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Research Article

INHIBITIVE STUDIES OF *AZADIRACHTA INDICA* (AI) BARK EXTRACT AS CORROSION INHIBITOR FOR ZINC IN 0.75 M HNO_3 SOLUTION: ADSORPTION THERMODYNAMICS AND KINETIC STUDY

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ABSTRACT

The study employed FT-IR, SEM, and gravimetric weight loss measurement to examine the inhibitive effect and adsorption behavior of *azadirachta indica* bark extract on zinc metal in a 0.75 M HNO_3 solution. The study measured weight loss in a 0.75 M nitric acid solution at four different temperatures (303-333K) and four different inhibitor concentrations (0.20-0.80g/L). The outcome of the experimental analysis demonstrates that while the extracts' inhibitory efficiency rises with increasing concentrations of the inhibitor, it falls with rising temperatures. FT-IR and SEM analysis verified that the adsorption of inhibitor molecules onto the metal surface reduces zinc corrosion in nitric acid solution. An analysis of adsorption isotherms demonstrates that experimental data follow the Freundlich isotherm and that adsorption mechanism follows physisorption. Thermodynamic studies on adsorption revealed a spontaneous and feasible process based on a negative value of ΔG_{ads}.

Keywords: Zinc, corrosion, inhibitor, *azadirachta indica* (AI) bark extract, adsorption.

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1. INTRODUCTION

Ordinarily, corrosion of metals or their alloys frequently arises from an electrochemical reaction with the environment. Surface impurities, pressure, temperature, and solution concentration exert an enormous effect on the corrosion process [1]. The natural occurrence of metal and alloy corrosion occurs when these materials interact with aggressive media or environments, oxidizing or returning to their anions and eventually forming thermodynamically stable forms [2]. In essence most of the corrosion agents or triggers are oils, water, liquid chemicals, gaseous materials and humidity in air [3]. Because metals are used continuously in industry and society at large, corrosion is a major concern. Metal corrosion is a damaging condition that can lead to mechanical failure and product devaluation. Additionally, it leads to the deterioration and eventual failure of industrial systems and component parts [4]. Hazardous side effects of corrosion include the potential for explosion, fire, and even loss of capital and equipment. It can also alienate employees [5].

There exist multiple strategies for reducing the degree of corrosion, but the most efficient and economical approach is to employ inhibitors [6]. Corrosion can be prevented by organic, inorganic, or a combination of the two inhibitors by interacting with the metal ions and creating a barrier-type precipitate on the metal surface, or by chemisorption on the metal surface [7]. Green inhibitors, which are plant-based extracts containing nitrogen, sulfur, and oxygen compounds that are highly effective as inhibitors in an aggressive medium, have drawn a lot of attention as a potential replacement for synthetic inorganic inhibitors, which are frequently hazardous, costly, and unfriendly to the environment [8-9].

Mostly, these heteroatoms are adsorbed either physically or chemically on the metal surface to block the destruction reaction with aggressive media [10-11]. One of the green plants that is employed as a corrosion inhibitor is the neem tree (*Azadirachta indica*). Neem tree are commonly known as “Dalbejiya” or “Dogon yaro” by hausa native people particularly in northern part of Nigeria. The tree is widespread throughout the world, but in Nigeria, it is typically found in large quantities in the northern region, where it grows year-round. Collecting the leaves that fall to the ground beneath the tree and removing the bark from it costs very little, if anything at all [12].

The bark of the neem tree was identified in the herbarium department of Bayero University Kano, where it was confirmed to belong to the following: kingdom; plantae, family; maliaceae, genus; *Azadirachta*, specie; *Azadirachta indica*, common name; neem tree (bark), and local name; darbejiya. Different parts of the plant were utilized as green corrosion inhibitors which includes the use of Oils of *Mentha piperita* and *M. pulegium* [13], Leaves of *Polyalthia longifolia* [14], Leaves of *Camellia Sinensis* [15], Leaves and Stem extract of *Sida acuta* [16], *Cocos nucifera* coir dust extract [17] and Okro leaf extract [18] as corrosion inhibitors in aggressive medium.

The aim of the current research work is to study the inhibition potential of bark extract of the Neem tree (*azadirachta indica*) against Zinc corrosion in a 0.75 M HNO_3 solution using weight loss measurement.

2. EXPERIMENTAL

a. Preparation of metal couple

Energy dispersed X-ray (EDX) was used to characterize the zinc metal sheet that was purchased from nearby marketers. Zinc metal specimen sheets, measuring 0.2 cm in thickness, were mechanically pressed and cut into various coupons, with each dimension measuring 2.0 × 2.0 cm. Every coupon was cleaned with ethanol to remove grease, dried in acetone, and then preserved in a desiccator. Using SiC polishing paper, the zinc coupons' working surface was delicately polished to remove the oxide layer and stop any potential reactions between the acid and zinc oxide layer [12].

b. Plant sample collection and preparation

A fresh sample of neem tree (Melipeaceae) bark was collected on the grounds of Bayero University, Kano old site, Nigeria. It was authenticated in the herbarium research laboratory, Bayero University, Kano (Herbarium Accession number BUKHAN 312) with the following identities: Kingdom – Plantae; Family – Meliaceae; Genus – *Azadirachta*; Specie – *Azadirachta indica*; Common name – Neem tree (Bark); Local name – Darbejiya. After a water wash, the sample was shredded and allowed to air dry at 30°C for a minimum of seven days. The sample was then ground into powder, sieved into fine powder, and kept in a plastic container with an airtight lid [19].

