



# Analysis of Inhibition Action of *Acacia nilotica* Ethanol Extract on Aluminium Corrosion in 1.0M HCl and NaOH

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## Abstract

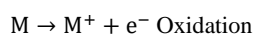
The proposed corrosion inhibition action of *Acacia nilotica* ethanol extract on aluminium corrosion in HCl and NaOH was investigated using weight loss method. The *Acacia nilotica* ethanol extract was found to be inactive in NaOH at all the concentrations of the inhibitor but active in HCl with increasing inhibition efficiency as inhibitor concentration and decreases as temperature increases with the highest inhibition efficiency of 95.31%. The kinetic and thermodynamics data shows that the adsorption process was feasible and endothermic adsorption process from the large negative values of Gibb's free energy ( $\Delta G$ ) and negative values of enthalpy ( $\Delta H$ ), The data indicated physisorption process of adsorption which was supported by FTIR spectra. The adsorption process was best fitted to Langmuir adsorption model.

**Keywords:** *Acacia nilotica*; Adsorption; Corrosion Inhibition; Kinetic; Thermodynamics.

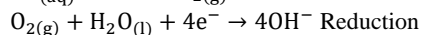
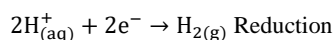
## 1. Introduction

The term metal corrosion is defined as the interaction of a metal with the surrounding environment, causing a slow, steady and irreversible deterioration of metal, in both physical and chemical properties (Rafael et al, 2014). It is the destruction of materials resulting from exposure and interaction with the corrosive environment. It is a major problem that must be confronted for safety, environment and economic reasons (Thomson et al, 2007). The basic processes of metallic corrosion in aqueous media consist of the anodic dissolution of the metals and cathodic reduction of oxidants present in the solution (Sharma, 2012).

The generic formula for anodic metal loss can be represented by the equation below:



The produced electrons are consumed at the cathodic site, with two possibilities in solution:



Aluminium is widely used for many industrial and domestic purposes. It is used in the field of aerospace, transportation, electronics, electricity, construction and in manufacturing chemical reactors, medical equipments, petroleum refining units, oil and gas pipelines, kitchen wears etc. The advantage of using aluminum is due to its excellent corrosion resistance properties and thus it becomes a priority in material selections in most industries (Hajar et.al, 2016).

Although aluminium has an adhesive protective passive oxide film, but this film has an atmospheric susceptibility and consequently the metal dissolves readily in acidic and basic solutions above and below the range of pH 4-9 (Aytac, 2010; Obot et.al, 2008).

Corrosion inhibitors are either organic or inorganic chemicals or more commonly formulations that are added in small amount to a corrosive environment in order to delay or decrease the corrosion process of the surface to be protected (Palou et al, 2014). The applications of corrosion inhibitor have been an accepted practice (Khan et al, 2015). Many of these inhibitor are toxic and do not conform with requirements of the environmental protection standards. As the alternative of toxic corrosion inhibitors and environmental friendly, plant extracts are receiving more attentions as better corrosion inhibitor (El-etere, 2007; Okafor et al, 2008). With regard to these findings, the current research investigated the corrosion inhibitive activity of *Acacia nilotica* fruits ethanol extract on the corrosion of aluminium in acidic and alkaline media.

## 2. Materials and Methods

**Preparation of coupons:** The metal was mechanically pressed cut into 2 x 2 cm with a very small hole close to the edge of the coupons, were degreased in acetone and kept in a dessicator.

**Preparation of inhibitor:** The fresh fruits of *Acacia nilotica* were obtained from a farm in Lengel, Kano, Nigeria. The fruits were washed, air dried, ground into powder. 100g of the fruit powder was weighed into 1.0dm<sup>3</sup> of absolute ethanol contained in an ambered bottle. It was left to stand for seven days with occasional shaking. The mixture was filtered and the filtered was concentrated using rotary evaporator and thick syrup was obtained which was dried further for total solvent removal (Mahalakshimi, 2016).

