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Original Research Article

Analysis of Corrosion Inhibitor Potential of *Acacia nilotica* Fruits on Aluminium Corrosion in Acidic and Alkaline Media

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ABSTRACT

In this study, the inhibitive action of *Acacia nilotica* fruits powder towards the corrosion behavior of aluminium in 1.0M HCl and 1.0M NaOH solutions has been studied without carrying out any solvent extraction of the fruits powder using weight loss method. *Acacia nilotica* showed corrosion inhibition efficiency of 98.83 and 71.64% in HCl and NaOH respectively in the presence of 0.5% w/v inhibitor concentration at 318K. The activation energy increases from that of the blanks (23.84 and 49.25 kJmol⁻¹) to the inhibited (55.92 and 65.92 kJ mol⁻¹) in HCl and NaOH respectively. The adsorption process was spontaneous as indicated by the large negative values of ΔG and ΔS . The values of enthalpy were positive indicating endothermic process of adsorption. The adsorption of *Acacia nilotica* on aluminium was best fitted to Langmuir adsorption model in both media. The result of FTIR Spectra also indicated physisorption mechanism as proposed by the thermodynamic data.

Keywords: Corrosion Inhibition, *Acacia Nilotica*, Solvent Extraction, Activation Energy, Enthalpy, Thermodynamics

Introduction

Corrosion is an undesirable phenomenon that needs to be controlled or prevented using corrosion inhibitors. From environmental and economic point of view, plant extracts are receiving increasing attention as green corrosion inhibitors because of their availability and their richness in natural biodegradable chemicals that are environmentally friendly [1, 2]. Most of the works reported using plant parts as corrosion inhibitors involve the use of solvent for the extraction of the active components of the plant parts. It was reported that all solvents affect human to greater or lesser extent. High doses over short period, can cause acute poisoning while small doses over long period, can lead to chronic damage [3]. Corrosion of metals and alloys is among the basic problems of industries. Hydrochloric acid is commonly used for pickling, cleaning, descaling and etching of metals and these greatly contribute to the corrosion of the metal surface [4]. The effect of corrosion can be appreciated by the annual cost of its prevention, of which survey on the cost revealed that the direct cost of corrosion was estimated at 276 billion dollars in the United States for 2002, which is approximately 4% of their gross national product [5]. 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 [6]. 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 [7]. There has been increasing search for green or organic corrosion inhibitors [8]. The plants inhibitors have been tested and found to be environmentally friendly, non-toxic, biodegradable, inexpensive and readily available [9]. This work is aimed at finding the corrosion inhibition potentials of *Acacia nilotica* fruits on aluminium in acidic and alkaline media without any solvent extraction using weight loss method.

Experimental

Inhibitor preparation

Fresh fruits of *Acacia nilotica* were obtained from Lengel, Ungogo, Kano, Nigeria. The fresh fruits were washed with deionized water and air dried. The dried fruits were ground into powder and sieved using 250nm mesh sieve.

Coupons preparation

The aluminium sheet was mechanically pressed-cut into 2cm x 2cm with a small hole close to the edge of the coupon. The coupons were degreased by washing in ethanol and rinsed with acetone, dried and kept in a dessicator [10].

Weight loss method

The prepared and weighed coupons were immersed in 100cm³ beakers containing the test solution of a given concentration with and without the inhibitor at a specific temperature which was maintained in a thermostatic water bath. The coupon was retrieved from the test solution at a given intervals of time, it was then washed with deionized water using brush, dried in acetone and weighed again. This was done in form of replicate and the difference in mass was recorded as weight loss. The weight loss (Δw), Corrosion rate (CR), degree of Surface Coverage (θ) and Inhibition Efficiency (%IE) were calculated using equation (1), (2), (3) and (4) respectively.

Where W_B and W_A are weights (g) of the coupon before and after immersion respectively, ΔW_{Free} and ΔW_{inh} are the weight losses (g) of free and inhibited metal respectively.

Infrared analysis

FTIR Spectrophotometer was used to determine the functional groups present in *Acacia nilotica* fruits and of the corrosion products in the presence of the inhibitor.