c. Medium

In order to achieve the required concentration of 0.75 M HNO_3 solution through serial dilution, analytical grade HNO_3 was diluted with distilled water to create the corrosive solution.

d. Extraction of the Plant Bark

250g of air-dried bark were weighed and ground with a mortar and pestle. The bark was then macerated in 1000 ml of 99% ethanol, and the mixture was shaken to allow the bark to be extracted into a large glass trough that was covered and kept at room temperature. The solution was shaken vigorously every day for at least a week in order to obtain a homogenous extract [12, 20]. After that, the bark was repeatedly filtered to produce a clear extract free of bark particles. A reddish extract was left in a beaker after the filtrate was evaporated under reduced pressure using rotary vapour and dried at 100°C for a few minutes in an oven to constant weight. The extract obtained was stored in desiccator for further used [21-23].

e. Weight loss measurements.

Weight loss measurement was used to analyze the zinc corrosion rates and inhibitory efficiency of the investigated extracts at various inhibitor concentrations (0.20, 0.40, 0.60, and 0.80g/L), varying temperature (303K – 333K), and utilizing 0.75 M HNO_3 as reported elsewhere [22, 24]. The weight loss (W_L) was determined using the following relation:

$$W_L = W_0 - W_f \qquad (1)$$

Where: W_0 is the zinc weight before immersion in the corrosive medium.

W_f is the zinc weight after immersion in the corrosive medium.

$$C_R = \frac{weight\ loss}{area \times time \times density} \times 8.76 \times 10^4 \qquad (2)$$

$where\ w$ is the corrosion weight loss of zinc (g), area of the coupon (cm^2), t (h), and density of zinc in ($g\ cm^{-3}$), Corrosion rate (C_R) in mm/year ([25]).

The inhibition efficiency of the extract was calculated using the following relation:

$$I.E.(\%) = \frac{W_u - W_i}{W_u} \times 100 \quad (3)$$

Where: W_u is weight loss without inhibitor, W_i is weight loss with inhibitor. The surface coverage (θ) of the zinc specimen for different inhibitor concentration in HNO_3 solution were evaluated by weight loss experiments using the following [22] equation:

$$\theta = \frac{W_u - W_i}{W_u} \quad (4)$$

f. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

To ascertain the structural organization of the neem bark extract under study, uncorroded metal, and corrosion products, FT-IR analysis was performed on neem bark extract, unreacted zinc, and that of the corrosion products in 0.75 M/0.80 g/L HNO_3 inhibited solution at 303 K following a 4-hour immersion time [19]. The analysis was carried out using Agilent Technology, FT-IR (Cary 630) Fourier Transform Infrared Spectrophotometer, by scanning the sample through full scale wave number range (4000-650 cm^{-1}).

g. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) model (PR: X: phenonm World 800-07334) was used to examine the zinc specimen's surface both before and after inhibition with neem bark extract. After four hours immersion time, scanned images of the unreacted, uninhibited, and inhibited metal at 0.00 g/L and 0.8 g/L inhibitor concentration at 303 K in 0.75 M HNO_3 concentration were determined at an accelerating voltage of 15.00kV and x 500 magnification.

3. RESULTS AND DISCUSSION

Weight loss measurement

A weight loss experiment using a zinc metal coupon was conducted at 303–333K with an inhibitor concentration of 0.20–0.80g/L in 0.75 M HNO_3 solution. The results of weight loss measurement are presented below.

Table 1. Weight loss measurement parameters of zinc corrosion in an aqueous solution of 0.75 M HNO_3 solution in absence and presence of different concentration of inhibitor

	0.75 M HNO_3											
	Temperature											
Conc. (g/L)	**303K**			**313K**			**323K**			**333K**		
	C_R **Mm/yr**	**IE %**	θ	C_R **Mm/yr**	**IE %**	θ	C_R **Mm/yr**	**IE %**	θ	C_R **Mm/yr**	**IE %**	θ
0.00	478.92	-	-	594.27	-	-	699.20	-	-	884.84	-	-
0.20	410.05	14.38	0.1438	630.96	10.65	0.1065	638.46	8.69	0.0869	826.53	6.59	0.0659
0.40	370.28	22.69	0.2269	479.92	19.24	0.1924	592.70	15.23	0.1523	782.18	11.60	0.1160
0.60	315.38	34.15	0.3415	425.74	28.36	0.2836	541.51	22.55	0.2255	734.28	17.02	0.1702
0.80	262.63	45.16	0.4516	388.67	34.60	0.3460	498.31	28.73	0.2873	688.22	22.22	0.2222

Table 2. Weight loss measurement at different contact time

Time (hour)	**0.75 M HNO_3**			
	C_R **(mm/yr)**		**IE (%)**	θ
	Uninhibited	**Inhibited**		
1.00	1383.01	876.00	36.66	0.3666
2.00	853.47	504.16	40.93	0.4093
3.00	591.79	338.00	42.88	0.4288
4.00	478.92	262.63	45.16	0.4516

a. Experimental weight loss analysis

Tables 1 and 2 show the results of a weight loss analysis conducted in a 0.75 M concentration of nitric acid solution. The results of the weight loss measurement of zinc metal in 0.75 M HNO_3 solution with varying inhibitor concentrations (0.20g/L to 0.80g/L) at 303K–333K are displayed in Table 1 along with the corrosion rate, inhibition efficiency, and surface coverage. It is pertinent to note from the above result that, at four different temperatures and in an acid concentration, the addition of the plant extract in 0.75 M HNO_3 solution reduces the rate of corrosion and weight loss when compared to the uninhibited solution. Further addition of the extract concentration from 0.20g/L to 0.80g/L lead to more decrease in corrosion rate from 478.92 mm/yr to 262.63 mm/yr in 0.75 M HNO_3.

