

# Study of the Inhibitive Property of *Azadirachta indica* (Neem Tree) Gum on Mild Steel Corrosion in Various Acidic Media

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## ABSTRACT

**Aims:** The aim of this work is to investigate the inhibitive properties of *Azadirachta indica* (neem) gum on mild steel corrosion in different acidic media using gravimetric method.

**Place and Duration of Study:** Chemistry Laboratory, Department of Chemistry, Kano University of Science and Technology, Wudil, between January 2018 and March 2018.

**Methodology:** Gravimetric method was used to analyze the effectiveness of *Azadirachta indica* (AZI) gum as a mild steel corrosion inhibitor in 1.0M nitric acid (HNO<sub>3</sub>), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl) solutions at 298K and 313K. Weight loss was obtained at different concentrations of the inhibitor; 0.50, 1.00, 1.50, 2.00 and 2.50% w/v. From the weight measurements, the degree of surface coverage and inhibitor efficiency were computed. Activation energy was calculated using the Arrhenius equation, and Gibbs free energy and heat of adsorption were determined to study the spontaneity and enthalpy of the corrosion process. Adsorption isotherms; Langmuir, Temkin and Freundlich were employed in order to have insight into the possible mechanism of adsorption involved.

**Results:** Gravimetric measurements of pure solvents used at several concentrations (0.5, 1, 1.5 and 2 M) showed that weight loss increases with temperature and concentration of the acids. When different concentrations of inhibitor were introduced into the solvents, similar trend was observed. Inhibitor efficiency increases with temperature and with concentration of the inhibitor. H<sub>2</sub>SO<sub>4</sub> was found to have the highest inhibition efficiency of 89.93% and 95.82% at 298K and 313K respectively in 2.5%w/v concentration of the inhibitor. Its strong hydrogen bonding and high surface tension may be a contributing factor. Corrosion rate was calculated and HNO<sub>3</sub> was found to be more corrosive than HCl and H<sub>2</sub>SO<sub>4</sub> both in the presence and absence of the inhibitor at 298K and 313K.

**Conclusion:** From the study, *Azadirachta indica* gum was found to retard corrosion of mild steel. HNO<sub>3</sub> acid was more aggressive and has the highest corrosion rate. Therefore corrosion retardation in this medium was least effective. This might be attributed to the strong oxidizing ability of HNO<sub>3</sub> than HCl and H<sub>2</sub>SO<sub>4</sub>. The rate of corrosion was more retarded in H<sub>2</sub>SO<sub>4</sub>. Free energy of the process was negative all through the inhibitor concentrations indicating that the action of the inhibitor on the metal surface was spontaneous. Data of the corrosion process also fitted well in to Langmuir isotherm suggesting that the mechanism of corrosion could be predominantly physisorption.

**Keywords:** Corrosion, neem gum, inhibition, mild steel, Acid media

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## 1. INTRODUCTION

Corrosion is a natural occurring process where it can be defined as the destruction or deterioration of a material's properties due to its interaction with its environment. Corrosion can lead to failures in plant infrastructure and machines which are usually costly to repair, in terms of loss of contaminated products, environmental damage and possibly costly in terms of human health [1].

Some insist there the definition should be restricted to metals but often the corrosion engineers must consider both metals and non-metals. Ceramics, rubber and other non-metallic materials, deterioration of paints and rubber by sunlight or chemicals, fluxing or lining of steel making furnace and attack of solid metal by another molten metal (Liquid metal Corrosion) are all considered to be corrosion [2].

The corrosion of metals is a serious problem in many industries, installations and civil services such as water and sewage supplies [3]. Corrosion can be fast or slow. Corrosion of metal can be considered as extractive metallurgy. Rusting is a term reserved for steel and iron corrosion, although many other metals form their oxides when corrosion occurs [2].

Corrosion inhibitors are chemical compounds usually used in small concentration which when added to a corrosive media retards the corrosion process and keeps its rate to a minimum. Among them, organic compounds containing heteroatoms such as nitrogen, oxygen, sulphur and phosphorus,  $\pi$  electrons in triple or conjugated double bonds possess the ability to act as good corrosion inhibitor as they are easily adsorbed onto the metal surface [1].

An attempt to find corrosion inhibitors that are environmentally safe and readily available has been a growing trend in the use of natural products such as essential oils as corrosion inhibitors for metals in acid cleaning processes. The effectiveness of inhibiting corrosion by an essential oil is closely related for its phytochemical constituents, which includes a non-polar, hydrophobic, consisting of hydrocarbon molecules and a polar, hydrophilic, which presents one or more functional groups [4].