**Weight loss method:** The weight aluminum coupons were separately immersed in the 100cm<sup>3</sup> opened beakers containing the test solution of a given concentration with and without a given concentration of the inhibitor at a particular temperature maintained in a thermostated water bath. At the given interval of time the coupons were retrieved from the test solution, washed with brush under running water, dried in acetone and weighed again. This was done in replicate. The weight loss ( $\Delta w$ ), corrosion rate (CR), surface coverage ( $\theta$ ) and inhibition efficiency were determined using the equation (1), (2), (3) and (4) respectively.

$$\Delta w = w_i - w_f \quad (1)$$

$$CR = \frac{\Delta w}{At} \quad (2)$$

$$\theta = \frac{w_o - w_1}{w_o} \quad (3)$$

$$\%IE = \frac{w_o - w_1}{w_o} \times 100 \quad (4)$$

**FTIR analysis:** The Fourier transform spectrophotometer (Cary 630) from Agilent technology was used for the determination of the functional group present in the extract and in the corrosion products on the metal surface in presence of the extract.

## 3. Result and discussion

**Effect of Immersion Time:** Weight loss for the corrosion of aluminium in 0.2M HCl and NaOH solutions at 298K for different immersion period in the absence of inhibitor were determined and the results were presented in figures 1 and 2. From figures 1 and 2, there was no weight loss observed in HCl for the time interval of 0.083 to 0.750 hours while weight loss for aluminium in NaOH was 0.0006 and 0.0216g at the same experimental conditions and the maximum immersion time possible was 5 hours for aluminium in NaOH and 24 hours in HCl. Generally weight loss was found to increase with the increase in immersion time. Similar results were reported in literature (Nwaedozie et al, 2015).

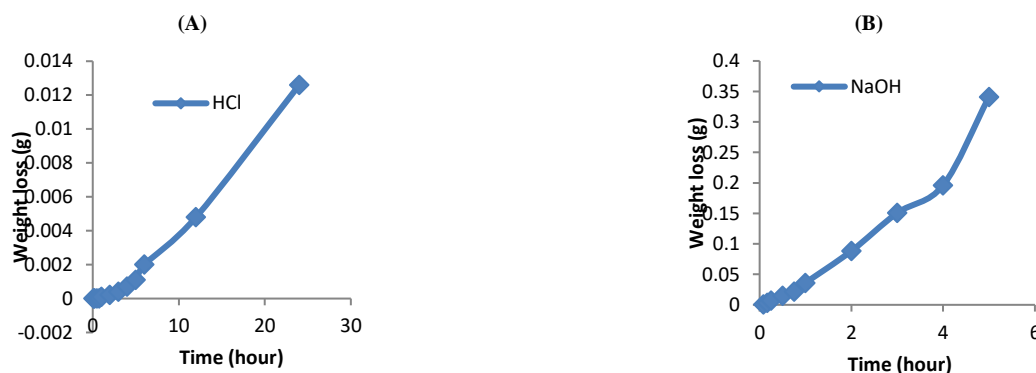


Fig. 1: Variation of Weight Loss with Immersion Time for Aluminium in 0.2M HCl (A) and NaOH (B).

**Effect of temperature:** The variations of weight loss, corrosion rate, surface coverage, inhibition efficiency as a function of temperature with and without 0.1% w/v are presented in table 1 and 2 respectively. At all tested temperature, the inhibitor was found to retard the weight loss and corrosion rate only in HCl and it was not active in NaOH. Weight loss and corrosion rate increases with temperature thereby decreasing surface coverage and inhibition efficiency. Result similar to this was reported in literature (Maibalangu et al, 2017). The increase in corrosion rate as temperature increases can be explained on the basis of desorption as a result of unstable nature of active phytochemicals when temperature is increased (Bouhlal et al, 2020).

Table 1: Variation of Weight Loss and Corrosion Rate with Temperature in HCl and NaOH without Inhibitor

Temperature (K)	HCl Weight loss (g)	Corrosion rate (gh <sup>-1</sup> cm <sup>-2</sup> )	NaOH Weight loss (g)	Corrosion rate (gh <sup>-1</sup> cm <sup>-2</sup> )
298	0.2151	0.0538	0.1207	0.0302
303	0.2406	0.0602	0.1661	0.0415
308	0.2860	0.0715	0.2292	0.0573
313	0.3306	0.0827	0.3029	0.0757
318	0.3622	0.0906	0.3801	0.0950