Results and Discussion

Effects of corrodent concentration

Weight loss of aluminium was determined at various corrodent concentrations without inhibitor and immersion time with the highest possible weight loss for each corrodent concentration was adopted as optimum immersion time and beyond this time interval the coupon dissolved completely. The weight loss and optimum immersion time for the various concentrations were presented in Table 1. The result presented in Table 1 showed that the rate of weight loss increases with increasing concentration of the corrodent and optimum immersion time decrease with increasing the corrodent concentration. For 1.0M corrodent concentration the optimum immersion time was 1hour in both HCl and NaOH with the weight loss of 0.3164g and 0.1745g respectively. Thus, higher rate of weight loss was indicated in 1.0M corrodent concentration. The increase in weight loss is due to the fact that, the rate of chemical reaction increases as the concentration of active species increases [11].

Table 1: Variation of optimum immersion time with corrodents concentration at 298K without inhibitor.

| Corrodent Concentration (mol/dm ³) | HCl | | NaOH | |
|--|-----------------|-------------------------------|-----------------|-------------------------------|
| | Weight loss (g) | Optimum immersion time (hour) | Weight loss (g) | Optimum immersion time (hour) |
| 0.2 | 0.0126 | 24 | 0.3410 | 5 |
| 0.4 | 0.1309 | 12 | 0.3349 | 4 |
| 0.6 | 0.3326 | 6 | 0.2774 | 3 |
| 0.8 | 0.1732 | 3 | 0.1326 | 1 |
| 1.0 | 0.3164 | 1 | 0.1745 | 1 |

Effect of temperature

The weight loss, corrosion rate and inhibition efficiency were investigated at various temperatures. Table 2 showed the increase in weight loss and corrosion rate but decrease in inhibition efficiency with increasing temperature. There were gradual decrease in inhibition efficiency from 97.65 to 95.02% and 63.12 to 46.13% in HCl and NaOH respectively as the result of decrease in surface coverage. Table 2 indicated the decrease in inhibitor activity with increasing temperature. Increase in temperature result in destabilizing the absorbed inhibitor molecules on the metal surface and decreasing its activity [7, 12]. Similar results were reported by [13].

Table 2: Variation of weight loss, corrosion rate, surface coverage (θ) and inhibition efficiency (%IE) with temperature.

| System | Temperature (K) | Weight loss (g) | | Corrosion rate ($\text{gh}^{-1}\text{cm}^{-2}$) | | θ | % IE |
|--------|-----------------|-----------------|-----------|---|-----------|----------|-------|
| | | Blank | Inhibited | Blank | Inhibited | | |
| HCl | 298 | 0.2040 | 0.0045 | 0.0510 | 0.0012 | 0.9765 | 97.65 |
| | 303 | 0.2256 | 0.0067 | 0.0564 | 0.0017 | 0.9703 | 97.03 |
| | 308 | 0.2972 | 0.0098 | 0.0743 | 0.0025 | 0.9670 | 96.70 |
| | 313 | 0.3152 | 0.0142 | 0.0788 | 0.0036 | 0.9549 | 95.49 |
| | 318 | 0.3680 | 0.0182 | 0.0920 | 0.0046 | 0.9502 | 95.02 |
| NaOH | 298 | 0.1184 | 0.0437 | 0.0296 | 0.0109 | 0.6312 | 63.12 |
| | 303 | 0.1640 | 0.0635 | 0.0410 | 0.0159 | 0.6130 | 61.30 |
| | 308 | 0.2172 | 0.1108 | 0.0543 | 0.0277 | 0.4899 | 48.99 |
| | 313 | 0.3428 | 0.1784 | 0.0857 | 0.0446 | 0.4794 | 47.94 |
| | 318 | 0.3900 | 0.2101 | 0.0975 | 0.0525 | 0.4613 | 46.13 |