Mild steel being the important alloy of iron has found a wide application in industries, constructional materials and machines due to its low cost and excellent mechanical properties despite of its tendency to corrosion in aqueous solution, especially in acidic media [1]. Mild steel and high carbon steels are classified as ferrous metals (they contain a large percentage of iron). Carbon steels are essentially iron-carbon alloys. For many years, mild steel plates and rod-sections have been used as structural members in bridges, buildings, pipelines, heavy vehicles, in welded plate form for the construction of ships storage vessels and numerous other applications. High carbon steel (having a higher carbon content than mild steel) is harder and stronger, and yet least ductile of all the carbon steels. It is mainly used for the manufacture of metal cutting tools like hammers, saws, forging die blocks, axes, knives, drills and wood [5].

*Azadirachta indica* is a small to medium-sized tree, usually evergreen, up to 15 (30 max.) m tall, with a round, large crown up to 10 (20 max.) m in diameter; branches spreading; bole branchless for up to 7.5 m, up to 90 cm in diameter, sometimes fluted at base; bark moderately thick, with small, scattered tubercles, deeply fissured and flaking in old trees, dark grey outside and reddish inside, with colourless, sticky foetid sap. Leaves alternate, crowded near the end of branches, simply pinnate, 20-40 cm long, estipulate, light green, with 2 pairs of glands at the base [6].

Neem gum is naturally extracted from neem tree by induced or natural injury. Neem Gum is clear, bright and amber-coloured material non-bitter in taste and is soluble in cold water. It is a by product obtained as a result of metabolic mechanism of plants and trees. Neem has been commercially tapped for using its gum which is used in large number of industries.

Neem cake as a byproduct of neem oil industry is used as livestock feed, fertilizer and natural pesticide. Neem oil is commonly used in soap production. Medicated neem soaps are gaining popularity. Neem based toothpaste is widely used in India and European countries. Neem is a source for many oral-hygiene preparations and dental care products. Neem bark yields gum and tannins which are used in tanning, dyeing etc. Neem seed pulp is used as a rich source of carbohydrate in fermentation industries and for methane gas production [7].

The main aim of this work is to investigate the inhibitive properties of *Azadirachta Indica* (neem) gum on mild steel corrosion in different acidic media using gravimetric method.

## 2. MATERIAL AND METHODS

### 2.1 Materials

Selected plant exudate: *Azadirachta Indica* (neem) gum. Metal : mild steel (3 × 4)cm × 1mm in diameter coupon. Set of 250ml beakers, measuring cylinder, volumetric flask and electric oven, mercury in glass thermometer, stirrer, sieve. Reagents: conc. Nitric (HNO<sub>3</sub>), sulphuric (H<sub>2</sub>SO<sub>4</sub>), hydrochloric (HCl) acids, sodium hydroxide (NaOH) and deionised water

### 2.2 Sample Collection And Identification

The Neem tree (AZI) exudates was extracted and collected from the trees located at Sankara ,Rigim jigawa state. It was then taken and identified at Herbarium of plant Science department Bayero Univesity Kano.

The identification was as follows:

Kingdom: Plantae

Division: Magnoliphyta

Order: sapindales

Family: Maliaceae

Genus: Azadirachta

Specie: *Azadirachta Indica*

Common name: Neem tree exudates

Local name: Karon darbejiya

### 2.3 Preparation of Inhibitor

The purified sample weighed 192g. This amount was then transferred into 1000ml beaker full of double strength chloroform water. On constant stirring, the exudate became sticky and was kept for about four days. The mucilage obtained was strained through a clean calico cloth and the gum was precipitated using 95% ethanol. The precipitate gum was filtered, washed with diethyl ether and then dried in hot air oven. The dried gum was pulverized and passed through sieve size No. 60 (250µm), [8].

### 2.4 Preparation of Mild Steel

Mild steel metals were collected from incubation center located at farm center Kano state. The metals were cut into rectangular shape having 3cm by 4cm and 1mm thickness having an approximate weight of 4g. The metals were washed with water and polished in ethanol and allowed to completely dried to remove moisture which might add some weight to it.