**Table 2:** Variation of Weight Loss, Corrosion Rate, Surface Coverage ( $\theta$ ) and Inhibition Efficiency (%IE) with Temperature in HCl with 0.1% Inhibitor

Temperature (K)	Weight loss (g)	Corrosion rate ( $\text{gh}^{-1}\text{cm}^{-2}$ )	$\theta$	%IE
298	0.0138	0.0035	0.9358	93.58
303	0.0383	0.0096	0.8407	84.07
308	0.0476	0.0119	0.8337	83.37
313	0.0694	0.0174	0.7602	76.02
318	0.0836	0.0209	0.7691	76.91

**Effect of inhibitor concentration:** The effect of inhibitor concentration on weight loss, corrosion rate, surface coverage and inhibition efficiency was investigated at 298K and the results were presented in table 3. The *Acacia nilotica* extract was found to be inactive in NaOH but weight loss was and corrosion rate were found to decrease with the increase in the concentration of the inhibitor in HCl, hence, increase in surface coverage and inhibition efficiency. A similar trend was reported by other authors (Ituen et al, 2013; Maibalangu et al, 2017; Ibrahim et al, 2019). The increase in inhibition efficiency with increasing the concentration of the inhibitor is due to the increase of the adsorbed amount and the coverage of the inhibitor molecules. (Fouda et al, 2013).

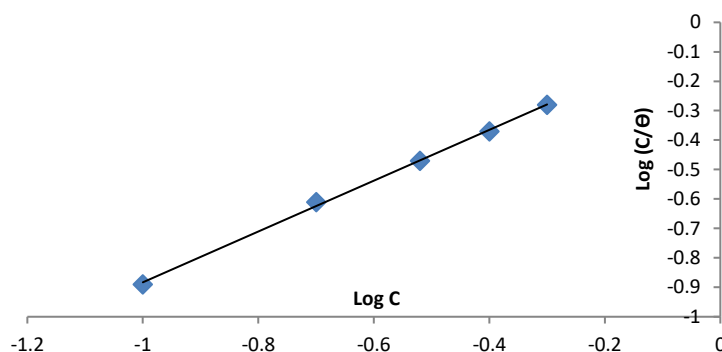
**Table 3:** Variation of Weight Loss, Corrosion Rate, Surface Coverage ( $\theta$ ) and Inhibition Efficiency (%IE) with Inhibitor Concentration in Hcl with At 318K

Inhibitor Conc. (%)	Weight loss (g)	Corrosion rate ( $\text{gh}^{-1}\text{cm}^{-2}$ )	$\theta$	%IE
0.1	0.0836	0.0209	0.7691	76.91
0.2	0.0652	0.0163	0.8199	81.99
0.3	0.0423	0.0106	0.8831	88.31
0.4	0.0231	0.0058	0.9361	93.61
0.5	0.0170	0.0043	0.9531	95.31

**Adsorption Isotherm:** The data obtained from the degree of surface coverage were used to test different adsorption isotherms. The adsorption of *Acacia nilotica* on aluminium surface was fitted to Langmuir adsorption model (equation 5).

$$\log\left(\frac{c}{\theta}\right) = \log c - \log k \quad (5)$$

Where  $c$  is the inhibitor concentration,  $\theta$  is the surface coverage and  $k$  is the adsorption equilibrium constant. The plot of  $\log\left(\frac{c}{\theta}\right)$  versus  $\log c$  was found to be linear and presented in figure 2.

**Fig. 2:** Langmuir Adsorption Model Plot.

**Thermodynamics and Kinetics:** Arrhenius plot of  $\log CR$  against  $1/T$  were plotted from Arrhenius equation (equation 6).

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (6)$$

Where  $CR$  is the corrosion rate,  $E_a$  is the activation energy,  $R$  is the molar gas constant and  $T$  is the temperature. The variation of  $CR$  with  $1/T$  is shown in figure 3 with the slope  $= \frac{E_a}{2.303R}$  and intercept  $= A$ . The calculated  $E_a$  are presented in table 4. The activation energy increases from that of the blank to the inhibited. The result suggest that the adsorption of *Acacia nilotica* on the aluminium involves physisorption as the activation energy is lower than the threshold value of  $80\text{KJmol}^{-1}$  required for chemisorptions (Hamdy and EL-Gendy, 2012).

