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Studies of Gmelina aborea fruits latex as environmental friendly inhibitor on aluminium corrosion in HCl

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Abstract

The ability of crude Gmelina aborea fruits latex without carrying out any solvent extraction of the fruits to inhibit the corrosion of aluminium in 1.0 M HCl solution was determined using weight loss method. The inhibition efficiency was found to increase with the increase in concentration of the inhibitor and decrease with the increase in temperature. The inhibition efficiency of 94.13% was the highest recorded in the presence of $5.0\ mL/L$ inhibitor concentration. The negative signs on the Gibb's free energy (ΔG) suggested a spontaneous process for the adsorption of Gmelina aborea on aluminium surface. The thermodynamics and kinetics data indicated exothermic and physisorption process which was supported by FTIR spectra. The adsorption mechanism was more fitted to Langmuir model of adsorption.

Keywords: Adsorption; aluminium; corrosion; inhibitor; kinetics; thermodynamics

1. Introduction

Although aluminium is the most abundant metal in earth's crust, its extraction is costly due to its reactivity. As the only industrial method of production, electrolysis method is costly, required a significant amounts of energy, causes serious environmental pollution, and high-grade bauxite is required [1]. Aluminium is used in making variety of products including cans, foils, kitchen utensils, window frames, electrical appliances, aeroplane body parts, packaging materials, automobiles, wind and solar energy equipment [2].

Corrosion of metals is an electrochemical reaction which involves oxidation of the anode into a positive ion, which is released from the solid metal. Aluminum exhibits a passive behavior in aqueous solution due to the protective Al_2O_3 film on its surface. However, the solubility of the protective film increases in acidic and alkaline medium [3]. The corrosion of aluminium in acidic medium involves anodic oxidation and catholic reduction. The rate of oxidation equals the rate of reduction in terms of electron production and consumption:

$$Al_{(s)} \rightarrow 2Al^{3+}_{(aq)} + 6e^{-} \qquad \text{Oxidation} \qquad (1)$$

$$6Al^{+}_{(aq)} + 6e^{-} \rightarrow 3H_{2(g)} \qquad \text{Reduction} \qquad (2)$$

$$Al_{(s)} + 6H^{+}_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3H_{2(g)} \qquad \text{Redox} \qquad (3)$$

Some control and prevention methods have been proposed to overcome the corrosion problems. The methods proposed include material selection, coatings, corrosion inhibitors, the cathodic protection and change in material design [4].

The use of corrosion inhibitor to arrest or control corrosion have become a common practice, however most of these inhibitors are expensive, toxic and not environmentally friendly [5]. There has been increasing search for green or organic corrosion inhibitors [6]. The plants inhibitors have been tested and found to be environmentally friendly, nontoxic, biodegradable, inexpensive and readily available [7]. The plant inhibitors are usually obtained from the plants parts such as leaves, roots, stems, barks and fruits by solvent extraction of these plant's parts. From economic point of view, these solvents are expensive and it has been reported that almost all the solvents are hazardous to health. Health hazards associated with solvent exposure include damage to nervous system, reproductive system, liver, kidney, respiratory impairment, cancer, and dermatitis [8].

The aim of this work is to investigate the environmentally friendly corrosion inhibition potential of Gmelina aborea fruit latex without carrying out any solvent extraction on the corrosion of aluminium in 1.0M HCl.

2. Materials and Methods

2.1. Coupon Preparation

Sheet of aluminium was pressed cut into coupons (2 cm × 2 cm). The coupons were degreased with acetone and washed with deionized water, dried in air and stored in desiccators.

2.2. Inhibitor Preparation

Unripe fresh fruits of Gmelina aborea were collected from the garden of Chemistry Department, Bayero University Kano, Nigeria. The Fruits were washed with deionized water and mechanically squeezed to obtain the latex.

2.3. Weight Loss Measurement

The prepared, weighed coupons were immersed in the 100 cm^3 test solution contained in an opened beaker with and without the inhibitor, at particular temperature maintained using thermostated water bath. The coupons were taken out of the test solution, washed with brush under running water, dried in acetone and weighed again. The weight loss (Δw), corrosion rate (CR), surface coverage (θ) and inhibition efficiency were determined using equation (1), (2), (3) and (4) respectively [9].

$$\Delta w = w_i - w_f \qquad (4)$$

$$CR = {}^{\Delta w}/_{At} \qquad (5)$$

$$\theta = \frac{\Delta w_{inh} - \Delta w_{free}}{\Delta w_{inh}} \qquad (6)$$

$$\theta = \frac{\Delta w_{inh} - \Delta w_{free}}{\Delta w_{inh}} \times 100 \qquad (7)$$

2.4. 2.4. FTIR Analysis

FTIR spectrophotometer was used to investigate the functional group in Gmelina aborea fruits latex and that present in the corrosion product on the metal surface.