### 2.5 Preparation of Acids

Four different concentrations (0.5,1.0,1.5,2.0)M were prepared each of H<sub>2</sub>SO<sub>4</sub>,HCl and HNO<sub>3</sub> using standard procedures [5]. Below is a demonstration of the work procedure. For example: to prepare 250ml of 0.5M HCl. There are several methods of doing so, but using direct formula will ease and quicken the work.

$$V_1 = \frac{\text{Molarity} \times \text{Molar mass} \times V_2}{\text{Specific gravity} \times \% \text{Purity}} \dots \dots \dots 1$$

### 2.6 Preparation of Quencher

Caustic soda (NaOH) was used as the base to quench the reaction of the acid with metal, before the metal is reweighed. 0.5M quencher was prepared using the below procedure.

$$\text{Mass (g)} = \text{Molarity} \times \text{Molar mass} \times \text{Volume} \dots \dots \dots 2$$

$$\text{Mass (g)} = 0.5\text{mol/L} \times 40\text{g/mol} \times 1\text{L} = 20\text{g}$$

i.e 20g of the Caustic soda (NaOH) was weighed and dissolved in 1000ml of water.

## 2.7 Preparation of Inhibitor Concentration

Five different concentrations (0.5, 1.0, 1.5, 2.0, 2.5)%w/v of inhibitor with 1M of each acid were prepared. To do so, 0.5g, 1.0g, 1.5g, 2.0g, 2.5g of inhibitor each was dissolve in 100ml volume of 1M acid. For example

To prepare 0.5 (%w/v) of inhibitor in 100ml of 1M acid ( $H_2SO_4$ ,  $HNO_3$  or  $HCl$ ), what mass of the inhibitor is required?

$$\frac{0.5}{100} = \frac{X(g)}{100ml} \dots\dots\dots 3$$

$$X = \frac{0.5 \times 100ml}{100} = 0.5g$$

i.e 0.5g of the inhibitor is dissolved in 100ml of 1M acid to prepare 0.5%(w/v) of the inhibitor.

The same procedure was applied for 1.0 (%w/v), 1.5 (%w/v), 2.0 (%w/v), 2.5 (%w/v)

## 2.8 Experimental Procedure

At the outset, 250ml of 0.5M, 1.0M, 1.5M, 2.0M each of the three acids were introduced into twelve (12) different beakers. After taking the weight of twelve set of mild steel, each was then suspended into the beaker containing acids using a thread which was tied to a stick and placed across the top of each beaker. All these twelve set up were left at 313K in an oven for exactly three (3) hours (i.e 11:42am – 2:42pm on 14<sup>th</sup> Feb., 2018). After the metals were brought out of the acids, they were introduced into a beaker containing the quencher in order to quench (stop) the reaction of the acid and metal. The metals were then stained, cleaned up and dried using a filter paper to remove dense that may add some weight to the metal, the final weight of the metal was then taking and recorded. The same procedure was repeated but this time around at room temperature (298K).

Secondly, the same procedure was repeated but this time around using 100ml of 0.5 (%w/v), 1.0 (%w/v), 1.5 (%w/v), 2.0 (%w/v), 2.5 (%w/v) inhibitor concentration each of 1M ( $H_2SO_4$ ,  $HNO_3$  and  $HCl$ ), i.e 15 different beakers and mild steel were used. The initial and final weight of each metal was recorded and it was done at 313K and repeated at 298K for duration of three (3) hours.

A table of data was made, followed by calculations of weight loss ( $\Delta W$ ), Corrosion rate (CR), degrees of surface coverage ( $\theta$ ) and inhibition efficiency (%IE) etc, which shall be discussed in the next chapter and finally conclusion was also reached.

## 2.9 Gravimetric Method

Weight loss: The weight loss of the coupons after time t (in hours) was determined by taking the difference between the weight of the coupon before and after immersion in the acid/inhibitor concentration as the case may be as shown below:

$$\Delta W = W_i - W_f \dots\dots\dots 4$$

Where

$W_i$  = initial weight

$W_f$  = final weight

From the weight loss of mild steel, the corrosion rate ( $gh^{-1}cm^{-2}$ ), inhibition efficiency (%IE) and degrees of surface coverage ( $\theta$ ) were calculated using equation 2 to 4 respectively

$$CR(gh^{-1}cm^{-2}) = \frac{\Delta W}{AT} \dots\dots\dots 5$$

$$IE = \theta \times 100 \dots\dots\dots 6$$

$$\theta = 1 - \frac{\Delta W_1}{\Delta W_2} \dots\dots\dots 7$$

Where,

$\Delta W_1$  and  $\Delta W_2$  are weight losses (g) of mild steel in the presence and absence of the inhibitor respectively,  $\theta$  is the degree of surface coverage, A is the area of the metal coupon (in  $\text{cm}^2$ ), t is the period of immersion (in hours) and  $\Delta W$  is the weight loss of mild steel (in g) after time t.