Effect of inhibitor concentration

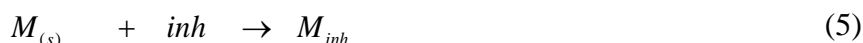
The effect of inhibitor concentration was investigated and the result is presented in Table 3. Various inhibitor concentrations in 1.0M corrodent concentration at 318K were used which result in gradual decrease in weight loss of the aluminium in both HCl and NaOH, thus decrease in corrosion rate and increase in inhibition efficiency. By increasing inhibitor concentration from 0.1 to 0.5% w/v at 318K, the inhibition efficiency increased from 95.02 to 98.83% and 46.13 to 71.64% in HCl and NaOH respectively. The increase in inhibition efficiency with increasing concentration of inhibitors is due to increase in the surface coverage, resulting in retardation of metal dissolution [14, 15]. The absorbed films of the inhibitor act as a physical barrier between the metal surface and the corrosive media [16].

Table 3: Variation of weight loss, corrosion rate, surface coverage (θ) and inhibition efficiency (%IE) with inhibitor concentration

| System | Inhibitor conc. (%) | Weight loss (g) | Corrosion rate ($\text{gh}^{-1} \text{cm}^{-2}$) | θ | %IE |
|--------|---------------------|-----------------|--|----------|-------|
| HCl | 0.1 | 0.0184 | 0.0046 | 0.9500 | 95.00 |
| | 0.2 | 0.0160 | 0.0040 | 0.9565 | 95.65 |
| | 0.3 | 0.0132 | 0.0033 | 0.9641 | 96.41 |
| | 0.4 | 0.0092 | 0.0023 | 0.9750 | 97.50 |
| | 0.5 | 0.0064 | 0.0016 | 0.9826 | 98.26 |
| NaOH | 0.1 | 0.2100 | 0.0525 | 0.4613 | 46.13 |
| | 0.2 | 0.1840 | 0.0460 | 0.5287 | 52.87 |
| | 0.3 | 0.1528 | 0.0382 | 0.6079 | 60.79 |
| | 0.4 | 0.1400 | 0.0350 | 0.6415 | 64.15 |
| | 0.5 | 0.1108 | 0.0277 | 0.7164 | 71.64 |

Adsorption Isotherms

The adsorption mechanism of inhibitor on the metal surface can be generally described by the general equation (equation 6) [17].



The study of the metal (M) inhibitor (Inh) interaction through different adsorption isotherms such as El-Awady, Florry-Huggins, Freundlich, Frumkin and Langmuir revealed that the interaction was more fitted to Langmuir adsorption model (equation 6) in both the acidic and basic media Where C is the inhibitor concentration, θ is the surface coverage and k is the equilibrium constant of adsorption. The plot of θ versus $\log c$ was found to be linear (Figure 1). The calculated values of adsorption constant (k), the linear regression coefficient and the slope of the plots were presented in Table 4.

