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Corrosion Inhibition of Aluminium in Acidic Medium by Ethanol Leaf Extract of *Azadirachta indica*

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Abstract: The inhibition of aluminium corrosion in hydrochloric acid solution by ethanol leaf extract of *Azadirachta indica* was studied by weight loss and thermometric methods. Results obtained show that *Azadirachta indica* leaf extract leaf extract is a good inhibitor of aluminium corrosion in HCl solution. The inhibition efficiency increased with increase in *Azadirachta indica* leaf extract concentration but decreased with increase in temperature. The inhibition efficiencies by both weight loss and thermometric methods followed the same trend. The calculated thermodynamic parameters revealed that the adsorption of *Azadirachta indica* leaf extract onto aluminium surface occurred spontaneously and conformed to the Langmuir adsorption isotherm.

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INTRODUCTION

The corrosion resistance of aluminium in many aggressive media is very good. This is attributed to the thin oxide film on it. However, in chloride solutions, aluminium is susceptible to pitting corrosion (Younis et al., 2012). Among the methods of preventing corrosion of metals, the most cost – effective is the use of corrosion inhibitors. The traditional inhibitors in use over the years have been inorganic and synthesized organic compounds. Their use is being limited due to environmental safety concerns. The focus of researchers nowadays has shifted to sourcing inhibitors from natural products. Such inhibitors are biodegradable, cheap, non-toxic and environmentally friendly.

Azadirachta indica (Neem) belongs to the family Meliaceae. The phytochemical analysis of *Azadirachta indica* leaf extract showed the presence of tannins and phenolic compounds, alkaloids, carbohydrates, reducing sugars, flavonoids, glycosides and saponins (Prashanth and Krishnaiah, 2014). The use of parts of *Azadirachta indica* for traditional medicinal practice in India has been reported (Chopra et al.,1956; Varma, 1976; Drabu et al., 2012). In south eastern Nigeria, the gin (ethanol) extract from *Azadirachta indica* leaf is used traditionally for the treatment of malaria fever.

Extracts from parts of *Azadirachta indica* have been reported as good inhibitors of metal corrosion in acidic media; this include mild steel (Eddy and Mamza, 2009; Okafor et al., 2010; Loto et al., 2011; Desai, 2015), zinc (Sharma et al., 2009), stainless steel (Obiukwu et al., 2013) and aluminium (Arab et al.,2008). Limited work (Ajanaku et al., 2015) has been done on the inhibitory effect of ethanol leaf extract of *Azadirachta indica* on aluminium corrosion in acidic medium. The aim of this work was to inhibit the corrosion of aluminium by ethanol leaf extract of *Azadirachta indica* in hydrochloric acid solution.

MATERIALS AND METHODS

Test materials

Aluminium sheet (purity 98.5%) of the type AA1060 used for this work was obtained from System Metal Industries Limited, Calabar, Nigeria. Each sheet was 0.4 mm in thickness and was mechanically press cut into 4 cm x 5 cm coupons. The surface treatment of the coupons involved degreasing in absolute ethanol, drying in acetone and storing in a moisture – free desiccator prior to use in corrosion studies.

Preparation of *Azadirachta indica* leaves extract

Fresh leaves of *Azadirachta indica* were collected from a farm in Calabar, Nigeria. They were plucked, washed and shade – dried at 30°C for seven days. They were then ground to powder. The dried ground samples of *Azadirachta indica* was macerated with 90% ethanol for seven days at room temperature in a large glass trough with cover. The mixture was then filtered. The filtrate was evaporated at 40°C in a water bath to constant weight, leaving a dark green extract in the beaker. Extract concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L, and 2.0 g/L, respectively in 0.5M HCl solution were used for the weight loss studies at 30°C and 60°C. The same extract concentrations were used in 2M HCl solution for the thermometric tests.

Weight loss measurements

The apparatus and procedure followed for the weight loss measurements were as previously reported (Abakedi and Moses, 2016). The corrodent concentration was kept at 0.5M HCl and the volume of the test solution used was 100 mL. The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss which was used to compute the corrosion rate given by (Abakedi, 2016):

$$CR\ (mg\ cm^{-2}hr^{-1}) = \left(\frac{W}{A\ t}\right) \qquad (1)$$

where W is the weight loss (mg), A is the surface area of the specimen (cm^2) while tisthe exposure time (hr).