## 2.10 Kinetic and Thermodynamic Study

### 2.10.1 Activation Energy

$$\ln \frac{CR_1}{CR_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \dots \dots \dots 8$$

### 2.10.2 Free Energy of Adsorption ( $\Delta G_{ads}$ )

The Free energy of adsorption was calculated using the relation:

$$\Delta G_{ads} = -RT \ln(55.5K) \text{kJmol}^{-1} \dots \dots \dots 9$$

The negative value of  $\Delta G_{ads}$  implies spontaneity.

### 2.10.2 Heat of Adsorption $\Delta H_{ads}$

Heat of adsorption was calculated using the formula below;

$$\Delta H_{ads} = 2.303R \left[ \left( \log \frac{\theta_2}{1 - \theta_2} \right) - \left( \log \frac{\theta_1}{1 - \theta_1} \right) \right] \frac{T_1 T_2}{T_2 - T_1} \text{ (kJmol}^{-1}) \dots \dots \dots 10$$

### 2.10.3 Adsorption Isotherms

Adsorption at the metal-solution interface has been considered as the primary step in the action of most organic corrosion inhibitors in acidic environment.

#### 2.10.3.1 Langmuir Adsorption Isotherm

Langmuir plot describes the relationship between the surface coverage and inhibition concentration of a material as:

$$\frac{C}{\theta} = \frac{1}{K} + C \dots \dots \dots 11$$

#### 2.10.3.2 Temkin Adsorption Isotherm

Temkin isotherm was used to determine if the extract adsorption on the metal surface is via chemisorptions which involves displacement of water molecules from the metal surface and the sharing of electrons between oxygen atom and iron. Temkin isotherm plot is expressed as:

$$\theta = \frac{1}{f} \ln(K_{ads}C) \dots \dots \dots 12$$

## 3. RESULTS AND DISCUSSION

### 3.1 Weight Loss

Weight loss of mild steel in different concentration of acids is shown in fig. 1 and 2. In these two figures, the effect of various concentration of  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  at 298 and 313K were shown respectively. Mass loss is higher at 313K than at 298K. This indicates mass loss increases with temperature. At both temperatures and at all concentrations, nitric acid has the highest value of weight loss, then sulfuric acid and lastly hydrochloric acid. In Fig 3 and 4, the variation of weight loss with different concentrations of inhibitor in different acidic media is shown. Here also, it can be observed that weight loss is higher at higher

temperature but decreases with increase in concentration of the inhibitor. At 298K nitric acid and sulfuric acid solutions have highest weight loss at 1%w/v and lowest at 2.5%w/v inhibitor concentration. While hydrochloric acid has its highest mass loss at 0.5%w/v and lowest mass loss at 2.5%w/v. At 313K, nitric acid and hydrochloric acid have high weight loss values at 1%w/v and lowest at 2.5%w/v inhibitor concentration. In sulfuric acid, highest mass loss value was observed at 0.5%w/v and lowest at 2.5%w/v. Generally nitric acid is observed to be more corrosive than hydrochloric acid or sulfuric acid both in presence and absence of inhibitor. This is due to its higher oxidative power than the two other acids even though they are much stronger acids.

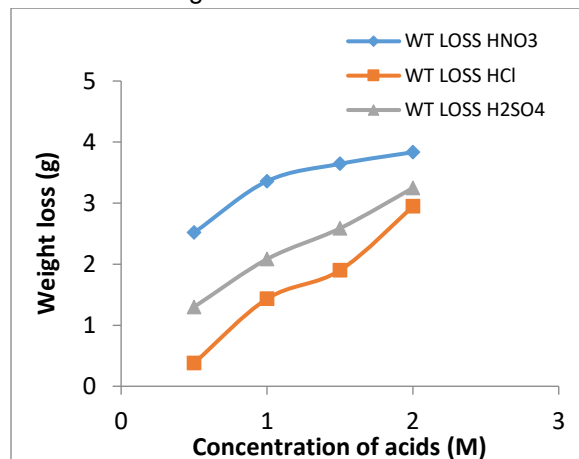


Fig.1. Variation of weight loss with concecntration of the acids at 313K without inhibitor

