C_{30}H_{50}O$), 3-Hexadecyloxycarbonyl-5-(2-hydroxyethyl) -4-methylimidazolium ion ($C_{24}H_{45}N_2O_3$) [12] etc.

2. MATERIALS

2.1. Preparation of Test Specimen

Rectangular specimen of Carbon steel was mechanically pressed, cut to form different coupons, each of dimension exactly 20cm^2 ($5 \times 2 \times 2 \text{cm}^2$) abraded with emery wheel of 80 and 120 and degreased using trichloroethylene, washed with distilled water, cleaned and dried, then stored in desiccator for throughout our present study.

2.2. Preparation of Inhibitor

Jatropha gossifolia leaves [JGL] were collected from western guards. Stock solution of the plant extract was obtained by drying the leaves under shadow and grinded to powdery form. Aproximately100g of the powder was immersed in alcohol for about 48hrs. Then the solvent was removed by evaporation process and the pure JGL extract was collected. The stock of the extract obtained was used for preparation of different concentrations of the extract by dissolving in 1.0N HCl, respectively.

2.3. METHODS

2.3.1. Weight loss studies

Carbon steel specimen were weighed initially and immersed in 100ml of test solution for 24 to 360 hours at the room temperature in the presence and absence of JGL inhibitor and the temperature studies was also carried out ranges from 303K to 333K for an hour. At the end of exposure period, specimens were washed and their final weight was recorded. The experiment was conducted in triplicates to avoid the error during analysis. From the mass loss measurements, corrosion rate was calculated using the following relationship:

Corrosion rate (mmpy) =
$$\frac{87.6 \times W}{DAT}$$
.....(1)

W=Mass loss (mg), D= Density (gm/cm^3) , A= Area of specimen (cm^2) , T=Time in hours

The percentage of degree of surface coverage (θ) and inhibition efficiency (IE) was calculated using equation (2) and equation (3) respectively.

IE % =
$$\frac{w_1 - w_2}{w_1} \times 100$$
(2)
 $\theta = \frac{w_1 - w_2}{w_1}$ (3)

Where, W_1 and W2 are the corrosion rate in the absence and presence of the JGL extract.

3. RESULT AND DISCUSSION

3.1. Mass loss Technique

3.1.1. Effect of Concentration

Mass loss measurements were carried out to study the inhibition performance of the plant extracts (JGL) for their different concentrations on the corrosion of Carbon steel in 1.0N HCl. The gain of corrosion rate and the inhibition efficiency (IE%) data are presented in Table-1. From this table, it was noted that corrosion rate gradually decreased on the successive addition of the extract, which indicates that the adsorption of inhibitor molecule on the metal surface or at solution interface on its increase of concentration which providing wider surface coverage. The created layer, of adsorbed molecules separates the metal surface from applicable aggressive medium which limits the dissolution of metal surface by preventing their corrosion sites which improves inhibition efficiency.

 Table 1: Calculated values of corrosion rate and inhibition efficiency (%) Using different concentration of JGL on Carbon steel in 1.0 N HCl

Conc.(ppm)	24	hrs	72	hrs	12	0 hrs	240	hrs	360	hrs
	CR	IE%	CR	IE%	CR	IE%	CR	IE%	CR	IE%
0	6.732	-	8.322	-	3.394	-	1.804	-	1.300	-
10	4.672	27.9	5.695	31.56	3.147	7.260	1.587	11.98	1.163	10.48
50	3.580	44.8	4.897	41.15	2.994	11.780	1.466	18.68	1.078	17.04
100	2.534	60.93	3.750	54.93	2.775	18.219	1.334	26.03	0.869	33.13
500	0.557	91.4	1.302	84.35	2.557	24.65	1.327	26.41	0.846	34.92
1000	0.511	92.11	0.333	95.99	0.776	77.12	1.086	39.81	0.576	55.66

3.1.2. Effect of Temperature

Corrosion parameters obtained from the mass loss measurements for Carbon steel in the presence and absence of inhibitor at various temperatures are summarized in Table 2. By the inspection of table 2, it can be concluded that maximum inhibition efficiency obtained was 88 % for JGL extract increased up to 313K. Slight decrease in IE was also observed beyond this temperature. This trend is due to the evaluation of H_2 gas which leads to dissolution process of Carbon steel and partial desorption of the inhibitor molecules from the metal surface. This effect can be explained by the decrease of strength of the adsorption process at high temperature and suggesting physisorption.

Table 2: Effect of temperature on the corrosion of Carbon steel in the presenceAnd absence of	various
concentration of JGL inhibitor in 1.0 N HCl	

Electrolyte	Corros	sion rate(mn	npy)	Inhibition Efficiency (%)			
(ppm)	303 K	313K	333 K	303 K	313 K	333 K	
0	80.904	95.969	109.360	-	-	-	
10	67.513	80.904	79.788	16	15	27.04	
50	58.028	65.281	50.774	28	31	53.57	
100	52.448	58.585	45.194	35	38	58.67	
500	33.477	41.289	36.267	58	56	66.83	
1000	22.318	10.601	13.949	72	88	87.24	

3.1.2.1. Corrosion Thermodynamic Parameters

The dependence of the corrosion rate on temperature can be expressed by the Arrhenius and transition state equations as presented in Eqn. (4) and (6), respectively.

