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Azardirachta Indica Leaves Ark's as Green Corrosion Inhibitor for Aluminum in HCl Solutions

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***Abstract*—**

The purpose of this paper to find out the effect of Azardirachta indica (Neem) leaves ark's on the corrosion of aluminum in 0.4, 0.5 and 0.6M hydrochloric acid (HCl), and elucidates the mechanism of the inhibition system. Gravimetric and galvanostatic polarization methods were used to investigate the effect of aluminum corrosion in HCl solutions. The outcome revealed that maximum inhibitor efficiency which corresponds to the lowest corrosion rate was obtained at most favorable inhibitor concentration of 1.25% with reduction in the corrosion rate observed to follow in order of increasing extract concentration. The adsorption study promote that Langmuir isotherm best described the metal surface interaction with the Azardirachta indica (Neem) leaves ark's with the best exposure time for the Azardirachta indica (Neem) leaves ark's to adsorb to the metal surface at all concentrations. Polarization study reveals that the inhibitors functions as a mixed inhibitor.

***Keywords*— Azardirachta indica (Neem), Corrosion, aluminum, Hydrochloric acid, Adsorption, Langmuir isotherm**

I. INTRODUCTION

Deterioration as a result of corrosion often accepted as an unavoidable fact of life and this has lead to widespread lack of awareness of the importance of economic aspects of corrosion. Corrosion is the destructive attack of metal by chemical or electro - chemical reaction with its environments [1]. They find wide application as components in pretreatment composition, in cleaning for industrial equipments. Hydrochloric acid is generally used for the removal of undesirable scale and rust in several industrial processes. Acid inhibitors are usually used in several industrial processes to control the corrosion of metals. Therefore, inhibitors are one of the most convenient methods for protection against corrosion, particularly in acid solutions to prevent unexpected metal dissolution and acid consumption. Majority of the acid inhibitors are organic molecules containing oxygen, nitrogen or sulfur atoms in a conjugated system have been reported to exhibit corrosion inhibition efficiency. Many researchers have investigated many N containing inhibitors for the corrosion inhibition of metal in acid solutions, N containing organic inhibitor acts as a strong inhibitor for metal in acid [2]-[11]. Commonly the reported inhibitors used in the industries are highly toxic and hazardous to the environment. The efficiency of inhibition is related to the amount of adsorbed inhibitor on the metal surface. The inhibitor after adsorption may form a surface film that acts as a physical barrier restricting the diffusion of ions/molecules to or from the metal/alloy surface and may prevent the metal atoms from participating in either the anodic or cathodic reactions of corrosion [12], [13].

Several works on plant extracts as green corrosion inhibitors have been done [14]-[21]. Uses of plants extracts as inhibitors are non-polluting, environment friendly, cheap and easily available from natural products. It has been shown that natural products of plant origin contain various organic compounds e.g. alkaloids, tannins, pigments, organic and amino acids, and most are known to have inhibitive action [22]-[29]. Neem is an evergreen of tropical and sub-tropical distribution, belonging to the Meliaceae family and is very popular for its pesticide properties [30]. Fresh leaves of Neem tree are also known [31] to contain among others, the following physico-chemical compounds: calcium (510 mg/100 g), phosphorus (80 mg/100 g), iron (17 mg/100 g), thiamine (0.04 mg/100 g), niacin (1.40 mg/100 g), vitamin C (218 mg/100 g), carotene (1,998 μg/100 g), tyrosine (31.50 mg/100 g), alanine (6.40 mg/100 g), proline (4.00 mg/100 g), glutamine (1.00 mg/100 g), glutamic acid (73.30 mg/100 g), aspartic acid (15.50 mg/100 g), carbohydrates (22.9%), minerals (3.4%), proteins (7.1%), fibre (6.25%) moisture (59.4%), and calorific value 1290 Kcal/Kg. The neem leaves are very bitter in test due essentially to the presence of an array of complex limonoids including azadirachtin in addition to its tannin content. We have been identified a number of potential green inhibitors for metal corrodent system [32], [33], [34]. Therefore, the paper is mainly focus on inhibitive action of Azardirachta indica leaves ark's on the corrosion of aluminum alloy in 0.4-0.6M HCl solutions using gravimetric and polarization method.