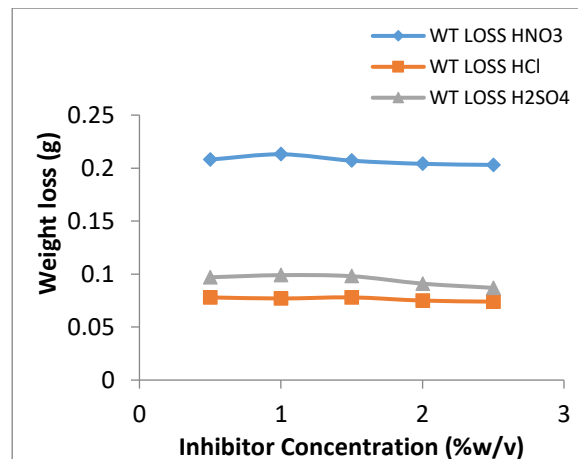


Fig.3. Variation of weight loss with concentration of the inhibitor at 298K.

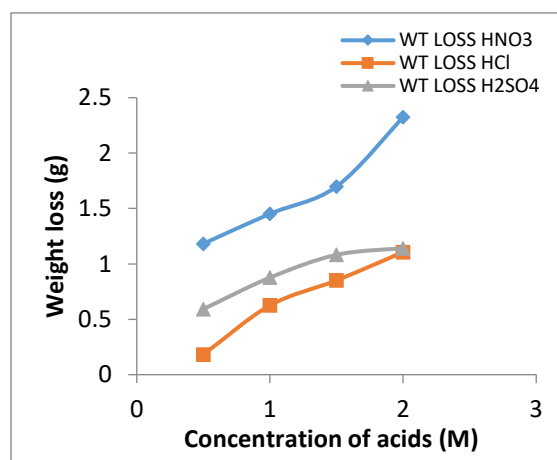


Fig.2. Variation of weight loss with concentration of the acids at 298K

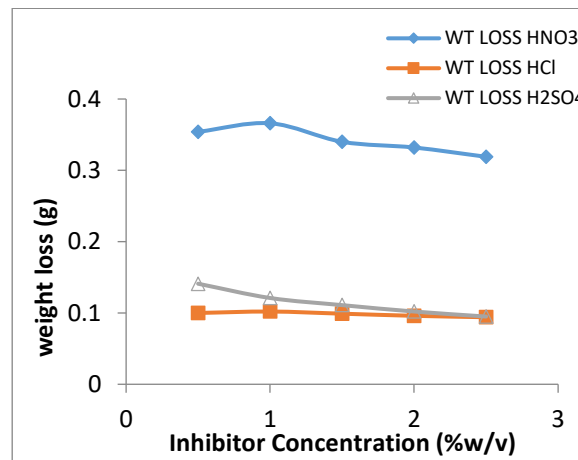


Fig.4. Variation of weight loss with concentration of the inhibitor at 313K

### 3.2 Corrosion Rate

The corrosion rate of the metals was calculated using the relation

$$CR(gh^{-1}cm^{-2}) = \frac{\Delta W}{AT}$$

Fig 5 and 6, show the corrosion rate of mild steel in different acid concentrations without inhibitor at 298K and 313K respectively. Fig 7 and 8 show the effect of inhibitor concentrations on the corrosion of mild steel in the acidic media used in this study i.e HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl, at 298K and 313K respectively. In figures 5 and 6, the trend shows that corrosion rate increases with increase in concentration of the acids. In HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl, the highest corrosion rate was observed in 2.0M and lowest in 0.5M of the acid. In Fig 7 and 8 i.e variation of corrosion rate with concentration of the inhibitor at 298K and 313K respectively, the trend shows that corrosion rate decreases with increase in concentration of the inhibitor. This indicates that the inhibitor is efficient in preventing corrosion on the metal surface.

Comparing all the figures show that corrosion increases with temperature and also nitric acid has the highest corrosion rate followed by sulfuric acid and lastly, hydrochloric acid. The corrosion attack in nitric acid is very significant because nitric acid is known to be a strong oxidizing agent. An autocatalytic mechanism has generally been proposed to explain the rate of corrosion in nitric acid medium [9],[10]. The primary displacement of hydrogen ion is followed by nitric acid reduction rather than hydrogen evolution since the acid reduction leads to a marked decrease in free energy. The reaction can be shown below



This reaction leads to the evolution of nitrogen (II) oxide and production of Fe(NO<sub>3</sub>)<sub>2</sub> which led to formation of brown colour in the medium.

