Azadirachta indica Leaf as a Corrosion Inhibitor for Coper in Nitric Acid

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The effect of Azadirachta indica leaf (AIL) extract on the corrosion of copper in 1M HNO_3 was investigated by weight loss technique. The result showed that the corrosion rate decreased in the presence of plant extract and inhibition efficiency increased with increasing the concentration of extract. The decreased corrosion rate was due to adsorption of plant extract which was discussed on the basis of Langmuir adsorption isotherm.

Keywords: Corrosion inhibition, copper, Azadirachta Indica, weight loss

Copper and its alloys have good corrosion resistance in water and have excellent heat conductivity, but these corrode easily in acidic solutions. Copper and its alloy are widely used in heating systems and condensers [1]. Acid solutions are often used in industry and some of the important fields of application are acid pickling, chemical cleaning and processing and ore production [2-4]. Copper requires strong oxidants in order to corrode. The most commonly used corrosive solution contains nitric acid, so this medium has induced a great deal of research on copper corrosion [5, 6]. The use of inhibitor is an important method of protecting materials against corrosion. Inhibitors are chemicals that often protective adsorbing themselves on the metallic surface, protecting the metal surface by forming a film [7, 8]. Most corrosion inhibitors are either synthesized from cheap raw materials or chosen from organic compounds containing electronegative functional groups and ð-electrons in triple or conjugated double bonds. The presence of aromatic rings and hetero atoms (such as S, N, O, P) are the major adsorption centers for these inhibitors [9-15]. Considerations of cost, biodegradability, toxicity, availability and environment friendliness are of considerable importance. Consequently, there exists the need to develop a new class of corrosion inhibitors with low toxicity and good efficiency. The exploration of natural products of plant origin as inexpensive eco-friendly corrosion inhibitors is an essential field of study. The plant extracts are rich sources of organic molecules which have appreciably high inhibition efficiency and hence termed as eco friendly or green inhibitors. These inhibitors are biodegradable and don't contain heavy metals or other toxic compounds [16-18]. The corrosion behavior of different inhibitors have been reported in the literature [19-24]. Azadirachta Indica (commonly known as Neem tree) is remarkable both for its chemical and for its biological activities. It is one of the richest sources of secondary metabolites in nature. More than 300 natural products have been isolated from different parts of the tree a number of them have been shown to have antifungal, antimalarial and antiviral properties [25-28].

The present work was on the growing interest in environmentally benign corrosion inhibitors. The corrosion inhibitor chosen is the low cost natural extract of the plant Azadirachta Indica. The present work aims to study (i) the corrosion inhibition of copper in 1M nitric acid (ii) to evaluate the activation energy and heat of adsorption (iii) to determine the best adsorption isotherm for the adsorption of the extracts of Azadirachta Indica onto the copper surface.

Experimental part

Materials

Rectangular specimens of copper were mechanically pressed cut to form different coupons, each of dimension exactly 5 X 1.8 X 0.3 cm. The specimens were mechanically polished; a hole drilled at one end for free suspension and numbered by punching. The specimens were degreased with acetone, washed with distilled water and polished well with emery paper, cleaned, rinsed and dried, then stored in desiccators for present study. All reagents for the present study were AR grade and double distilled water was used for their preparation. Each specimen was suspended by a glass hook and immersed in a beaker containing exactly 100 mL of the test solution and left exposed to air. After the exposure, the test specimens were cleaned with acetone. Triplicate experiments were performed in each case and mean values of the mass loss were calculated.

Chemicals used

1M HNO_3 acid was prepared using analytical grade concentrated HNO_3 and double distilled water. The 1M HNO_3 acid solution was used for corrosion analysis and for extract preparation.

Extraction of plant materials

Azadirachta Indica leaves were collected from Chennai city of India. The leaves of the plant are shade dried and powdered. Plant materials were dried in shade so as to enrich the active principles in them, by reducing their moisture content. The stock solution of the inhibitor is prepared by refluxing 5 g dry powder with 100 mL of 1M nitric acid for 3 h. The refluxed solution is allowed to stand overnight and filtered through ordinary filter paper. The residue is repeatedly washed with small amounts of 1M HNO_3 and the filtrate made up to 100 mL. From this stock solution, different concentrations of inhibitor solutions ranging from 10 to 150 ppm are prepared.