II. EXPERIMENTAL

Details of the chemical composition of test specimen of metal aluminum contains Al = 98.02 %; Mg = 0.37 %; Si = 0.49 %; Fe = 0.68 %; Mn = 0.16 % and Cu = 0.082 % were used in this study. Each sheet, which was 0.12 cm in thickness, was mechanically press-cut into coupons of dimension 5 x 2 cm with small hole of about 5 mm diameter near the upper edge. These coupons were used in the "as cut" condition, inhibition efficiency without further polishing, but were de-greased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use.

Neem Leaves Extract: The Neem leaves were dried, grind to powder form and boiling with double distilled water to making extract of different concentrations 0.25, 0.5, 0.75, 1.0 and 1.25 %.

All chemicals and reagents used were of analytical grade and used as source without further purification. The aggressive media were respectively 0.4, 0.5 and 0.6 M HCl solution. All inhibitors were used in the concentration range 0.25 to 1.25%.

1) Weight loss method

Corrosion damage is most commonly assessed by weight loss method, rectangular specimen having area of 0.2259 dm^2 with small hole of about 5 mm diameter near the upper edge of the specimen for suspension have been used.

After cleaning and weighting each specimen was suspended to same depth of 1.5 cm below the surface of the liquid. The volume of the corrosive media for, all experiment was kept 230ml. Only one specimen was suspended in each glass beaker of 250ml capacity. Triplicate experiments were performed in each case. In long duration tests the level of corrosive media was maintained. Experiments were conducted at room temperature (303 $\pm$ 1 K). For satisfactory assessment of corrosion, it is essential to remove corrosion products from the specimen at the same time. The cleaned and dried specimens were weighed before immersion in the respective test solutions of 0.4, 0.5 and 0.6M HCl using CAH 123 electronic weighing balance with the accuracy of ±0.001. Tests were conducted with different concentrations of inhibitor. At the end of the tests, the specimens were removed from the corrosive environment and were cleaned after the test with chromic-phosphate mixture solution and then reweighed. Triplicate experiments were performed in each case and the mean values reported.

The specimens were immersed in 0.4, 0.5 and 0.6M HCl solution with and without inhibitors for 24 hour duration at room temperature. The effects of Neem, leaves ark were used as inhibitor in 0.25, 0.50, 0.75, 1.00 and 1.25% concentration. The corrosion rate was reported in mpy. Then the rate of corrosion, inhibition efficiency and degree of surface coverage were determined. The experiment was conducted at 303K.

2) Polarization

When electrochemical corrosion occurs, the current that flows between anode and cathode causes a change in the electrode potential, this change is termed as polarization. Electrochemical experiments were carried out in a conventional three-electrode glass cell of capacity 230ml, using a GAMRY Potentiostat/ Galvanostat electrochemical computer unit. For the polarization study, metal specimens of rectangular design having an area of 1 mm^2 were exposed to corrosive solutions. Aluminum was used as a working electrode, SCE was used as reference electrode and the auxiliary graphite electrode was placed in corrosive media through which external current was supplied automatically from the computerized polarization instrument. The change in potential was measured by potentiostate / galvanostate on the potentiostate mode with 5 mV/ sec scan rate. Polarization has been taken with and without inhibitors in 0.4 M HCl. The curves show polarization of both the anodes and cathodes.

III. RESULTS AND DISCUSSION

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The results are presented in Tables I to II and Figures 1 to 4. To assess their protective value, Azardirachta indica leaves extract was added to solutions of HCl. Corrosion rate was calculated by the following equation:

$$CR\ (mpy) = \frac{534\mathrm{W}}{\mathrm{DAt}} \qquad (1)$$

Where, ‘W’ is the weight loss of Aluminum in grams, ‘A’ is the surface area of specimen in inches square, ‘D’ is the density of aluminum and ‘t’ is the time in hours. The effects of acid concentration on the aluminum alloy are shown in Figure 1. The results revealed that on increasing acid concentration there is an increase of corrosion rate in the absence and presence of Azardirachta indica leaves extract. The increase in corrosion rate in the absence of extract is higher acid concentration studied, suggests more aggressiveness of free acid solution. The increase in corrosion rate with increase in acid concentration may be probably due to decreasing strength of adsorption.