$CR = A_{exp(-E_a/2)}$	RT) • • • • •	•••••	(4)
$\log CR = \frac{-E_a}{2.303RT}$	+logA	۱	(5)
$\log \frac{CR}{T} = \log \frac{Rh}{N} +$	$\frac{\Delta s}{2.303R}$	ΔH 2.303RT	(6)

where *CR* is the corrosion rate, E_a is the apparent activation energy, *R* is the universal gas constant (8.314 J mol-1 K-1), *T* is temperature, A is the Arrhenius preexponential factor, *h* is the Plank's constant (6.626176 x 1034 Js), *N* is the Avogadro's number (6.02252 x 10^{23} mol-1), ΔS is the entropy of activation and ΔH is the enthalpy of activation.



Fig.1: Arrhenius plot for Carbon steel corrosion 1.0 N HCl in the presence and absence of different concentration of JGL



Fig. 2: Transition plot for mild steel corrosion 1.0 N HCl in the presence and absence of different concentrations of JGL

The plot of log *CR* against 1/T is presented in Fig: 1. The slope of the line is $(-E_a/2.303 \text{ RT})$ and the intercept of the line extrapolated gives log *A*. The result shows that the activation energy in the presence and absence of inhibitors gives insight knowledge on the possible mechanism of inhibitor adsorption.

 E_a values in the presence and absence of inhibitor are shown in the table 3. Observed values (5.404 KJ/mol to-12.880 KJ/mol), lower than the threshold value (80KJ/mol) required for chemisorptions, this indicates that the weak adsorption of the inhibitor molecules on the metal surface.

The transition state equation was used to evaluate some thermodynamic parameters (Δ H, Δ S and Q) for the adsorption of inhibitor on the Carbon steel surface.

The plot of log (CR/T) against 1/T was linear, the slopes and intercept of the transition state plot (Fig:2) are equal

to $(-\Delta H/2.303R)$ and $(\log R/Nh+\Delta S/2.303R)$, respectively. The computed value of enthalpy (ΔH) calculated from the slope of the plot, were positive in uninhibited solution and negative in the inhibited solution, this shows that the adsorption of *JGL extract* on Carbon steel surface exhibited exothermic reaction. On the other hand the values of entropy (ΔS) generated from the intercept of the transition state plot decreased. However negative values of ΔS of the inhibitor point to an activated complex in the rate determining step, performs an association rather than a dissociation step, meaning that a reduction in disorder occurs through the transition from reactant to the activated complex [13].

$$Q=2.303R[\log(\theta_{2}/1-\theta_{2})-\log(\theta_{1}/1-\theta_{1})] x(T_{1}xT_{2})/(T_{2}-T_{1})$$
.....(7)

Calculated values of Q (Table 3) were positive and ranged from 17.490 to 26.776 kJ/mol.

Concentration (ppm)	$\Delta H (KJ / mol)$	$-\Delta S (KJ/K mol)$	E _{ads} (KJ /mol)	$Q_{ads}(KJ /mol)$
0	2.782	59.173	5.402	-
10	-1.230	52.857	1.378	17.490
50	-9.786	40.122	-7.159	30.035
100	-10.208	39.149	-7.563	26.902
500	-3.960	46.504	-1.326	9.852
1000	-15.565	27.290	-12.886	26.776

Table 3: Corrosion Thermodynamic parameters of JGL in 1.0NHCl on Carbon steel

3.1.2.2. Adsorption Isotherm

The mechanism of corrosion protection was explained on the basis of adsorption behavior. Adsorptions isotherms are very important in determine the mechanism of organo electrochemical reaction. The adsorption of organic compounds happens due to the interaction energy between the inhibitor and a metallic surface either through electrostatic or covalent bond formation. In order to gain adsorption isotherms, the surface coverage (θ) gained by the function of inhibitor's concentration. The data of θ are then graphed to fit the more appropriate adsorption model [14] such as, Langmuir, Temkin, Frumkin, Flory- Huggins, Freundlich, Bockris-Swinkles, Hill-de Boer, Parsons and the El-Awady and best results judged by the correlation coefficient R^2 are listed in table-4. All these isotherms can be represented as follows:

Where $f(\theta, \mathbf{x})$ is the configuration factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm. θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, \mathbf{x} is the size ratio, a is molecular interaction parameter and k is the equilibrium constant of the adsorption process.



Fig.3: Langmuir adsorption plot for JGL on Carbon steel in 1.0N HCl.

Langmuir adsorption isotherms were found to best describe the adsorption mechanism for JGL extract as it fits the experimental results as 303k to 333k.

Langmuir adsorption isotherm is expressed according to Equation (9):

$$\frac{c}{\theta} = \frac{1}{\kappa} + C....(9)$$

Where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is degree of surface coverage of the inhibitor.