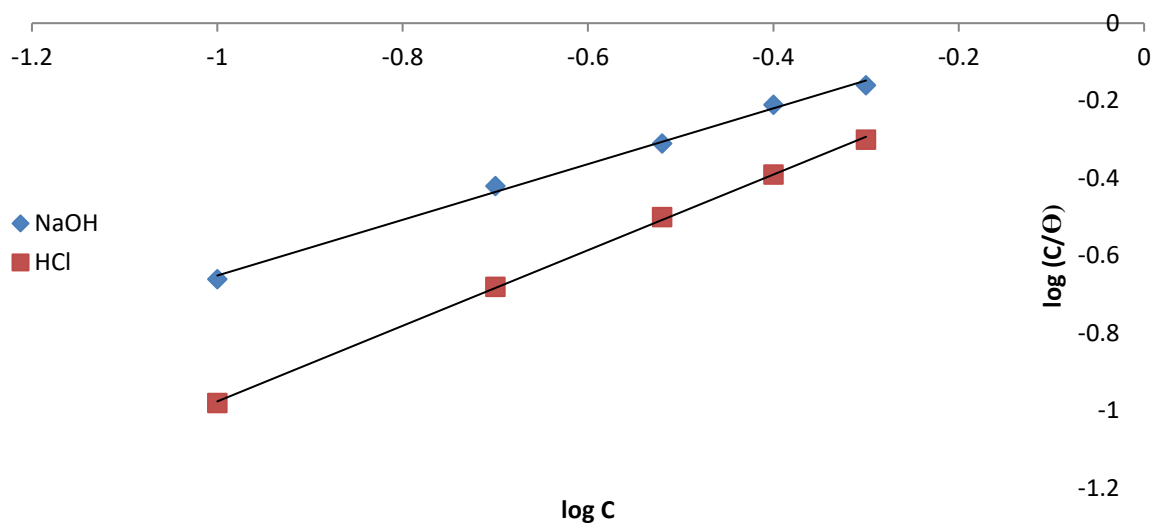


Figure 1: Langmuir adsorption isotherm

Table 4 showed the linear regression coefficient (R^2), adsorption constant k and the slope for the Langmuir adsorption isotherm.

| System | R^2 | Slope | K |
|--------|-------|-------|------|
| HCl | 0.999 | 0.975 | 1.00 |
| NaOH | 0.996 | 0.718 | 1.17 |

Thermodynamic and Kinetics

The Arrhenius equation (equation 7) was used to determine the activation energies (E_a) for the corrosion of the Free and the inhibited metal

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (7)$$

Where CR is the corrosion rate, T is the absolute temperature, R is the gas constant and A is the Arrhenius pre-exponential. The variation of logarithm of corrosion rate with reciprocal of absolute temperature is shown in Figure 2 with the $Slope = \frac{E_a}{2.303R}$ and the intercept = A . The

calculated values of E_a are presented in table 5. In the presence of 0.1% w/v of the inhibitor, the activation energy increases from that of the blank ($23.84 \text{ kJ mol}^{-1}$) to the inhibited ($55.92 \text{ kJ mol}^{-1}$) in HCl and from that of the blank ($49.25 \text{ kJ mol}^{-1}$) to the inhibited ($65.92 \text{ kJ mol}^{-1}$) in NaOH. The increase in E_a is as the result of adsorption of the inhibitor on the metal surface which formed a barrier for mass and charge transfer. The E_a in both media are less than the threshold value of 80 kJ mol^{-1} required for chemisorption [18]. Therefore the E_a values suggest physisorption mechanism [7, 12].

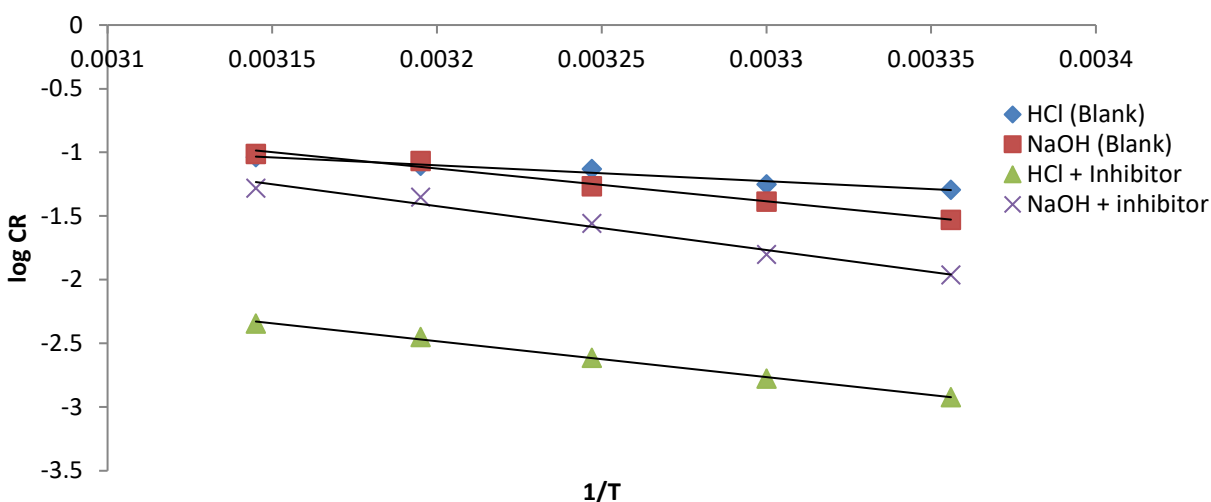


Figure 2: Arrhenius Plot

The enthalpy (ΔH) and entropy (ΔS) were obtained from Eyring transition state equation