Also, as the concentration of the inhibitor increased, the extracts' inhibition efficiency increased as well, reaching 45.16% after four hours in 0.75 M/0.80g/L HNO_3. These findings is in agreement with the findings of Jyothi and Ravichandran (2013), Kathirvel *et al*. (2014) and Arinkoola *et al*. (2020) [9, 26-27]. Moreover, the result in Figure 4 indicated that corrosion rate increases with rise in temperature due to increase in kinetic energy of the corrosive medium. In addition, there appears to be a strong interaction between extract molecules and the metal surface, as evidenced by the increase in inhibition efficiency observed with an increase in inhibitor concentration [20]. Accordingly, earlier findings suggested that the plant extract can function as an effective corrosion inhibitor to delay the rate at which zinc metal deteriorates in a solution containing nitric acid.

As Figure 4 illustrates, the system's temperature has an impact on the extracts' performance of inhibition efficiency; as the temperature rises, the inhibition efficiency of the extracts decreases. The observed decrease in the extracts' inhibition efficiency with rising temperatures may be attributed to the possible desorption of certain inhibitor molecules that have been adsorbed onto the metal surface. As a result, the inhibitor molecules' behaviour on the metal surface suggested that the molecules were physically adsorbed there, and the adsorption mechanism can therefore be referred to as a physisorption mechanism [28-30].

b. **Effect of contact time**

Table 2 displays the findings of the corrosion rate and inhibition efficiency changes over time for a 0.75 M HNO_3 solution. The findings showed that as contact time increases, the corrosion rate in both the inhibited and uninhibited solutions decrease. However, it was discovered that the extract's inhibition efficiency increased as contact time increased, which is in good agreement with the findings of Venkatesha *et al*. (2008), Murugavel and Gunavathy, (2012) and Jane and Nakara, (2019)[4, 31-32]. The results of variation of inhibition efficiency with time and corrosion rate with time for 0.75 M are presented in Figure 1 & 2 respectively.