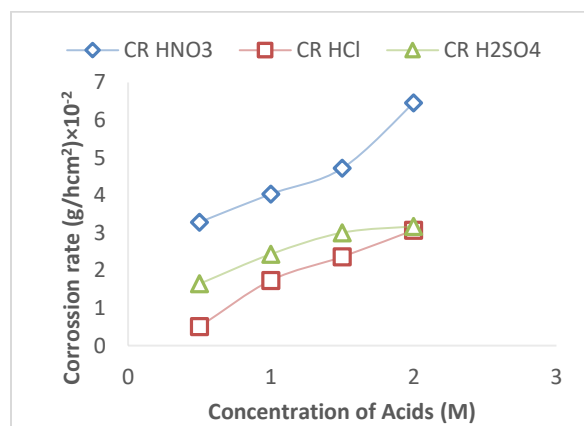


Fig.5. Variation of corrosion rate with concentration of the acids at 298K

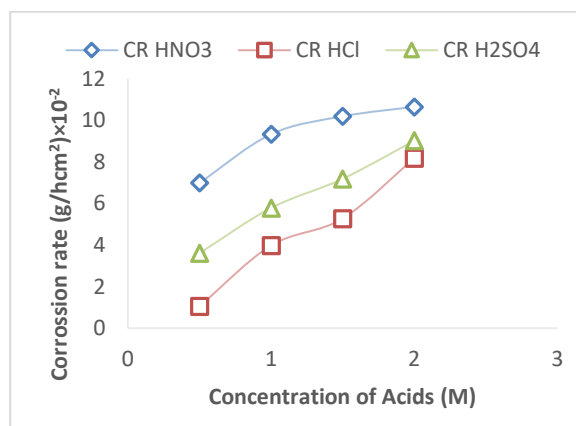


Fig.6. Variation of corrosion rate with concentration of the acids at 313k

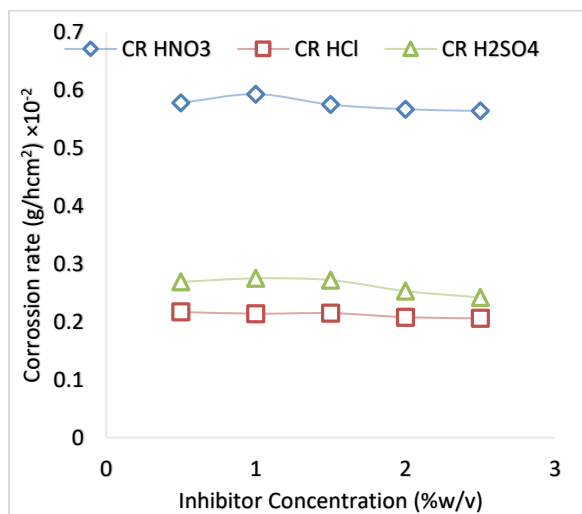


Fig.7 Variation of corrosion rate with concentration of the inhibitor at 298K.

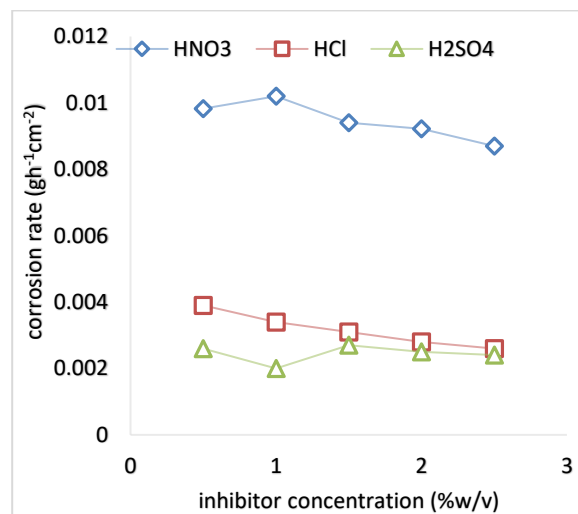


Fig.8. Variation of corrosion rate with concentration of the inhibitor at 313K

### 3.3 Degree of Surface Coverage ( $\theta$ )

The degree of surface coverage was calculated using the relation below;

$$\theta = 1 - \left[ \frac{\Delta W(\text{presence of inhibitor})}{\Delta W(\text{absence of inhibitor})} \right]$$

Weight loss is inversely proportional to the degree of surface coverage. The higher the weight loss, the lower will be the surface coverage. Nitric acid gave the highest weight loss and therefore the lowest surface coverage. This shows that the inhibitor is less active in the solvent as compared to other solvents used. At both 298k and 313k, sulfuric acid has the highest inhibitor coverage, followed by hydrochloric acid and lastly nitric acid. At 313k, surface coverage was observed to decrease when compared to 298K showing that corrosion increases with increase in temperature.