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Weight loss Studies

The weight loss studies were carried out at 30°C by immersing previously weighed copper in 100 mL of the test solution in the presence and absence of the bio-inhibitor. The metal specimens were withdrawn from the test solutions after two hours. The mass loss was taken as the difference in weight of the specimens before and after immersion determined using, digital balance with a resolution of ± 1mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported. From the mass loss measurements, the corrosion rate was calculated using the following relationship [29].

$$\text{Corrosion Rate (mmpy)}, \; vR_{CORR} = \frac{87.6\,w}{D\cdot A\cdot T} \qquad (1)$$

where, mmpy = millimeter per year, w = Mass loss (g), D = Density (g/cm^3), A= Area of specimen (cm^2), T = time in hours.

The percentage inhibition efficiency (% IE) and degree of surface coverage (q) were calculated using equation -2 and 3, respectively;

$$\%\,IE = \frac{W_1 - W_2}{W_1}\,X\,100 \qquad (2)$$

$$\theta = \frac{W_1 - W_2}{W_1} \qquad (3)$$

where W_1 and W_2 are the weight loss in the absence and presence of the bio-inhibitor.

Results and discussions

The effect of acid concentration

The inhibition effects of various concentrations of nitric acid have been studied. The corrosion rates are summarized in table 1. The inspection of these values shows that the weight loss increases with increasing the concentration of acid. This attributed to presence of water air and H^+ which accelerate the corrosion process. This indicates that the corrosion rate of copper is a function of the concentration of acid solutions. This observation agrees with the fact that the rate of a chemical reaction increases with increasing concentration and probably due to the increase in the rate of diffusion and ionization of active species in the corrosion reaction. This conforms to reports by Omodudu and Oforka [30].

Table 1

EFFECT OF ACID CONCENTRATION ON THE CORROSION RATE OF COPPER AT 30°C

Concentration of acid (M)	Weight Loss (g)	Corrosion rate (mmpy)x10^{-3}
0.5	0.2596	3.4
1	0.5567	7.4
1.5	0.6769	9.0
2	0.9140	12.1
2.5	0.9145	12.1

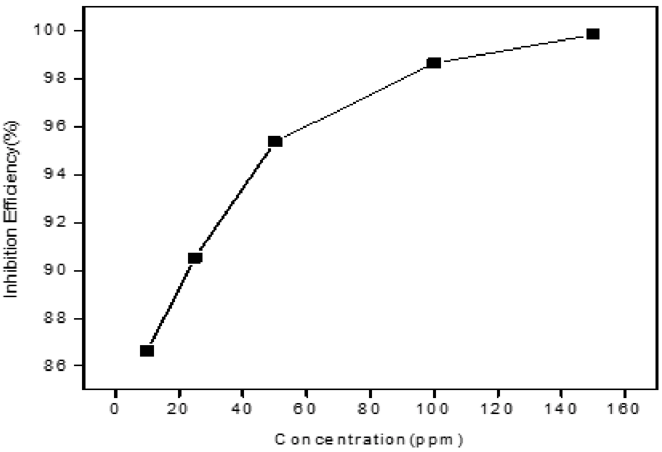

Fig. 1. Inhibition efficiencies of copper in various concentration of AIL extract at 303 K in 1M HNO_3

Effect of inhibitors concentration

The corrosion inhibition of copper in 1M HNO_3 containing different concentration (10-150 ppm) of AIL extracts by weight loss method after two hours exposures were carried out and the results are given in table 2. From table 2, it is obvious that the inhibition efficiency increases with the increase in the concentration of plant extract. This suggests that as the concentration of plant extract is increased, the number of molecules adsorbed over the copper surface increases which block the active sites where direct acid attack proceeds, thereby protecting the metal from corrosion. Figure 1 shows the variation of percent inhibition efficiency with concentration of inhibitor in ppm. The degree of the surface coverage q which represents the part of the metal surface covered by inhibitor molecules was calculated using equation 3. Inspection of this table, the data revealed that as the plant extract concentration is increased, the corrosion rate decreased while the inhibition efficiency percent IE % and surface coverage q, increase. This behavior may be attributed to be the increased the surface coverage due to increase of the number of adsorbed molecules on copper surface [31].