The inhibition efficiency (I%) of ethanol leaf extract of *Azadirachta indica* (AZI) in 0.5M HCl was calculated using the formula:

$$\%I = \left(\frac{CR_0 - CR_1}{CR_0}\right) \times 100 \qquad (2)$$

where CR_0 and CR_1 are the corrosion rates of aluminium coupons in the absence and presence of inhibitors, respectively, in the corrodent at the same temperature.

Thermometric measurements

The reaction vessel and procedure for determining the corrosion behaviour by this method is as described in literature (Mousa et al., 1988; El – Etre, 2001). In the thermometric technique the corrodent concentration was kept at 2M HCl. The volume of test solution used was 50 mL. The initial temperature in all experiments was kept at 30.0°C. The progress of corrosion reaction was monitored by determining the changes in temperature with time using a calibrated thermometer (0 -100°C) to the nearest ± 0.1°C. This method enabled the computation of the reaction number (RN) defined as (Oza and Sinha, 1982):

$$RN\ (°C\ min^{-1}) = \frac{T_m - T_i}{t} \qquad (3)$$

where T_m and T_i are the maximum and initial temperatures, respectively, while 't' is the time (min) taken to reach the maximum temperature. The inhibition efficiency (%I) was evaluated from percentage reduction in the reaction number, via the equation:

$$\%I = \left(\frac{RN_0 - RN_1}{RN_0}\right) \times 100 \qquad (4)$$

where$RN_0$is the reaction number in the absence of inhibitors (blank) and $RN_1$is the reaction number in the presence of studied inhibitor.

RESULTS AND DISCUSSION

Effect of extract concentration on inhibition efficiency

Figure 1 shows that there was a significant reduction in the corrosion rates of aluminium in0.5M HCl solution in the presence of *Azadirachta indica* (AZI) leaf extract concentration compared to the blank at 30°C. A similar result was also obtained at 60°C, though with higher corrosion rates. This indicates that the metal coupons corrode less in the HCl solution containing the additives than in their absence (Ita et al., 2013). Figure 2 illustrates that the inhibition efficiency, at a particular temperature, increases with increase in the concentration of AZI leaf extract (Figure 2). An increase in inhibition efficiency with increase in extract concentration indicates a strong interaction between the extract and metal surface (Ita et al., 2013).

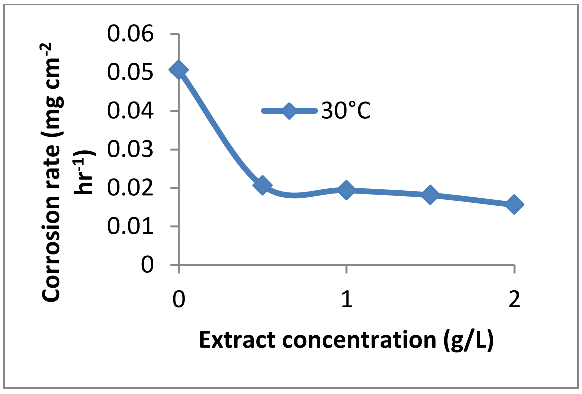

Figure 1:Variation of corrosion rate against AZI leaf extract concentrations for aluminium in 0.5M HCl at 30°C

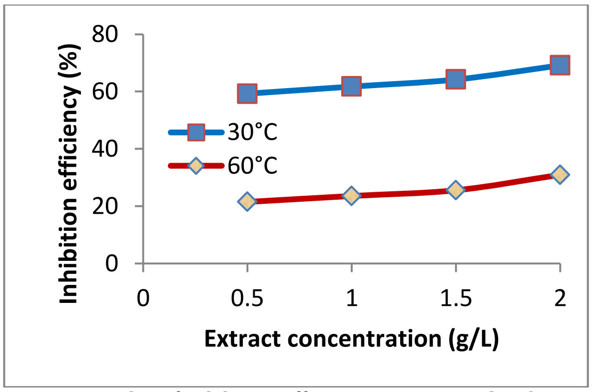

Figure 2: A plot of inhibition efficiency against *Azadirachta indica* (AZI) leaf extract concentrations for aluminium corrosion in 0.5M HCl at 30°C and 60°C

Thermometric studies

Figure 3 illustrates the thermometric measurements for aluminium corrosion in 2M HCl solution containing *Azadirachta indica* leaf extract. Inspection of Figure 3 shows that as the concentration of AZI leaf extract increases, the time required to reach the maximum temperature increases while the maximum temperature decreases. The calculated values of reaction number and inhibition efficiency are presented in Table 1. The data in Table 1 reveal that the inhibition efficiency of AZI leaf extract increased with increase in extract concentration. The inhibition efficiency by the thermometric method followed a similar trend as that of the weight loss method.