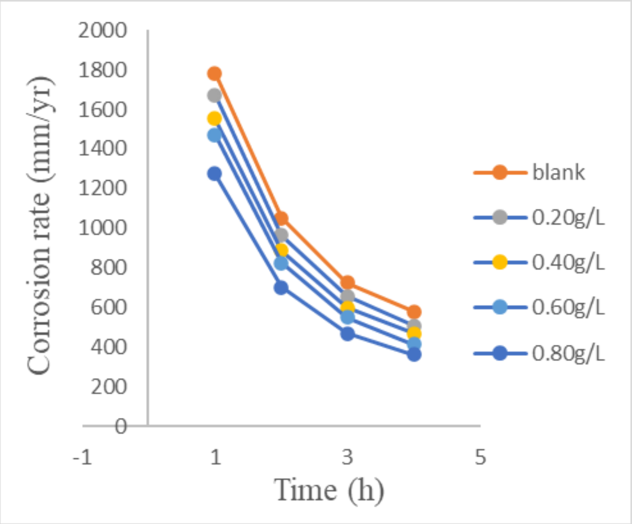

Fig.1. Variation of corrosion rate with time for 0.75 M HNO_3

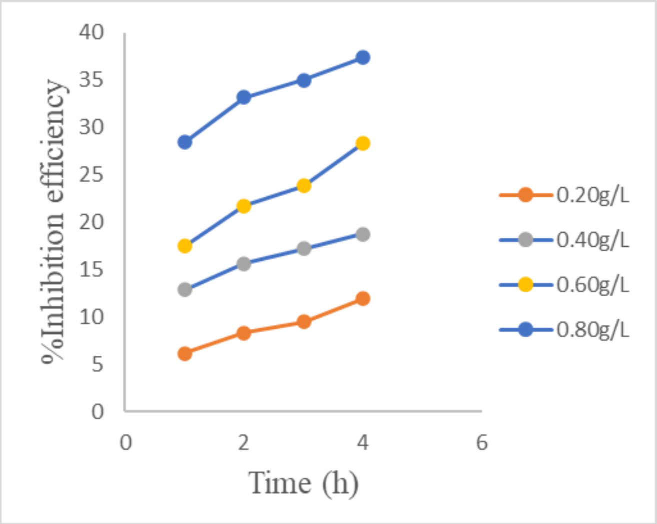

Fig.2. Variation of %Inhibition efficiency with time for 0.75 M HNO_3

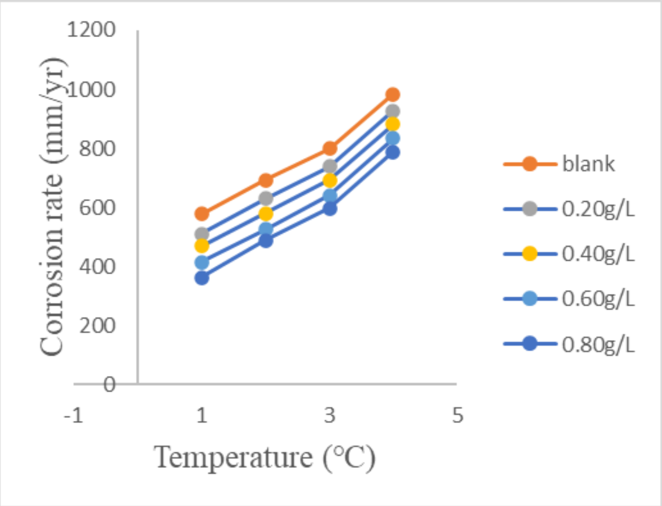

Fig.3. Variation of corrosion rate with temperature for 0.75 M HNO_3

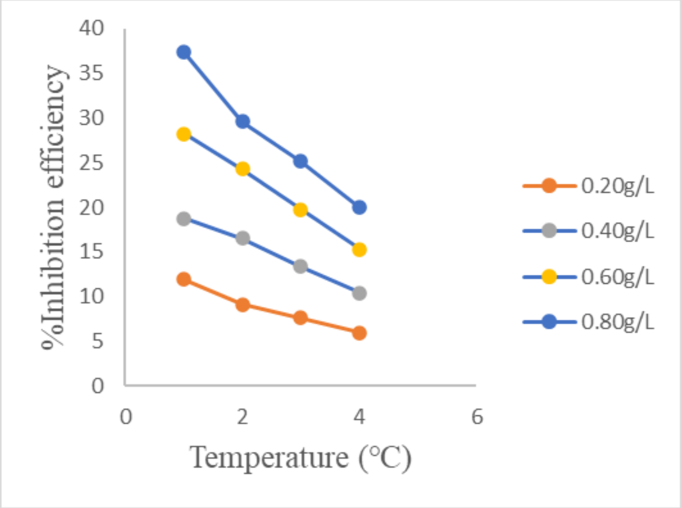

Fig.4. Variation of %Inhibition efficiency with temperature for 0.75 M HNO_3

The result displayed in Figure 1-4 illustrates how the extract's corrosion rate and inhibition efficiency change with temperature and time in a 0.75 M HNO_3 solution. The results, which are shown in Figures 1 and 3 of the 0.75 M HNO_3 solution, showed that the corrosion rate increased with contact time but decreased with temperature. The rationale for the decrease in corrosion rate with increasing time is that more corrosion product covers the metal's surface over time, reducing the area on the metal surface that is available for acid attack, while on the other hand, increase in temperature increase the kinetic energy of the acidic solution thereby increasing the level of corrosion reaction on metal surface as such corrosion rate increases.

Furthermore, as shown in Figures 2&4 for a 0.75 M HNO_3 solution, the inhibition efficiency in nitric acid was found to increase with time but decrease with temperature. These can be explained by the fact that longer contact times between the inhibitor solution and the metal surface enable the inhibitor to make better contact with the metal, protecting it more and enhancing the extract's ability to inhibit it. Conversely, higher temperatures cause more acid to attack the metal surface, decreasing the extract's ability to inhibit it in an acidic solution. The results also show that inhibition efficiency was higher in the highest inhibitor concentration.

The inhibition ability of *azdirachta indica* bark extract like other plant extracts can be ascribed to the adsorption of phytochemical constituent present (flavonoids, alkaloids, saponins, glycosides, terpenoids, etc.) on the surface of zinc metal [33-35].

c. **Fourier Transform Infrared (FT-IR) Spectroscopy**

The functional groups that are present in the adsorption film that are produced when inhibitor molecules adsorb on the surface of zinc were discovered using Fourier transform infrared (FT-IR) spectroscopic techniques. The plant extract used as corrosion inhibitor contain several organic compounds. These analyses were used to find the carbon base and inorganic functional groups present, as well as to examine the structural organization of the extract and corrosion product [19, 28]. The FT-IR spectra of *azadirachta indica* bark extract, uninhibited zinc surface and that of corrosion product in 0.75 M HNO_3 in 0.80g/L inhibitor concentration are presented in Figure 9a, 9b and 9c respectively.