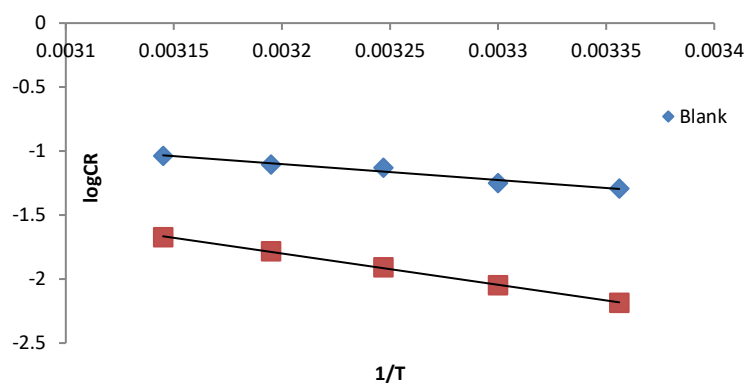


Fig. 3: Arrhenius Plot.

Eyring transition state equation (equation 7) was considered for the determination of enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ).

$$\log \frac{CR}{T} = \log \frac{R}{N_h} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (7)$$

Where  $N$  is the Avogadro's constant and  $h$  is the Plank constant. The plot of  $\frac{CR}{T}$  against  $1/T$  (figure 13) gives a straight line graph with the slope =  $\frac{\Delta H}{2.303R}$  and intercept =  $\left(\frac{R}{N_h}\right) + \left(\frac{\Delta S}{2.303R}\right)$ . The calculated values of enthalpy and entropy were presented in table 4. The findings suggest that the endothermic nature of the process from the positive values of  $\Delta H$ . The absolute values of  $\Delta H$  is  $49.99 \text{ kJmol}^{-1}$  which is slightly higher than the threshold value of  $40 \text{ kJmol}^{-1}$  associated with physical adsorption and far less than  $100 \text{ kJmol}^{-1}$  associated with chemical adsorption signifying mixed-type adsorption nature with predominance of physisorption (Ituen et al, 2017). The negative value of entropy of adsorption shows that the destruction on the metal surface has been lowered as the result of decrease in disorderliness of the system (Ogunlaye et al, 2020).

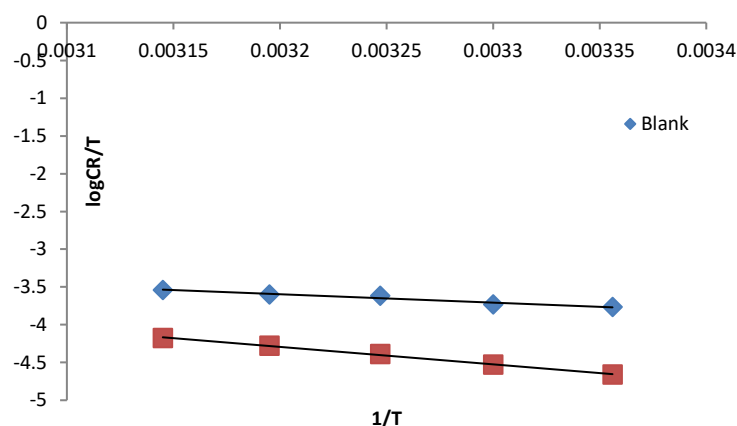


Fig. 4: Transition State Plot.

Table 4: The Calculated Values of Activation Energy, Enthalpy and Entropy with and Without 0.1% Inhibitor

System	$E_a$ ( $\text{kJmol}^{-1}$ )	$\Delta H$ ( $\text{kJmol}^{-1}$ )	$\Delta S$ ( $\text{kJmol}^{-1}$ )
Blank	24.00	21.30	-0.21
HCl + Inhibitor	46.81	44.29	-0.14

The values of Gibb's free energy of adsorption ( $\Delta G$ ) were calculated using equation 9 and presented in table 5.