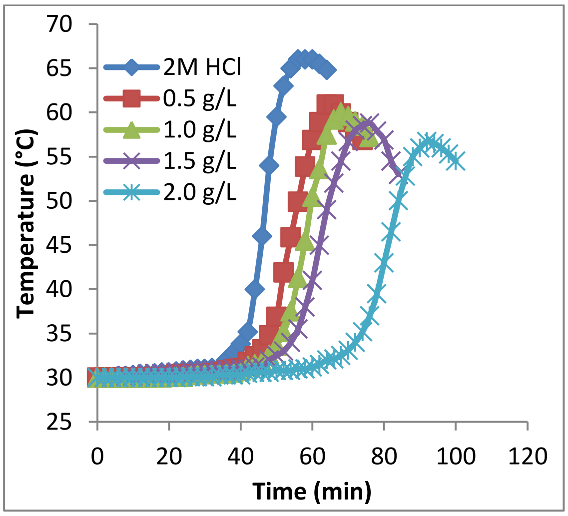

Figure 3: Temperature – time curves for aluminium corrosion in 2M HCl obtained in absence and presence of *Azadirachta indica* leaf extract

Effect of temperature on inhibition efficiency

Inhibition efficiency decreased with increase in temperature at all the concentrations of AZI leaf extract studied (Table 2). A decrease in inhibition efficiency with increase in temperature indicates a weakening of adsorption bonds between metal and inhibitor as well as physical adsorption mechanism. Consequently, AZI physically adsorbed onto the aluminium surface.

The activation energy (E_a) of the corrosion process in the absence and presence of the leaf extract was evaluated using the Arrhenius equation (Ita and Abakedi, 2006):

$$log\left(\frac{CR_2}{CR_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (5)$$

where CR_1 and CR_2 are corrosion rates at T_1 (303K) and T_2(333K),respectively, and R is the universal gas constant (8.314 JK^{-1} mol^{-1}).

The values of heat of adsorption (Q_{ads}) presented in Table 3 were calculated using the equation (Bhajiwala and Vashi, 2001):

$$Q_{ads} = 2.303R\left[log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\frac{T_1T_2}{T_2 - T_1}\right] \quad (6)$$

where $\theta_1$and θ_2 are the degrees of surface coverage at T_1 and T_2, respectively, and R is the universal gas constant.

The calculated values of activation energy (E_a) from equation (5) are presented in Table 3. It is observed that the E_a values in the presence of AZI leaf extract are higher than the E_a value for the blank (107.737 kJ mol^{-1}). The higher E_a values in the presence of inhibitor compared to the blank coupled with a decrease in the inhibition efficiency with increase in temperature can be interpreted as an indication of physical adsorption of the inhibitor on the metal surface (Dehri and Ozcan, 2006).The Q_{ads} values for aluminium corrosion in 0.5M HCl containing AZI leaf extract as presented in Table 3 are negative and ranged from – 46.681 kJ mol^{-1} to – 44.975 kJ mol^{-1}. Negative values of Q_{ads} indicate that the adsorption of AZI leaf extract onto aluminium surface and hence the inhibition efficiency decreased with increase in temperature (Anozie et al., 2011).Negative Q_{ads} values are consistent with physical adsorption (physisorption) characteristics (Ejikeme et al., 2014).

Table 1: Effect of *Azadirachta indica* leaf extract on inhibition efficiency of aluminium corrosion in 2M HCl solution (Thermometric measurements)

Extract concentration (g L^{-1})	Initial temperature T_i (°C)	Maximum temperature T_m (°C)	Time taken to reach maximum temp. t (min)	Reaction number RN (°C min^{-1})	Inhibition efficiency (%)
2M HCl	30.0	66.0	56	0.6429	-
0.5	30.0	61.2	65	0.4800	25.34
1.0	30.0	57.0	66	0.4091	36.37
1.5	30.0	58.8	76	0.3789	41.06
2.0	30.0	56.7	92	0.2902	54.86

Table 2: Calculated values of corrosion rate and inhibition efficiency for aluminium corrosion in 0.5M HCl solution (blank) containing *Azadirachta indica* (AZI) leaf extract (Weight loss measurements)