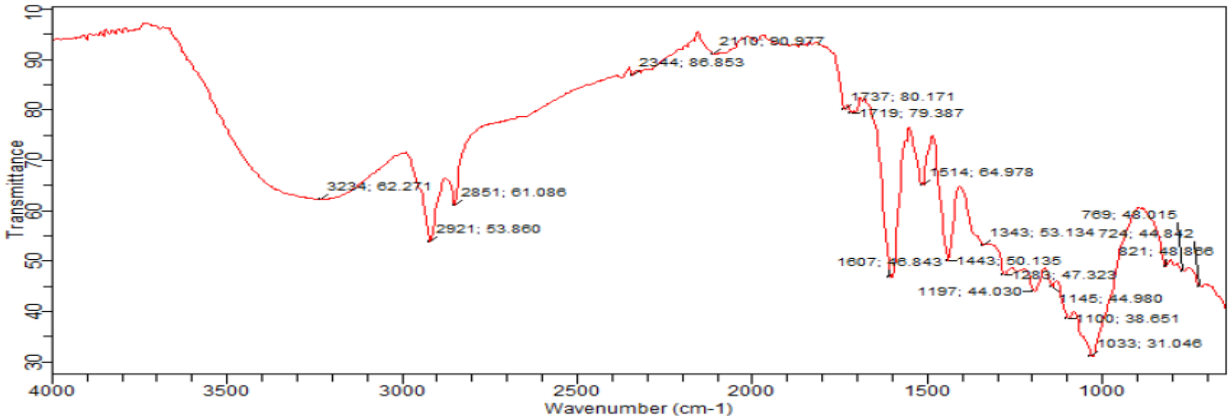

Fig.9a. FT-IR Spectrum of the neem (AI) bark extract

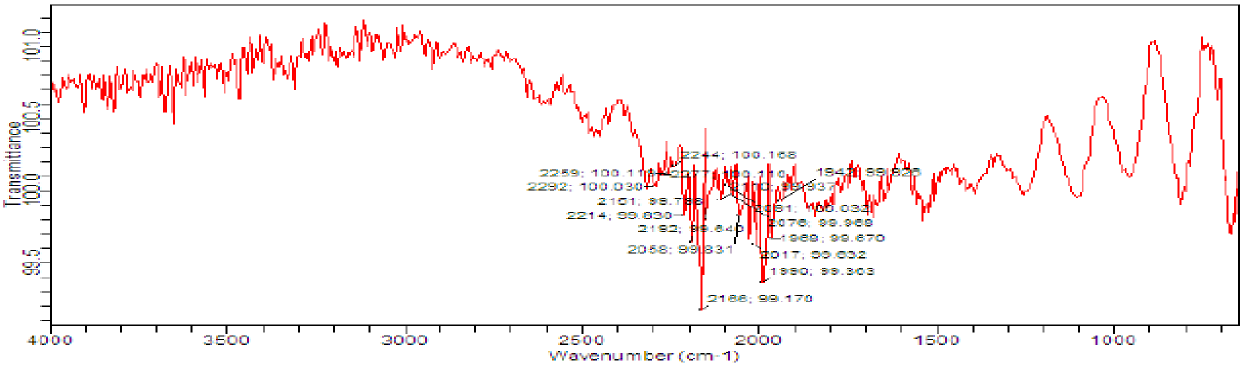

Fig.9b. FT-IR Spectrum of uninhibited zinc in nitric acid

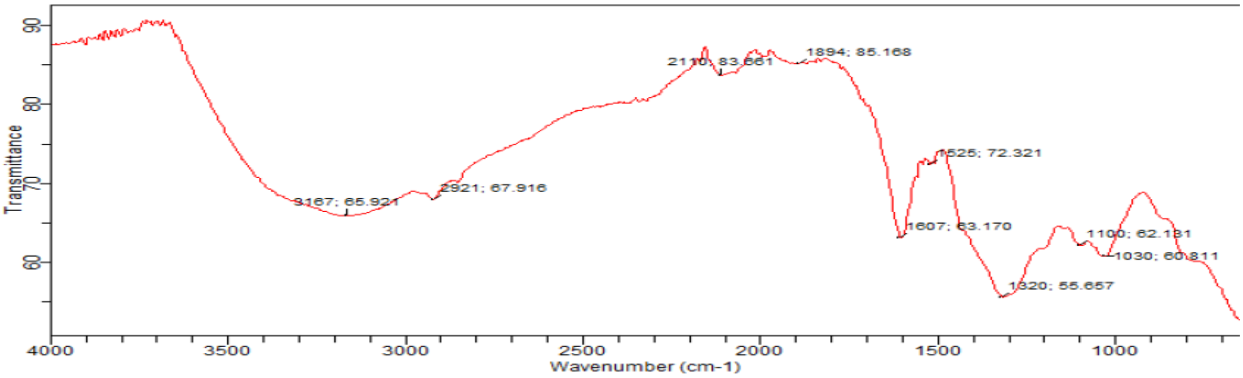

Fig.9c. FT-IR Spectrum of zinc corrosion product immersed in inhibited 0.75M nitric acid

It is evident that Figure 9c and Figure 9a share similar constituents. This is because some of the extract's constituent phytochemical compounds have adhered to the metal surface after adsorption. Consequently, the result from Figure 9a shows that adsorption band at 3234 cm^{-1} was assign to –OH stretching vibration, peak at 2921 cm^{-1} correspond to C-H Stretch vibration, peak at 2344 cm^{-1} was assign to C≡N Stretching vibration, and absorption band at 2110 cm^{-1}

was correspond to C=C stretching vibration. The peak at 1607 cm^{-1} was assign to N-H bending vibration, and adsorption band at 1514 cm^{-1}, 1343 cm^{-1}, and 1033 cm^{-1} correspond to C-H bending vibration, C-O bending vibration, and C=O bending vibration respectively. Accordingly, the result in Figure 9c –OH stretching vibration was assign to 3167 cm^{-1}, C≡N Stretching vibration appeared at 2110 cm^{-1}, C=C stretching vibration at 1894 cm^{-1}, C-H bending vibration assigned to 1525 cm^{-1}, C-O bending vibration assigned to 1320 cm^{-1}, and C=O bending vibration was assigned to 1030 cm^{-1}.