3. Results

3.1. Effect of Temperature

Variations of weight loss, corrosion rate, surface coverage and inhibition efficiency were investigated and the results are presented in Table 1. As shown in Table 1, the weight loss and corrosion rate were found to increase with the increase in temperature but lower weight loss and corrosion rate were observed in the presence of Gmelina aborea at all the temperature recorded. These records of findings suggest that Gmelina aborea inhibited the corrosion of aluminium in the acidic medium. Similar results were reported in the literature [10, 11]. Similarly, from Table 1 surface coverage and inhibition efficiency decrease with increase in temperature. These findings conform to those reported in the literature [12].

3.2. Effect of Inhibitor Concentration

Variation of weight loss, corrosion rate, surface coverage and inhibition efficiency were investigated and presented in Table 2. Weight loss and corrosion rate were found to decrease with increase in the concentration of the Gmelina aborea while the surface coverage and inhibition efficiency were found to increase with increase in concentration of the inhibitor with the highest Inhibition efficiency of 94.13 % in the presence of 5.0 mL/L inhibitor concentration. The increase in inhibition efficiency with increasing concentration of inhibitors was due to increase in the surface coverage, resulting in the retardation of the metal dissolution [13]. Generally, the result suggested that there is gradual retardation of the metal dissolution with increasing concentration of the inhibitor. Similar results have been reported in the literature [14].

3.3. Adsorption Isotherm

The data obtained for the adsorption of Gmelina aborea on the aluminium surface were analysed using Langmuir, El-Awady, Florry Huggins and Freundlich adsorption models, equation (5), (6), (7) and (8). The adsorption of the inhibitor was found to be best fitted to Langmuir model with the linear regression coefficient (R^2) more closely to unity. The linear regression coefficient (R^2), adsorption constant (K) and slope were obtained from Langmuir, El-Awady, Florry Huggins and Freundlich and presented in Table3.

$$\boldsymbol{log\left(\frac{c}{\theta}\right) = logc - logk} \qquad (8)$$

$$\boldsymbol{log\left(\frac{\theta}{1-\theta}\right) = logk + ylogc} \qquad (9)$$

$$\boldsymbol{log\left(\frac{\theta}{c}\right) = logk + xlog(1-\theta)} \qquad (10)$$

$$\boldsymbol{log\theta = logk + nlogc} \qquad (11)$$

Where c is the inhibitor concentration, θ is surface coverage, k is adsorption equilibrium constant, where x is the number of molecule occupying an active site, n is the freundlich interaction coefficient.

3.4 Thermodynamic and Kinetic Parameters

The thermodynamic and kinetic data for the corrosion of aluminium in HCl in the presence and absence of the inhibitor were determined using equation 12, 13 and 14 while the results were presented in Table 4 and 5.

$$logCR = logA - \frac{E_a}{2.303RT} \qquad (12)$$

$$log\frac{CR}{T} = log\frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (13)$$

$$\Delta G = -2.303RTlog(55.5k) \qquad (14)$$

The activation energy for the inhibited and uninhibited metals were determined using equation 12. Where CR is the corrosion rate, T is the absolute temperature, R is the gas constant and A is the Arrhenius pre-exponential. The plot of logarithm of corrosion rate against reciprocal of absolute temperature is shown in figure 1 with the slope = $\frac{E_a}{2.303R}$ and the intercept = A. As the result of adsorption of the inhibitor on the surface of aluminium, the activation energy was found to increase from that in the absence of the inhibitor to that with the inhibitor (Table 4). The increase in the energy of activation is as the result of the barrier formed between the metal and the corrosive media. The calculated activation energy value is below 80 kJmol-1. It has been reported earlier that for an adsorption to be considered as physical adsorption, it is expected that, the average values of E_a be ≥ 80 Kjmol-1[15, 16]. The enthalpy (ΔH) and entropy (ΔS) were determined using Erying transition state, equation 13. Where CR is the corrosion rate, T is the absolute temperature , R is the molar gas constant, N is the Avogadros constant and h is the plank's constant. The Erying plot gives straight line graph (figure 2) with the slope $=\frac{\Delta H}{2.303RT}$ and intercept of $=\frac{R}{Nh}+\frac{\Delta S}{2.303R}$ .The values of ΔH and ΔS were negative (Table 4), signifying exothermic process and the associative mechanism of the corrosion process respectively whereby a decrease in disorder occur in transition from the reactant to the activated complex [17, 18].The calculated values of Gibb's free energy (ΔG) were determined from equation 14. Where R is a gas constant, T is absolute temperature and 55.5 is the water concentration and k is the adsorption equilibrium constant. The values of ΔG were all negative (Table 5) at all temperature indicating that the adsorption process is feasible and spontaneous [19].