Where CR is corrosion rate, T is absolute temperature, R is molar gas constant, N is Avogadro's Constant and h is Planck's constant. The plot of $\log CR/T$ against $1/T$ gives a straight line graph (figure 3) with the slope = $\Delta H/2.303R$ and intercept = $(R/Nh) + (\Delta S/2.303R)$. The calculated values of ΔH and ΔS are presented in table 4. The positive values of ΔH both in the presence and absence of inhibitor justify the endothermic nature of the metal dissolution process. Large and negative values of entropies reflect that the activated complex in the rate-determining step represents an association rather than dissociation occurring going from reactants to the activated complex, thereby increasing the probability of inhibitor molecules to settle on the surface of the metal [19, 20].

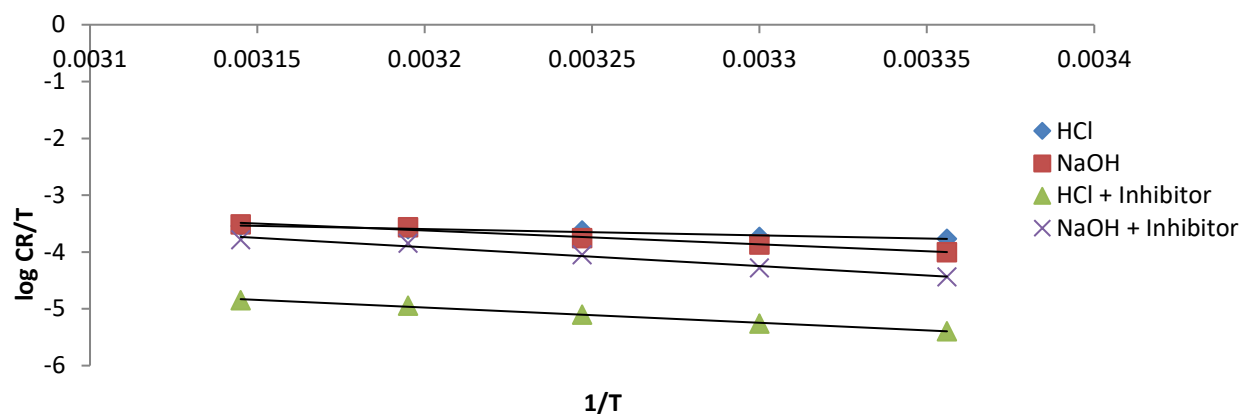


Figure3: Transition state plot

Table 5: The calculated values of activation energy (E_a), enthalpy (ΔH) and entropy (ΔS) in the presence and absence of 0.1% inhibitor.

| System | | E_a (KJ mol ⁻¹) | ΔH (KJmol ⁻¹) | ΔS (KJ mol ⁻¹ k ⁻¹) |
|--------|-----------|-------------------------------|-----------------------------------|--|
| HCl | Blank | 23.84 | 21.29 | - 0.20 |
| | Inhibited | 55.92 | 51.37 | - 0.13 |
| NaOH | Blank | 49.25 | 46.65 | - 0.12 |
| | Inhibited | 65.92 | 63.37 | - 0.07 |

The values of Gibb's free energy of adsorption (ΔG) were calculated using equation (9) and presented in table 6.

$$\Delta G = - 2.303RT \log (55.5 k) \quad (9)$$

Where R is the molar gas constant, T is the absolute temperature, 55.5 is the water concentration and k is the adsorption equilibrium constant. The signs of ΔG were negative which reflect that the adsorption of the inhibitor was feasible and spontaneous process [21]. The highest value of the Gibb's free energy was $-11.04 \text{ KJmol}^{-1}$. Generally values of $\Delta G \leq 20 \text{ KJmol}^{-1}$ are consistent with electrostatic interaction between the metal and inhibitor molecules, which infer physical adsorption, while value more negative than -40 KJmol^{-1} signifies chemical adsorption [22].