This clearly shows that the adsorption bands of the corrosion product and the plant extract differed only slightly, suggesting that phytochemicals in the plant extract may have physically adhered to the zinc surface through adsorption in acidic media [1, 26]. The interaction between the zinc surface and plant extract was indicated by these shifts in the absorption band of the corrosion product's FT-IR spectra. Additionally, it is noted that some functional groups are absent from the corrosion product's spectra. This indicates that the inhibitor may have been adsorbed through the missing bonds, and the extract possesses an inhibitory effect on the rate of zinc corrosion in nitric acid solution [36-37].

d. Scanning Electron Microscopy (SEM)

The surface morphology of zinc metal in uninhibited 0.75 M HNO_3 solution and inhibited solution by *azadirachta indica* bark extract was examined using SEM micrograph analysis, which will corroborate our findings. The SEM analysis results for unreacted zinc sample, uninhibited zinc in 0.75 M HNO_3 solution and inhibited sample by bark (AI) extract are presented in Plate 1, 2 and 3 respectively.

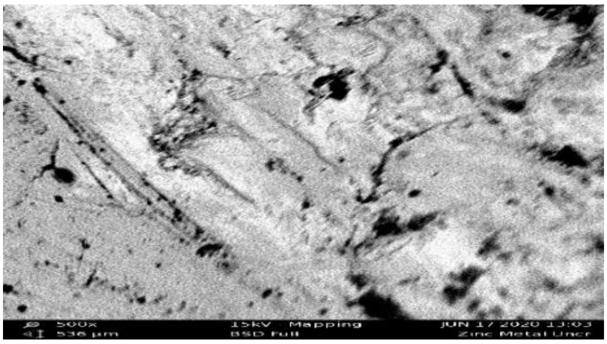

Plate 1. SEM micrograph for unreacted zinc

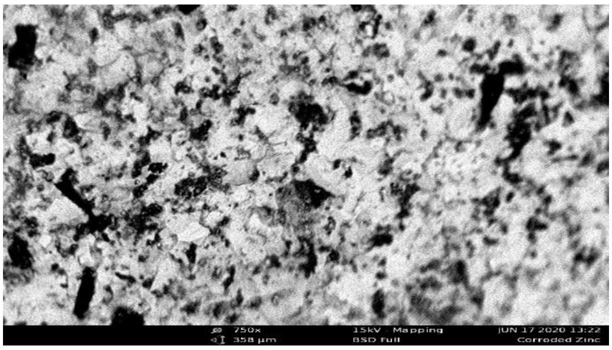

Plate 2. SEM micrograph for uninhibited zinc in 0.75 M HNO_3 solution

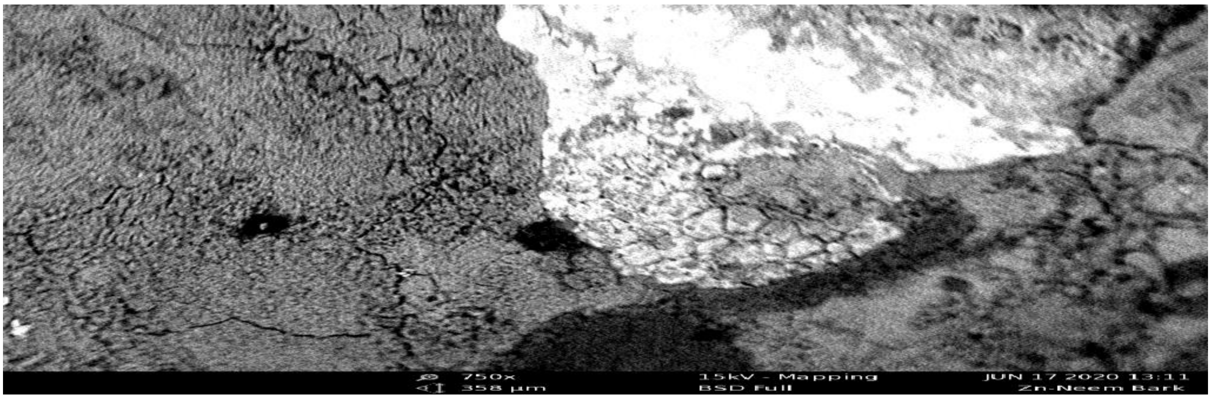

Plate 3. SEM micrograph for bark (AI) inhibited zinc in 0.75 M HNO_3 solution

As the sample did not take part in any reaction, the result in Plate 1 for the unreacted zinc sample displays the smooth, finely polished surface of zinc along with some scratches that occurred during polishing. In contrast, the result in Plate 2 for the reacted zinc sample in the uninhibited solution of 0.75 M nitric acid appeared to be severely roughened due to severe corrosion attack by 0.75 M HNO_3 acid media. Furthermore, the results in Plate 3 shows the micrograph for inhibited zinc sample in 0.75 M HNO_3 solution. The formation of a protective film on the surface of zinc metal was visible in these micrographs, which is not present when zinc is in an uninhibited nitric acid solution.

e. **Adsorption Isotherms**

Adsorption behavior provides the most compelling explanation for the mechanism underlying the plant extract's inhibitory effect. Based on weight loss data for the nitric acid concentration, the degree of surface covered (θ) for various inhibitor concentrations was computed. The data were analyzed graphically by fitting them into various isotherms under study. The surface coverage θ, which was computed in equation 4, was used to study five different adsorption isotherms: the Freundlich, Temkin, Flory-Huggins, Langmuir, and Frumkin isotherms. The high correlation coefficient (R^2) indicated that the Freundlich isotherm in nitric acid concentration best fit the experimental data. The results of Freundlich isotherm are presented in Figure 10, which was plotted using linear graph of $log\theta$ against $logC$. The nature and surface charge of the metal, the distribution of charge within the molecule, the type of aggressive media, and the chemical structure of organic compounds all had an effect on the inhibitor molecules' ability to adsorb onto the zinc surface [38]. Therefore, adsorption isotherm studies can suggest the nature of metal-inhibitor interaction and described the adsorption behaviour of the inhibitor molecules.