3.4. FTIR Spectra

The FTIR spectra of the inhibitor sample and of the corrosion products show the presence of hydroxyl (OH) and carbonyl groups (figure 3). However there were shift of stretching frequency from that of the Gmelina aborea to that of the corrosion product on the metal surface. This shift of the frequency was as the result of interaction between the Gmelina aborea molecule and aluminium surface [20]. Similar results were reported [21]

aluminium in HCl with and without 1mL of the inhibitor.

Temp (K)	Inhibited				Uninhibited			
	WL (g)	CR ($gh^{-1}mm^{-2}$)	Θ	IE (%)	WL (g)	CR ($gh^{-1}mm^{-2}$)	Θ	IE (%)
298	0.0121		0.9407	94.07	0.2040		-	-
303	0.0231		0.8975	89.75	0.2256		-	-
308	0.0386		0.8700	87.00	0.2972		-	-
313	0.0427		0.8650	86.50	0.3152		-	-
318	0.0523		0.8578	85.78	0.3680		-	-

Table 1: Weight loss (WL), corrosion rate (CR), surface coverage (θ) and inhibition efficiency (IE) for the corrosion of

aluminium in HCl at 318K at various inhibitor concentrations

Inh. Conc. (mL/L)	WL (g)	CR ($gh^{-1}mm^{-2}$)		IE (%)
1.0	0.0524		0.8578	85.78
2.0	0.0404		0.8909	89.09
3.0	0.0260		0.9298	92.98
4.0	0.0228		0.9385	93.85
5.0	0.0216		0.9413	94.13

Table 2: Weight loss (WL), corrosion rate (CR), surface coverage (θ) and inhibition efficiency (IE) for the corrosion of

Table 3: The linear regression coefficient (R^2) adsorption constant (k) and the slope for different adsorption models.

Adsorption model	R^2	Slope	K
Langmuir	0.997	0.946	0.959×10^0
El-Awady	0.960	0.660	6.670×10^1
Florry-Huggins	0.954	0.501	6.800×10^{-3}
Freundlich	0.964	0.062	0.991×10^0

Table 4: The calculated values of activation energy (E_a), enthalpy(ΔH) and entropy(ΔS) in the presence and absence of

Inhibition	( )	( )	( )
Blank	23.84	21.29	-0.20
Inhibited	53.53	49.99	-0.13

inhibitor.

Temperature (K)	298	303	308	313	318
ΔG (KJmol^{-1})	-10.11	-10.58	-10.75	-10.93	-11.10

Table 5: The calculated values of Gibb's free energy of adsorption with 0.1% Gmelina aborea