Table 6: The calculated values of Gibb's free energy of adsorption at various temperatures.

| System | ΔG (KJ mol ⁻¹) | | | | |
|------------------|------------------------------------|---------|---------|---------|---------|
| | 298K | 303K | 308K | 313K | 318K |
| HCl + Inhibitor | - 09.95 | - 10.12 | - 10.29 | - 10.45 | - 10.62 |
| NaOH + Inhibitor | - 10.34 | - 10.52 | - 10.69 | - 10.86 | - 10.86 |

Infrared analysis

The FTIR Spectra indicated the presence of phenolics hydroxyl (OH) and carbonyl (CO) groups in the *Acacia nilotica* powder. However, the spectra of the inhibited metal surface indicated the shift of frequencies of the hydroxyl and carbonyl groups. The shift in the frequencies observed is suggesting that the active phytochemical constituents present in the inhibitor bind to the metal surface [23]. Also the changes in the adsorption band suggest that adsorption between inhibitors and aluminium take place through this functional group [24].

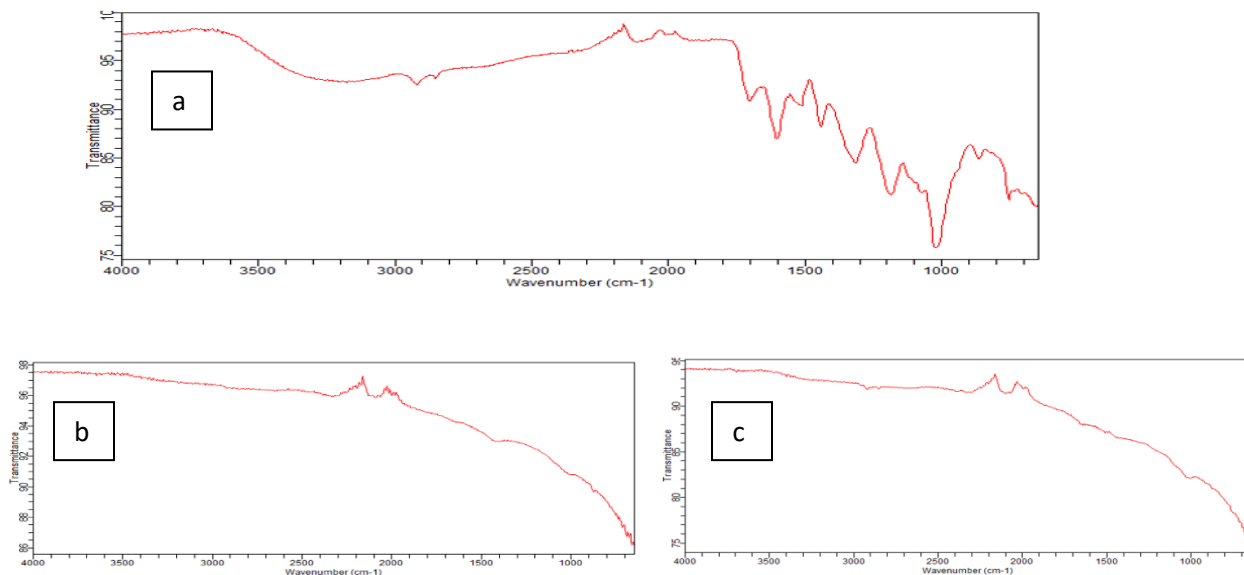


Figure 4: FTIR spectra for (a) *Acacia nilotica* powder, (b) aluminium in HCl with *Acacia nilotica*, (c) aluminium in NaOH with *Acacia nilotica*.

Conclusion

The findings from this research show that the *Acacia nilotica* fruit powder was found to be effective corrosion inhibitor for aluminium in both HCl and NaOH. The inhibitor was found to have better activity in HCl than in NaOH. The adsorption was more fitted to Langmuir adsorption model. The thermodynamics and kinetic data suggested that *Acacia nilotica* was physically adsorbed on the surface of aluminium through spontaneous and exothermic process.

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