Effect of Temperature

To gain insight into the nature of the inhibitor adsorption, the effect the temperature on the corrosion behavior and the inhibition efficiency of copper in 1M HNO_3 solution in presence of different concentration of extract were studied by weight loss method for a fixed immersion time of two hours and the results are given in table 3. The data in table 3 indicate that the corrosion rate of copper in absence and presence of the plant extracts increased with increasing temperature. This is because an increase in temperature usually accelerates corrosion processes, particularly in acid media in which H_2 gas evaluation accompanies corrosion, giving rise to higher dissolution rates of the metal. The values

Table 2

EFFECT OF EXTRACT CONCENTRATIONS ON (R_{CORR}), (IE %) AND (q) FOR COPPER IN 1M HNO_3 SOLUTION AT 30°C

Concentration of inhibitor (ppm)	R_{CORR} x10^{-2} (mmpy)	IE %	θ
10	2.62	86.63	0.8663
25	2.17	90.52	0.9052
50	0.38	95.35	0.9535
100	0.20	98.63	0.9863
150	0.05	99.83	0.9983

of IE % of the extracts decrease with increasing temperature and the highest inhibition efficiency being 30°C. This decrease in inhibition efficiency with rise in temperature, suggests the possible desorption of some of the adsorbed inhibitor from the metal surface at higher temperatures. This gives a clue that the mechanism of adsorption of the inhibitor may be mainly due to physisorption, because the physisorption which is due to weak Van der Waal's forces, disappears at elevated temperatures. It may be further attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of copper that may otherwise inhibit the corrosion process. Thus, as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency [32-34].

The heat of adsorption on copper in the presence of bio-inhibitor is calculated by the following equation [35];

$$Q_{ads} = 2.303R[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)]\ (T_2T_1/T_2-T_1) \qquad (4)$$

where R is the gas constant, q_1 and q_2 is the degree of surface coverage at temperatures T_1 and T_2 respectively. The calculated values of Q_{ads} are reported in table 3. These values range from -39.85 to -74.71 KJ/mol. The negative values are indicated that the adsorption of bio-inhibitor on copper surfaces is exothermic [36].

Adsorption isotherm

The nature of corrosion inhibition has been deduced in terms of the adsorption characteristics of the inhibitors. The adsorption of organic compounds can be described by two main types of interaction; physical adsorption and chemisorptions [37]. These are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. The interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm. In order to obtain a proper adsorption isotherm, Langmuir adsorption isotherm is used. By plotting values a log C/q versus log C, linear plots are generated (fig. 2) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of plant extract on copper surface. This involves the assumption of no interaction between the adsorbed inhibitor constituents on the copper surface [38]. The equilibrium constant of adsorption of AIL extract on the surface of copper is relate to the free energy of adsorption DG^0_{ads} by the following equation;

$$\Delta G^o_{ads} = -2.303\ RT \log(55.5K) \qquad (5)$$

where R -gas constant, T- temperature and K is the equilibrium constant of adsorption. The negative values of DG°ads ensure the spontaneity of adsorption process and stability of the adsorbed layer on the copper surface. Generally, the values of DG°ads around 20 KJ/mol or lower are consistent with physisorption while those around -40 KJ/mol or higher involve chemisorptions [39]. The values of free energy, DG°ads are shown in table 4 which in consistent with literature survey and therefore authenticates physical adsorption [39]. This implies that the plant extract adheres on the surface of the corroding system and so gives a very strong inhibitor.

Table 3
EFFECT OF INHIBITIOR CONCENTRATIONS ON (R_{CORR}) AND (IE %) FOR COPPER IN 1M HNO_3 SOLUTION AT 30°C AND 60°C

Concentration of inhibitor (ppm)	AIL				
	R_{CORR} x10^{-2} (mmpy)		IE %		$-Q_{ads}$ (KJ.mol^{-1})
	30°C	60°C	30°C	60°C	
10	1.41	0.1468	86.63	70.06	70.17
25	0.80	0.1231	90.52	74.88	72.15
50	0.53	0.0957	95.35	80.48	74.71
100	0.44	0.0616	98.63	87.42	65.39
150	0.38	0.0203	99.83	89.31	39.85