The inhibition efficiency (η%) and degree of surface coverage (θ) at each concentration of ark of Azardirachta indica (Neem) leaves were calculated by comparing the corrosion loss in absence (W_u) and presence of inhibitor (W_i) using the relationships:

$$\eta\% = \frac{\mathrm{W_u} - \mathrm{W_i}}{\mathrm{W_i}} \times 100 \qquad (2)$$

$$\theta = \frac{\mathrm{W_u} - \mathrm{W_i}}{\mathrm{W_i}} \qquad (3)$$

From the Figure 2, at constant acid concentration the inhibition efficiency of Neem leaves ark increase with increases in inhibitor concentration, e.g. the inhibition efficiency increases from 78.04 to 90.92% as the inhibitor concentration increases from 0.25 to 1.25% respectively in 0.4M acid concentration.

The enhanced effectiveness of the inhibitor with concentration is explicable in the light of the extent of adsorption of the inhibitor molecules on the metallic surface. It may be assumed that the film formed by the adsorbed molecules of the inhibitors on the metal surface is the sole criteria for lowering the surface area of cathodic and anodic reactions.

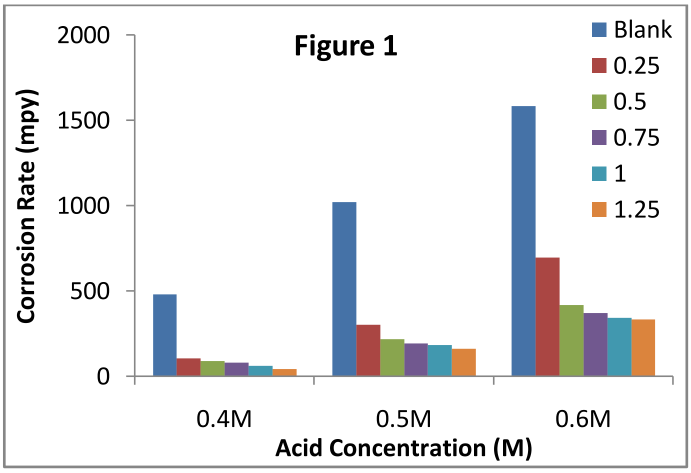

Fig. 1 plot of Corrosion rate of presence and absence inhibitor at various acid concentrations for 24 hours.

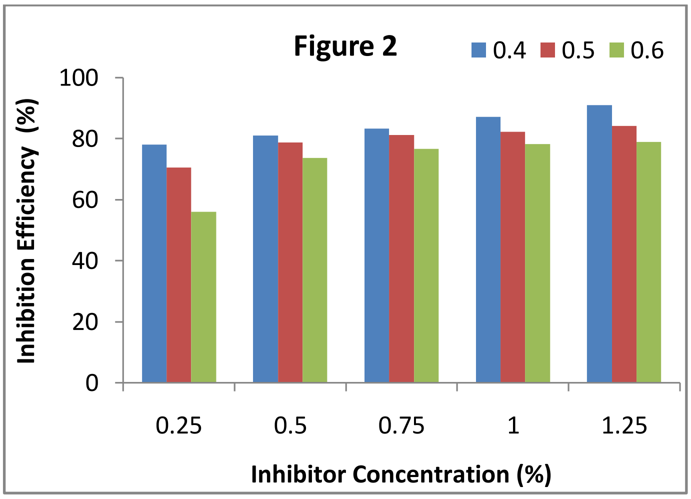

Fig. 2 Plot between inhibition efficiency η(%) and concentration of inhibitor in various concentration of HCl.