Furthermore, since the experimental data was best fitted into Freundlich isotherm, the adsorption mechanism can be described as physical adsorption mechanism, which means the adsorbed compounds of the extract were physically adsorbed on zinc surface and it also involved multilayer of adsorbate on the outer surface of the adsorbent [28, 39-40]. Also, the value of the Freundlich factor n is less than 1 which implies ease of adsorption of inhibitor molecule on to the zinc surface. The Freundlich equations can be expressed as follows:

$$log\theta = logK + \frac{1}{n}logC \qquad (5)$$

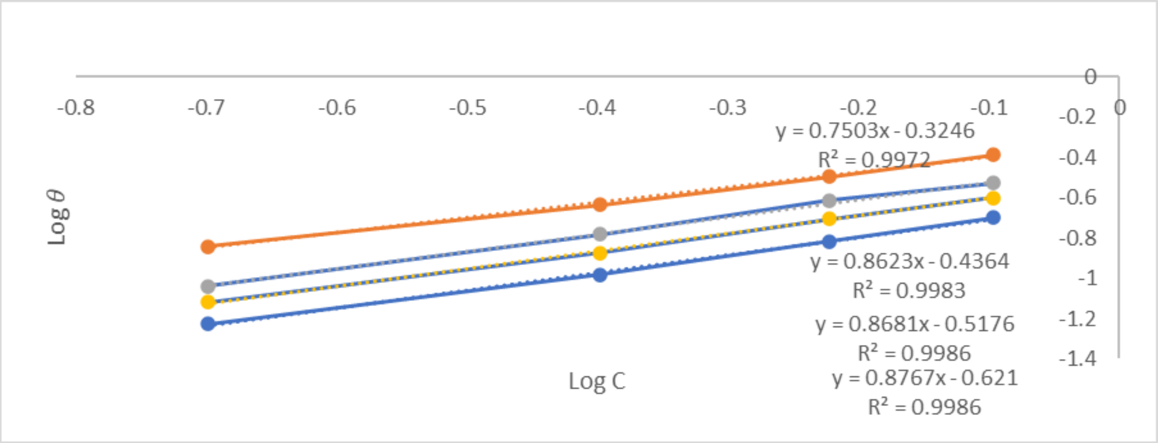

Fig.10. Freundlich Isotherm for neem bark extract at 0.75 M HNO_3 and at various Temperature

f. **Thermodynamic and Kinetic Studies**

In order to ascertain the process's practical application and predict whether the adsorption process is spontaneous or nonspontaneous, thermodynamics parameters were assessed. Thermodynamics parameter such as free energy of adsorption, enthalpy and entropy were calculated and presented in Table 3 & 4. The above mentioned thermodynamic parameter were calculated using equation below:

$$\Delta G^0_{ads} = -RTln\,(55.5K_{ads}) \qquad (6)$$

$$log\frac{C_R}{T} = \left(log\frac{R}{Nh} + \frac{\Delta S}{2.303R}\right) - \frac{\Delta H}{2.303RT} \qquad (7)$$

Where R is the universal gas constant and T is the thermodynamic temperature, 55.5 is the concentration of water in the solution in 1 mol.dm^{-3}, ΔG^0_{ads} is the standard free energy (kJ.mol^{-1}). Equation (7) is called transition state equation, where C_R is the corrosion rate, h is the Plank's constant (6.626176×10^{-34} Js), N is the Avogadro's number (6.02252×10^{23} mol^{-1}), R is universal gas constant. The plot of log C_R/T versus 1/T gives a straight line with slope of [-ΔH/2.303R] and intercept of [log R/Nh + ΔS/2.303R] from which the values of ΔH and ΔS were calculated [35].

Table 3. Change in Gibbs Free-Energy, K_{ads} values and Correlation coefficient at various Temperature

0.75 M HNO_3											
ΔG (kJmol^{-1})				**K_{ads}**				**R^2**			
303K	313K	323K	333K	303K	313K	323K	333K	303K	313K	323K	333K
-7.28	-8.29	-9.01	-9.80	0.3246	0.4364	0.5176	0.621	0.9972	0.9983	0.9986	0.9986

The decrease in the materials' Gibbs free energy value is one of the main causes of corrosion [41]. Thus, the free energy result shown in Table 3 showed that, in 0.75 M nitric acid, the negative value of Gibbs free energy increases with temperature, and as a result, metal corrosion also decreases. The negative sign of Gibbs free energy implies that the adsorption process was spontaneous and the adsorbed layer of inhibitor formed on the surface of zinc metal was stable. Hence, all the values of Gibbs free energy of adsorption presented in the result are less than -20KJmol^{-1} and joined with decrease in inhibition efficiency of the extract with rise in temperature suggested the physical adsorption mechanism succeeded for the adsorption of inhibitor on to metal surface, otherwise if the values of free energy are more negative than -40KJmol^{-1} chemical adsorption mechanism will prevailed [42-43].