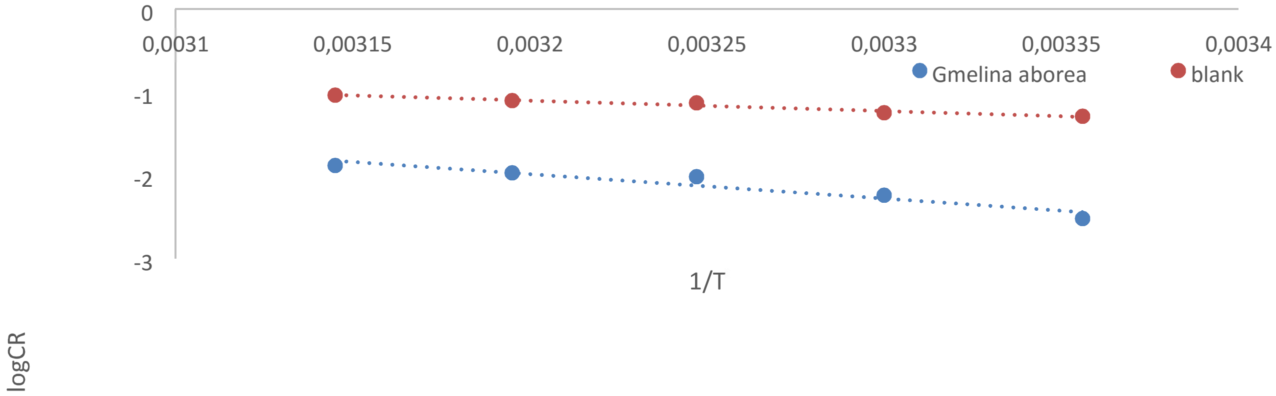


Figure 1. Arrhenius plot

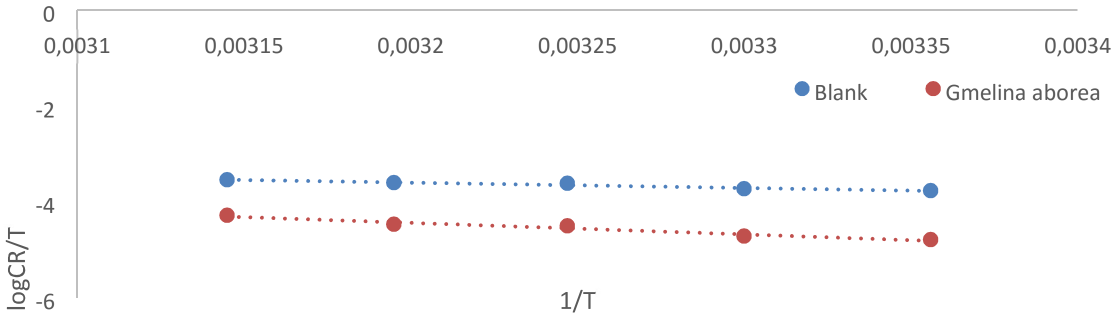
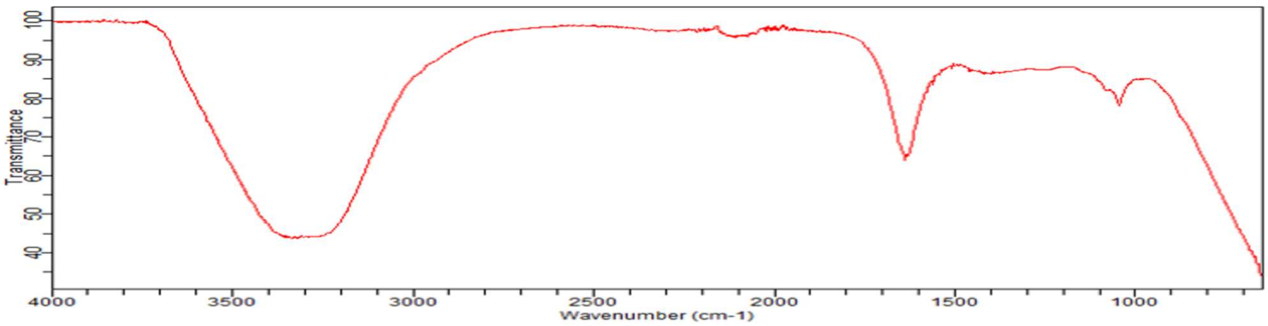
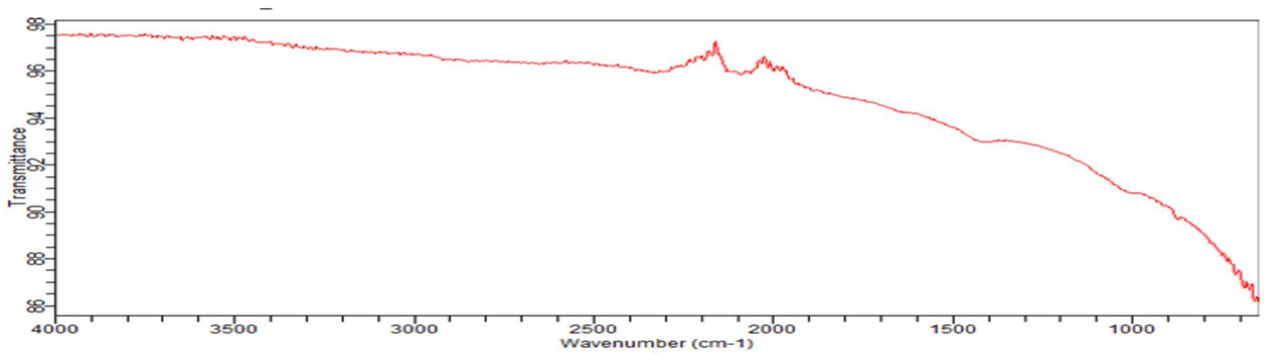


Figure 2. Transition state plot



3a



3b

Figure 3. FTIR spectra for *Gmelina aborea* (3a) and inhibited corrosion product on aluminium surface (3b)

4. Conclusion

The findings of this research work shows that the Gmelina aborea fruit latex was found to be effective evirounmentally friendly corrosion inhibitor for corrosion of aluminium in 1.0 M HCl.The adsorption of the inhibitor was found to be more fitted to Langmuir adsorption model. The thermodynamic and kinetic data suggested that the Gmelina aborea was adsorbed on the aluminium surface through physiosorption mechanism and this was supported by infrared spectra which indicated the interaction between the metal surface and the Gmelina aborea molecules.

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