At any instant a fraction 'θ' of the metal surface is covered by the inhibitor molecules and uncovered fraction (1-θ) reacts with acid as it does in the absence of the inhibitor. The nature of the inhibitor interaction with the corroding surface has been deduced from the adsorption characteristics of the inhibitor. Surface coverage, values are very useful in explaining the adsorption characteristics. (Table I)

Table I Surface Coverage Area of Aluminum In HCL Containing Azardirachta Indica Inhibitors for 24 Hours.

Inhibitor	**Inhibitor Concentration**	**Acid Concentration**		
		0.4 M	**0.5 M**	**0.6 M**
	%	**θ**	**θ**	**θ**
Azardirachta indica (Neem)	0.25	0.7804	0.7043	0.5602
	0.5	0.8086	0.7862	0.7360
	0.75	0.8329	0.8116	0.7658
	1	0.8711	0.8208	0.7822
	1.25	0.9092	0.8416	0.7882

Adsorption isotherm provides useful insights into the mechanism of corrosion inhibition. The adsorption equilibrium constant, K_{ads}, is expressed as:

$$K_{ads} \cdot C = \theta / (1-\theta) \qquad (4)$$

Where C is the concentration of Neem in g/l; θ is the fractional surface coverage and K_{ads} is the adsorption equilibrium constant. The fractional surface coverage, θ was evaluated. The fractional surface coverage θ and the adsorption equilibrium constant K_{ads}, was found large at higher concentration of Neem, hence it is concluded that higher concentration of Neem is essential for maximum adsorption over aluminum metal surface.

The linear plot (Figure 3) with high correlation coefficient and slope of about unity clearly (values of R^2 in range; 0.837 to 0.977) will reveal that the surface adsorption process of Neem on the aluminum alloy surface obey the Langmuir adsorption isotherm. Therefore, one can infer that physical adsorption occurred.

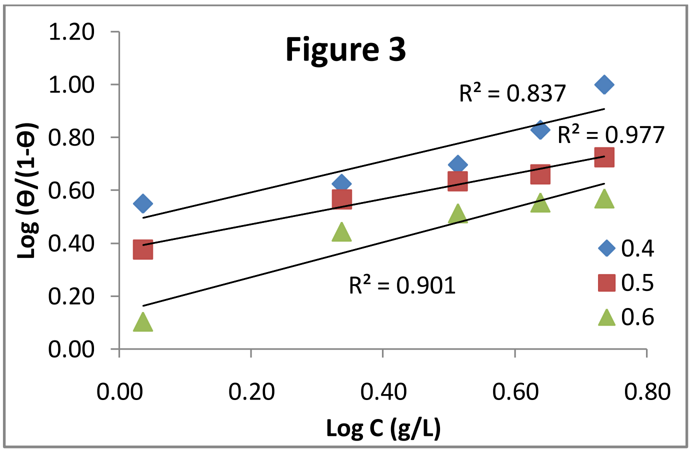

Fig. 3 Plot of log (θ /1- θ) versus log C for Neem leaf extract at various concentrations of HCl for 24h at 301K.