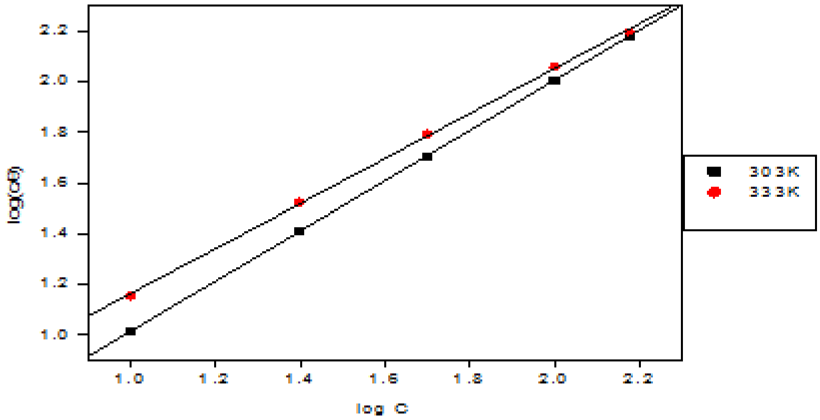

Fig. 2. Langmuir isotherm for the adsorption of AIL extract on copper in 1M HNO_3 at 303K and 333K

Table 4
LANGMUIR ADSORPTION PARAMETERS FOR THE ADSORPTION OF AIL EXTRACT ON COPPER IN 1M HNO_3

Name of the Inhibitor	Adsorption isotherm	Temperature (Kelvin)	Slope	log K	R	$-\Delta G_{ads}$(KJ/mol)
AIL	Langmuir	303	0.992	1.6447	0.999	10.25
		333	0.889	0.5626	0.999	12.87

Inhibition mechanism of plant extract

The obtained results indicated that plant extract performs a good inhibition for the corrosion of copper in HNO_3 solution. The inhibition efficiency depends on many factors including, number of adsorption sites, functional groups, molecular size and mode of interaction [40]. Plant extracts are viewed as an incredible rich source of naturally synthesized chemical compounds. These large numbers of different chemical compounds may form adsorbed intermediates (organo-metallic complexes) [41] which may either inhibit or catalyze further metal dissolution. Most investigators claim a particular compound in plant extract as solely responsible for the inhibition ability of the extract. This in the real sense is not true, since most plant extract are composed of numerous organic compounds capable of either inhibiting or accelerating the corrosion process. The net (antagonistic and synergistic) action of the phytochemical components of the plant is what is actually recorded as the inhibition efficiency of the plant extract [42]. Like most medicinal plants, Azadirachta indica is composed of numerous naturally occurring organic compounds. Most of these compounds have complicated molecular structures, large molecular weights and significant number of oxygen, sulphur and nitrogen atoms incorporated in the structure. These compounds can adsorb on the metal surface via the lone pairs of electrons present on their oxygen, sulphur and nitrogen atoms. The adsorption of such compounds on the metal surface creates a barrier for charge and mass transfer leading to a decrease in the interaction between the metal and the corrosive environment [43]. Analysis of the temperature dependence of inhibition efficiency in absence and presence of inhibitor give some insight into the possible mechanism of inhibitor adsorption. An increase in inhibition efficiency with rise in temperature, in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of chemically adsorption film. While a decrease in inhibition efficiency with rise in temperature, in the presence of inhibitor compared to its absence, is ascribed to physical adsorption mechanism. The trend in inhibition efficiency with temperature obtained (table 3) suggests physisorption of the phytochemical constituents of the plant extract on the surface of the metal.

Conclusions

Azadirachta Indica extract acted as corrosion inhibitor for copper in 1M HNO_3 solution. The inhibition efficiency of copper in 1M HNO_3 increase with the increase in plant extracts concentration but decreased with increase in temperature. The corrosion process is inhibited by adsorption of the plant extracts onto the copper surface following the Langmuir adsorption isotherm. The values of free energy of adsorption calculated indicate strong, spontaneous and physical adsorption of the extracts on the copper surface. This present study provides new information on the inhibiting characteristics of plant extract under specified conditions. The environmentally friendly inhibitor could find possible applications in metal surface anodizing and surface coating in industries.

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