From the charts, it can be shown that surface coverage also gradually increase with increase in concentration of the inhibitor at an almost regular pattern across the solvents used. At 313K a fall in inhibitor coverage was observed for HCl at 1%w/v and at 1% and 1.5% for H<sub>2</sub>SO<sub>4</sub>. At 298K, surface coverage steadily increases with concentration of the inhibitor for all solvents. The trend shows H<sub>2</sub>SO<sub>4</sub> gave highest coverage, then HCl and then HNO<sub>3</sub>.



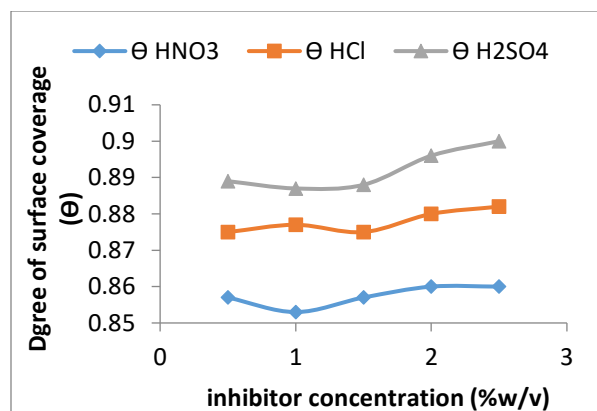


Fig. 10. The variations of surface coverage ( $\theta$ ) with different inhibitor concentration at 313K are shown in below in the fig below:

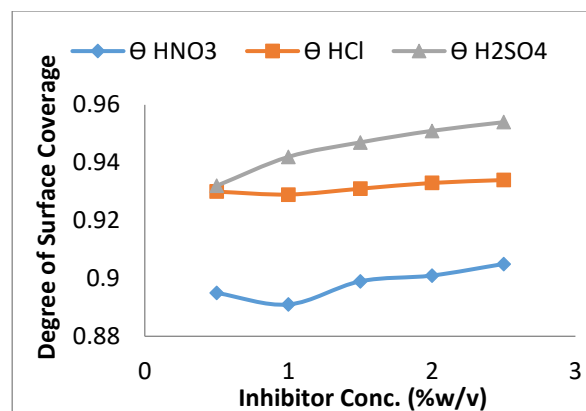


Fig.9. variation of degree of surface coverage ( $\theta$ ) with concentrations of the inhibitor at 298

### 3.4 Inhibitor Efficiency IE

Inhibition efficiency was calculated using the relation;  $IE = \theta \times 100$

Inhibitor efficiency is simply the surface coverage expressed as a percentage. It is an important indicator that gives insight into the possible mechanism of adsorption on the metal surface. A decrease in inhibitor efficiency with rise in temperature and analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence is frequently interpreted as possible formation of an adsorption film on the metal surface (physisorption). The reverse effect, corresponding to an increase in inhibitor efficiency with rise in temperature and lower activation energy in the presence of inhibitor as compared to its absence suggests a mechanism of chemisorption [11], [12], [13]. As the concentration of the inhibitor increases, the inhibitor efficiency also increases. Table 1 shows inhibitor efficiency for all three solvents used at 298K and 313K across all concentrations. At 298K,  $H_2SO_4$  show highest inhibitor efficiency, followed by HCl and then  $HNO_3$ . Similar pattern is observed at 313K. When comparing efficiencies at both temperature, it was observed that at 313K the inhibitor efficiency was higher than at 298K across all solvents. This observation makes it clear the chemical adsorption mechanism may have took place.