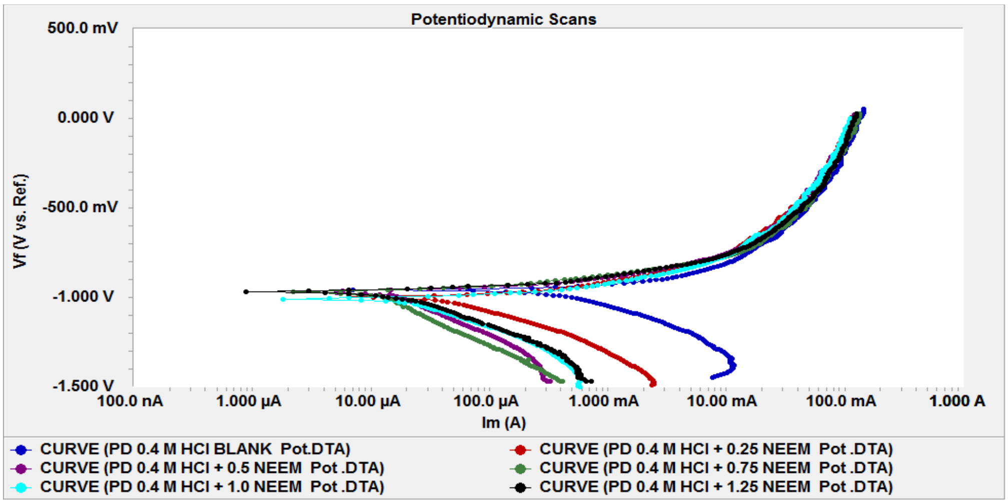

Fig.4 Polarization curves for aluminum in 0.4 M HCl with and without Neem leaves ark as inhibitor.

Table II Polarization Data and Inhibition Efficiency of Neem for Aluminum in 0.4 M HCL.

Inhibitor Concentration	**E_{corr} mV**	**i_{corr} (µA/cm^2)**	**Tafel slope (V / decade)**		**Inhibition efficiency (%)**	
			anodic +βa	**Cathodic -βc**	**Polarization method (i_{corr})**	**Weight loss method**
Blank	-958	203.0	6.87E-02	2.53E-01	-	-
0.25%	-997	30.6	3.75E-02	1.60E-01	84.93	78.04
0.50%	-966	13.6	2.82E-02	2.85E-01	93.30	80.86
0.75%	-970	12.5	3.83E-02	4.13E-01	93.84	83.29
1.00 %	-999	11.9	3.33E-02	8.77E-02	94.14	87.11
1.25 %	-967	6.37	2.58E-02	8.71E-02	96.86	90.92

Anodic and Cathodic polarization curves for aluminum in 0.4M HCl at 0.25 to 1.25% inhibitor concentration of the presence and absence of inhibitors are shown in Fig. 4. It is evident from the figure that cathodic tafel slopes (βc) remain almost unchanged with increasing inhibitor concentration. This indicates that hydrogen evolution is activation controlled and the addition of inhibitor did not change the mechanism of cathodic hydrogen evolution reaction [35], [36]. It is clearly observed from the figure the addition of Azardirachta indica extract in acid solution indicates that the corrosion current density (i_{corr}) and corrosion rate significantly decreases with respect to the blank. There is significant change in the anodic and cathodic slopes after the addition of the inhibitor. If the change in corrosion potential E_{corr}value was more than 85 mV, a chemical compound could be recognized as an anodic or a cathodic type inhibitor. The maximum shift in Ecorr was 41 mV towards cathodic direction indicating mixed mode of corrosion with predominately cathodic effect. The values for the Tafel parameters obtained from this plot with and without inhibitors are reflected in Table II. The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency *(η %)* was calculated using the following equation (5).

$$\eta\% = \frac{i_{corr}\,(u) - i_{corr}\,(i)}{i_{corr}\,(u)} \times 100 \qquad (5)$$

The hydrogen evolution type of attack is predominating and no other factors influence the corrosion process, corroded by the hydrochloric acid should be maximized. Nimbin was the first bitter compound isolated from Neem oil, and thereafter more than 135 compounds have been isolated from Neem and several reviews have also been published on the chemistry and structural variety of these compounds which are divided into two major classes: isoprenoids [37] and others. The isoprenoids include diterpenoids (namely sugiol, nimbiol, margasone) and triterpenoids containing protomeliacins, liminoids, azadirone and its derivatives, genudin and its derivatives, vilarin type of compounds and C-secomeliacins such as nimbin, salannin and azadirachtin.All of above compunds contain one five membered heterocyclic ring with oxygen heteroatom and is liable to resist the corrosion process [32].

IV. CONCLUSIONS

Azardirachta indica (Neem) leaves extract was found to inhibit the corrosion of aluminum in 0.4-0.6M hydrochloric acid solution and inhibition efficiency increases with increasing extract concentration. At the highest concentration of 1.25%, the inhibition efficiency increased clearly to a maximum value of 91%. Potentiodynamic polarization curves proved that the neem leaves extract was a mixed-type inhibitor. The adsorption isotherms obey the Langmuir adsorption isotherms.

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