Extract concentration	Corrosion rate (mg cm^{-2} hr^{-1})		Inhibition efficiency (%)	
	30°C	60°C	30°C	60°C
0.5M HCl (blank)	0.0506	2.3831	-	-
0.5 g/L AZI	0.0206	1.8706	59.26	21.51
1.0 g/L AZI	0.0194	1.8213	61.73	23.58
1.5 g/L AZI	0.0181	1.7663	64.20	25.58
2.0 g/L AZI	0.0156	1.6450	69.14	30.97

Table 3: Calculated values of activation energy and heat of adsorption for aluminium corrosion in 0.5M HCl solution containing *Azadirachta indica* (AZI) leaf extract

Extract concentration	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})
0.5M HCl (Blank)	107.737	-
0.5 g/L AZI	126.098	- 46.681
1.0 g/L AZI	127.029	- 46.257
1.5 g/L AZI	128.112	- 46.199
2.0 g/L AZI	130.279	- 44.975

Adsorption isotherm

The adsorption of AZI leaf extract was found to obey the modified Langmuir adsorption isotherm defined as:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \qquad (7)$$

where C is the inhibitor concentration, θ is the degree of surface coverage while K_{ads} is the equilibrium constant of the adsorption process. Plot of C/θ against C gives straight lines (Figure 4). The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 4. The equilibrium adsorption constant, K_{ads}, is related to the standard free energy of adsorption (ΔG^0_{ads}) by the formula (Verma and Khan, 2016):

$$\Delta G^0_{ads} = -RT\ ln(55.5K_{ads}) \qquad (8)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant while T is the absolute temperature. The negative values of ΔG^0_{ads} indicate that the adsorption of AZI leaf extract on aluminium surface occurred spontaneously. Furthermore, values of ΔG^0_{ads} less negative than -20 kJ mol^{-1} are attributed to electrostatic interaction between the charged inhibitor and the charged metal surface implying a physical adsorption process. Conversely, values of ΔG^0_{ads} less negative than -40kJ mol^{-1} are generally considered to involve charge sharing between the inhibitor and the metal surface and signifies a chemical adsorption process (Khaled and Al-Qahtani, 2009). The values of ΔG^0_{ads} in this work being less negative than -20kJ mol^{-1} coupled with a decrease in the inhibition efficiency with increase in temperature indicates that the adsorption of *Azadirachta indica* leaf extract on aluminium surface occurred by a physical adsorption mechanism.

CONCLUSION

This work reveals that *Azadirachta indica* leaf extract inhibited the corrosion of aluminium in hydrochloric acid solution. The inhibition efficiency was found to increase with increase in extract concentration but decreased with increase in temperature. The adsorption of *Azadirachta indica* leaf extract onto aluminium surface best fit the modified Langmuir adsorption isotherm. The negative values of ΔG^0_{ads} reflect the spontaneity of the corrosion inhibition process. Based on a decrease in the inhibition efficiency with increase in temperature, physical adsorption (physisorption) mechanism has been proposed for the adsorption of the leaf extract on aluminium surface.

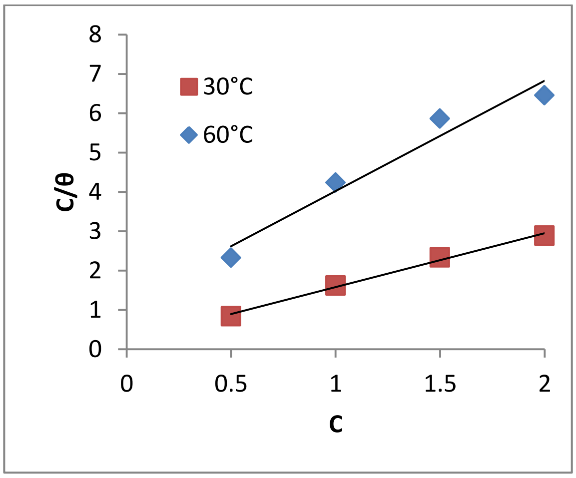

Figure4**:** Plot of C/θ vs. C(Langmuir isotherm) for aluminium corrosion in 0.5M HCl containing AZI leaf extract

Table 4. Some parameters of the linear regression of Langmuir adsorption isotherm for aluminium corrosion in 0.5M HCl solution containing AZI leaf extract

Temperature	R^2	n	$1/K_{ads}$(g L^{-1})	K_{ads} (g^{-1} L)	ΔG^0_{ads} (kJ mol^{-1})
303K	0.9947	1.37	0.2074	4.8216	-14.0807
333K	0.9549	2.80	1.2160	0.8224	-10.5783

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