Taking logarithm of both sides of Equation (9) yields Equation (10).

$$\log \frac{c}{a} = \log c - \log k...(10)$$

Plotting of log C/θ against log C is shown in Figure 2. Straight line slope with unity indicating Langmuir adsorption isotherm. Langmuir isotherm assumes that the metal surface contains a fixed adsorption sites and each site holds one adsorbate. Since the average regression coefficient is almost unity (0.9973), the adsorption behavior is believed to obey Langmuir adsorption isotherm at all the studied temperature. This indicates that mono-layer of the studied inhibitor adsorbed to Carbon steel surface without interaction between the adsorbed molecule.

Table 4. Adsorption Isotherms values for Carbon steel in 1.0N HCl with different concentration of JGL extract

Isotherm	R^2	TEMP (K)	K	SLOPE
Langmuir		303	12.501	0.679
	0.9973	313	13.440	0.6501
		33	5.342	0.7755
Frumkin		303	0.0947	2.7273
	0.9847	313	0.0872	2.7997
		333	0.0579	2.9133
Temkin		303	0.6889	0.2807
	0.9667	313	0.5910	0.3334
		333	1.0868	0.2647
El-Awady		303	0.0481	0.5561
	0.9609	313	0.0285	0.7214
		333	0.1129	0.5442
Frendlich		303	0.0800	0.3201
	0.9483	313	0.0744	0.3498
		333	0.1749	0.2437
Florry-		303	0.1513	1.5788
Huggin	0.526	313	0.1624	1.7902
		333	0.279	1.0156

3.2. Characterization Studies Of Corrosion Products

3.2.1. EDX Studies

EDX spectroscopy was used to determine the elements present on the Carbon Steel surface in the inhibited and uninhibited of compounds. Figs: 4 (a, b) represents that the EDX spectra of the corrosion products on metal surface in the presence and absence of optimum concentrations of JGL extract in 1.0N hydrochloric acid. In the absence of inhibitor molecules, the spectrum may conclude the existence of elements present in the metal and its environment (4a). However, in the presence of the inhibitor concentrations, the hetero atom such as Oxygen and sulphur are found to be present in the corrosion product on the metal surface (4b). It clearly indicates that sulphur and oxygen elements present in the inhibitor molecules may be involved in thin film formation with the metal ion during the adsorption process and prevent further dissolution of metal against corrosion.



Fig. 4: (a, b)EDX spectrum of the corrosion product in Presence and absence of inhibitor on Carbon steel surface in 1.0N HCl.

3.2.2. FT-IR Analysis

Fig.5 (a) and (b) shows that the FT-IR spectrum of the pure ethanol JGL extract and the corrosion productive

band formed on the Carbon steel surface in the presence spectras Fig.5(a) and (b) the –OH stretch was shifted from 3376 cm⁻¹ to 3275 cm⁻¹, the >C=O stretch for carbonyl group was shifted from 1707.95 cm⁻¹ to 1621.77 cm⁻¹, the -C-O-C- stretch shift of ester group from 1161.61 cm⁻¹ to 1105.51cm⁻¹was appeared. The above changes in stretching frequency indicate that there of inhibitor in 1.0N HCl. Upon comparing both of these was an interaction between the inhibitor molecules and the surface of the metal. Thus the Carbon steel exposed to JGL extract shows the retention of the characteristic peaks of JGL extract and is found to be shifted which is due to the participation of the compounds present in the extract in the corrosion inhibition process.



Fig: 5(a) FTIR Spectrum of JGL plant extract in 1.0N HCl



Fig.5: (b) FTIR Spectrum of Carbon steel in JGL extract in 1.0N HCl



Fig. 6: (a -c) SEM image of the Polished Carbon Steel surface, Before and After Immersed in 1.0N Hydrochloric acid with JGL extract.

Image of Scanning Electron Micrographs (SEM) were taken and detected in order to support the findings of present work. Fig: 6 (a-c) shows that the polished specimens (blank), in 1.0N HCl and in presence of inhibitor were observed are shown. Fig: 6(a) evident that the polished Carbon steel surface before exposure to the corrosion solution, which is associated with polishing scratches. It is clear from Fig: 6(b) that the surface of the Carbon steel was heavily corroded in 1.0 N HCl, and leads to plug type of corrosion. But in the presence of inhibitor the entire surface was protected with thin film formation by the inhibitor molecules suggesting that the metal surface prevent further dissolution from corrosion.

4. CONCLUSION

The extract of Jatropha gossyfolia leaf extract acts as excellent and efficient inhibitor for the corrosion of Carbon steel in 1.0N Hydrochloric acid medium. Inhibition efficiency increased with inhibitor concentration and maximum inhibition efficiency for the extract was found to be 95.99%. The inhibitor follows Langmuir adsorption isotherm ($R^2=0.99$). The values of apparent activation energy decreased (5.402 to-12.886 KJ/mol) with the increase of inhibitor concentration shows that the physisorption based mechanism. The negative value of the enthalpy (2.782 to -15.565K J/mol) of adsorption indicates that the reaction of the JGL is exothermic. The analysis of corrosion composite by using EDX, FT-IR and image of SEM clearly revealed that the formation of the strong protective thin film formed on the surface.

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