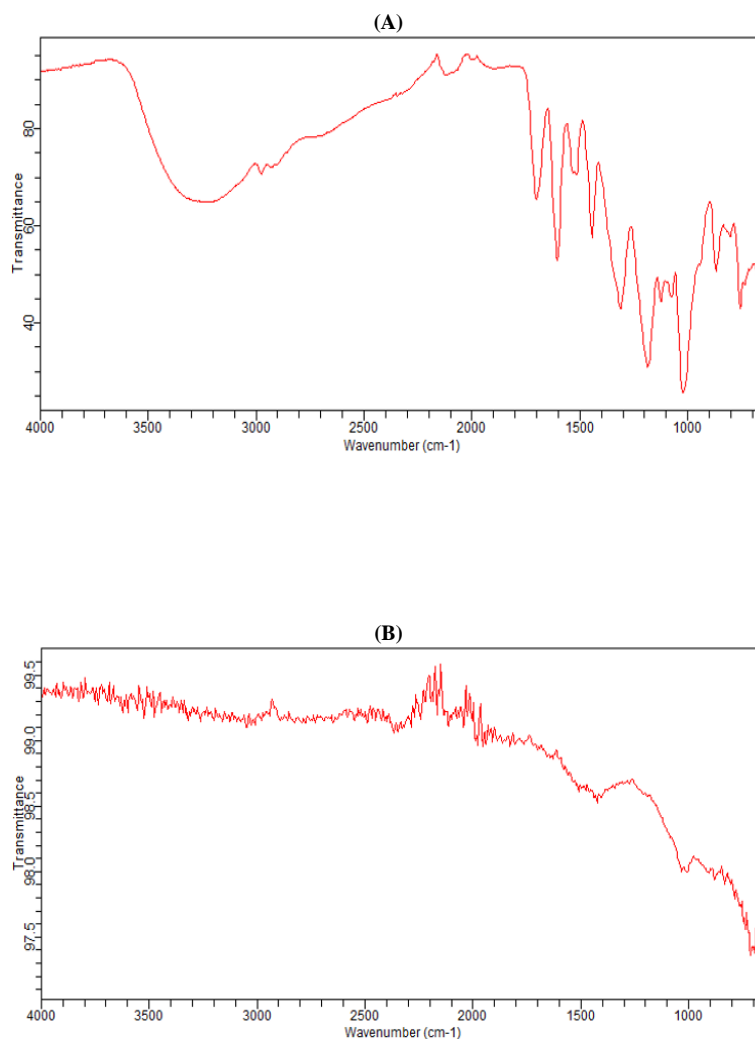
$$\Delta G = -2.303RT \log(55.5k) \quad (8)$$

Where  $R$  is a gas constant,  $T$  is the absolute temperature,  $55.5$  is the water concentration and  $k$  is the adsorption equilibrium constant. The negative sign of ( $\Delta G$ ) indicate spontaneous process of adsorption. The values  $\Delta G$  are less than the threshold value of  $-40 \text{ kJmol}^{-1}$  required for chemisorption, suggesting that the adsorption of *Acacia nilotica* on the aluminium surface is through physisorption mechanism (Dominic and Monday, 2016).

Table 5: The Calculated Values of Gibb's Free Energy with 0.1% Inhibitor at Different Temperature

System	Temperature (K)	$\Delta G$ ( $\text{kJmol}^{-1}\text{k}^{-1}$ )
1.0M HCl + 0.1% Inhibitor	298	-09.55
	303	-09.61
	308	-09.59
	313	-09.93
	318	-10.09

**FTIR:** The FTIR spectra of *Acacia nilotica* indicates the presence of phenolic hydroxyl (OH) and carbonyl group (CO). However, the corrosion products in the presence of *Acacia nilotica* shows that the stretching frequencies of the OH and CO shifted from  $3360\text{cm}^{-1}$  to  $3339\text{cm}^{-1}$  and  $1639$  to  $1640\text{cm}^{-1}$ . The shifts in peaks of the FTIR spectra of the corrosion product in the presence of *Acacia nilotica* suggest that, there was interaction between the metal and some molecules of the inhibitor (Dominic and Monday, 2016).



**Fig. 5:** FTIR Spectra for *Acacia nilotica* Ethanol Extract (A) and Corrosion Products in the Presence of *Acacia nilotica* (B).

## 4. Conclusion

The findings of this work showed that *Acacia nilotica* fruits ethanol extract is a good inhibitor for the corrosion of aluminium in HCl but inactive in NaOH. The thermodynamic and kinetic data proposed that *Acacia nilotica* adsorption was spontaneous and exothermic process and followed physical adsorption process.

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