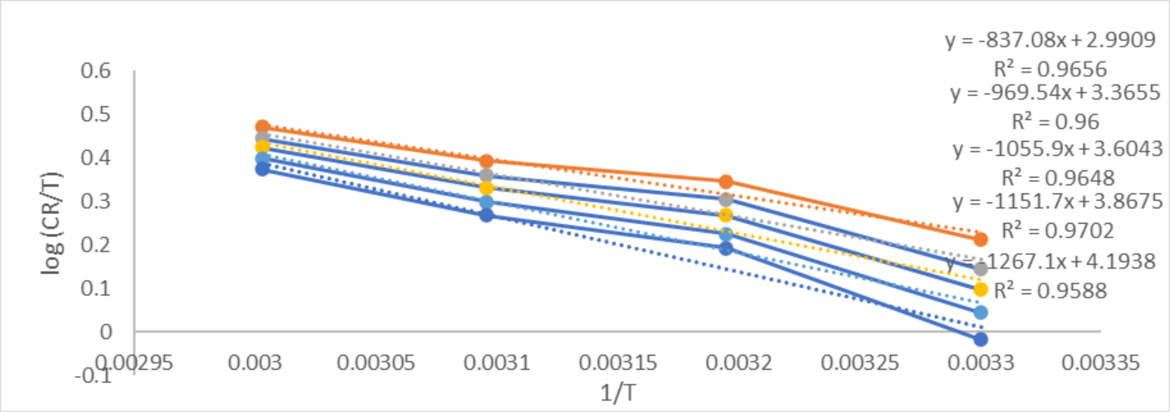

Fig.12. Plot for transition state equation at 0.75 M HNO_3

The results of enthalpy ΔH_{ads} and entropy ΔS_{ads} of adsorption at different inhibitor concentration were calculated and presented on Table 4, and the plot for transition state equation are presented on Figure 12 for 0.75 M HNO_3 solution. The result of activation enthalpy in the presence of inhibitor extract was higher when compared to the uninhibited solution which indicates that there was increase in the energy barrier of the corrosion reaction, as such the dissolution of zinc metal became difficult [23]. Also, the positive values of enthalpy indicate the endothermic nature of zinc dissolution process [44].

Subsequently, the values of activation entropy are negative in both inhibited and uninhibited solution. This can be ascribed to the free movement of the inhibitor molecules in the bulk solution, which were adsorbed on to the metal surface, and also implies that the association mechanism succeeded rather than dissociation i.e. there is decrease in solution agitation from reactant to activated complex taking place [24, 45].

Table 4. Activation energy, Enthalpy and Entropy of adsorption for 0.75 M and 1.0 M HNO_3 solution at different inhibitor concentration

Inhibitor Con. (g/L)	**0.75 M HNO_3**		
	Activation energy (E_a) $kJmol^{-1}$	**Enthalpy (ΔH_{ads}) $kJmol^{-1}$**	**Entropy (ΔS_{ads}) $Jmol^{-1}$**
0.00	18.66	16.02	-0.0829
0.20	21.19	18.56	-0.0757
0.40	22.85	20.21	-0.0711
0.60	24.68	22.05	-0.0661
0.80	26.89	24.26	-0.0598

The result of activation energy was presented in Table 4, which was calculated from the plot of ln C_R against 1/T that gives a straight line with slope of $-E_a / R$ using Arrhenius equation [46].

$$\ln C_R = \ln A - \frac{E_a}{RT} \tag{8}$$

The Arrhenius plot at various inhibitor concentration are presented on Figure 12. The result of activation energy shows that increase in inhibitor concentration increases activation energy of the system. Also, the result of activation enthalpy and that of activation energy for 0.75 M nitric acid concentration are higher in inhibited solution as compared to uninhibited solution, suggesting that the energy barrier of the corrosion reaction increases in the inhibited solution without changing the mechanism of dissolution [43].

In addition, the fact that inhibited solution has a higher activation energy than uninhibited ones implies that the dissolution of zinc takes time. Hence, when the inhibitor concentration of the extract increases so did the activation energy. This means that the inhibitor act as a physical barrier to the corrosion process (physisorption), which becomes stronger as the concentration becomes higher [47-50].

4. CONCLUSION

The potential of *azadirachta indica* bark extract to inhibit zinc corrosion in 0.75 M HNO_3 acid solution was investigated through weight loss measurement in an experimental analysis that also included thermodynamic and kinetic studies and an examination of the adsorption isotherm. The findings' conclusions are summed up here:

- Zinc corrosion was effectively reduced by the *azadirachta indica* bark extract in a 0.75 M HNO_3 acid solution. It was discovered that while the inhibitor's inhibition efficiency decreased with rising temperatures, it increased with increasing concentrations.
- At an inhibitor concentration of 0.80g/L, the extract's inhibition efficiency was observed to reach 47.37.
- The adsorption of phytochemical compounds present in the extract is responsible for the inhibitor extract's adsorption onto the metal surface.
- The study of adsorption isotherms demonstrates that the experimental data comply with the Freundlich isotherm and that the adsorption mechanism is based on physisorption.
- Thermodynamic studies on adsorption revealed a spontaneous and feasible process based on a negative value of ΔG_{ads}. The values of enthalpy are all positive indicating endothermic nature of the adsorption process.
- The activation energy result showed that the presence of the inhibitor increased the energy barrier of the zinc dissolution process compared to its absence.

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