Concentration (%w/v)	Inhibitor efficiency at 298k (%)			Inhibitor efficiency at 313k (%)		
	HNO <sub>3</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	HCl	H <sub>2</sub> SO
0.5	85.68	87.52	88.58	89.46	90.15	95.53
1.0	84.78	87.68	88.36	89.10	91.55	96.59
1.5	85.74	88.72	88.81	89.88	92.25	95.29
2.0	85.95	88.00	89.16	90.12	92.88	95.63
2.5	85.02	88.16	89.93	90.50	93.37	95.82

**Table 1.** Variation of inhibitor efficiency for different solvents with concentration and temperature

### 3.5 Kinetic and Thermodynamic Study

### 3.5.1 Effect of Temperature Corrosion Study

$$\ln \frac{CR_1}{CR_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Where  $CR_1$  and  $CR_2$  are corrosion rates for mild steel at  $T_1$  (298K) and  $T_2$  (313K) respectively.  $E_a$  is the activation energy for adsorption of neem gum on mild steel.  $R$  is the molar gas constant. Calculated values of  $E_a$  are shown in table 2. Activated energy values are within the range of values typical of chemisorption and tend to decrease with increase in concentration of the inhibitor for  $HNO_3$  and  $HCl$ . For  $H_2SO_4$ ,  $E_a$  values have an irregular pattern as the concentration of the inhibitor increases. It is important also to note that activation energy calculated for the blank is higher than those calculated for all the acids used as corrosive media across all concentrations of the inhibitor.  $E_a$  (inhibited) >  $E_a$  (uninhibited) coupled with decrease in inhibition efficiency with increase in temperature have been ascribed to physical adsorption mechanism [14]. Therefore decrease in activation energy for the inhibited coupled with increase in inhibitor efficiency with rise in temperature could be described as chemisorption. In the present study, it is seen that all activation energy values fall below that of the blank pointing therefore towards possible chemisorption.

Inhibitor Concentration	HNO <sub>3</sub>		HCl		H <sub>2</sub> SO <sub>4</sub>	
	$E_a$ (kJmol <sup>-1</sup> )	$\Delta H_{ads}$ (kJmol <sup>-1</sup> )	$E_a$ (kJmol <sup>-1</sup> )	$\Delta H_{ads}$ (kJmol <sup>-1</sup> )	$E_a$ (kJmol <sup>-1</sup> )	$\Delta H_{ads}$ (kJmol <sup>-1</sup> )
Blank	43.40	-	42.78	-	44.80	-
0.5	27.28	18.08	29.60	13.77	-3.83	52.41
1.0	26.58	19.83	24.91	21.73	-17.95	68.09
1.5	24.96	20.17	22.66	21.43	0.00	48.39
2.0	24.86	20.66	14.87	29.78	-2.82	50.85
2.5	22.41	22.60	11.04	32.95	-6.09	54.22

**Table 2.** Activation energy and heat of adsorption for  $HNO_3$ ,  $HCl$  and  $H_2SO_4$  across concentrations of the inhibitor

### 3.5.2 Heat of Adsorption $\Delta H_{ads}$

Heat of adsorption was calculated using the formula below;

$$\Delta H_{ads} = 2.303R \left\{ \left( \log \frac{\theta_2}{1 - \theta_2} \right) - \left( \log \frac{\theta_1}{1 - \theta_1} \right) \right\} \frac{T_1 T_2}{T_2 - T_1} \text{ (kJmol}^{-1}\text{)}$$

Table 2 shows heats of adsorption  $\Delta H_{ads}$  of neem gum extracts on mild steel in different solvents, ie.  $HNO_3$ ,  $HCl$  and  $H_2SO_4$ .  $\Delta H_{ads}$  values were found to be positive for all the three solvents used. A positive value of the heat of adsorption signifies that the degree of surface coverage increased with rise in temperature. Such behavior is often interpreted as being indicative of chemical adsorption of organic matter on the steel surface [15],[16]. This shows that setting a particular value range to distinguish between physical and chemical adsorption based on heat of adsorption is not always valid. Also, from the table, it could be seen that  $H_2SO_4$  has the highest  $\Delta H_{ads}$  value at all concentrations and  $HNO_3$  the lowest. This is because the inhibitor is more efficient in  $H_2SO_4$  than in  $HNO_3$ .

### 3.5.3 Free Energy of Adsorption ( $\Delta G_{ads}$ )

The Free energy of adsorption was calculated using the relation:

$\Delta G_{ads} = -RT \ln(55.5K) \text{ kJmol}^{-1}$ . The negative value of  $\Delta G_{ads}$  implies spontaneity.

Adsorption at the metal-solution interface has been considered as the primary step in the action of most organic corrosion inhibitors in acidic environment.

#### 3.5.3.1 Langmuir Adsorption Isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases [17]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Langmuir plot describes the relationship between the surface coverage and inhibition concentration of a material as:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

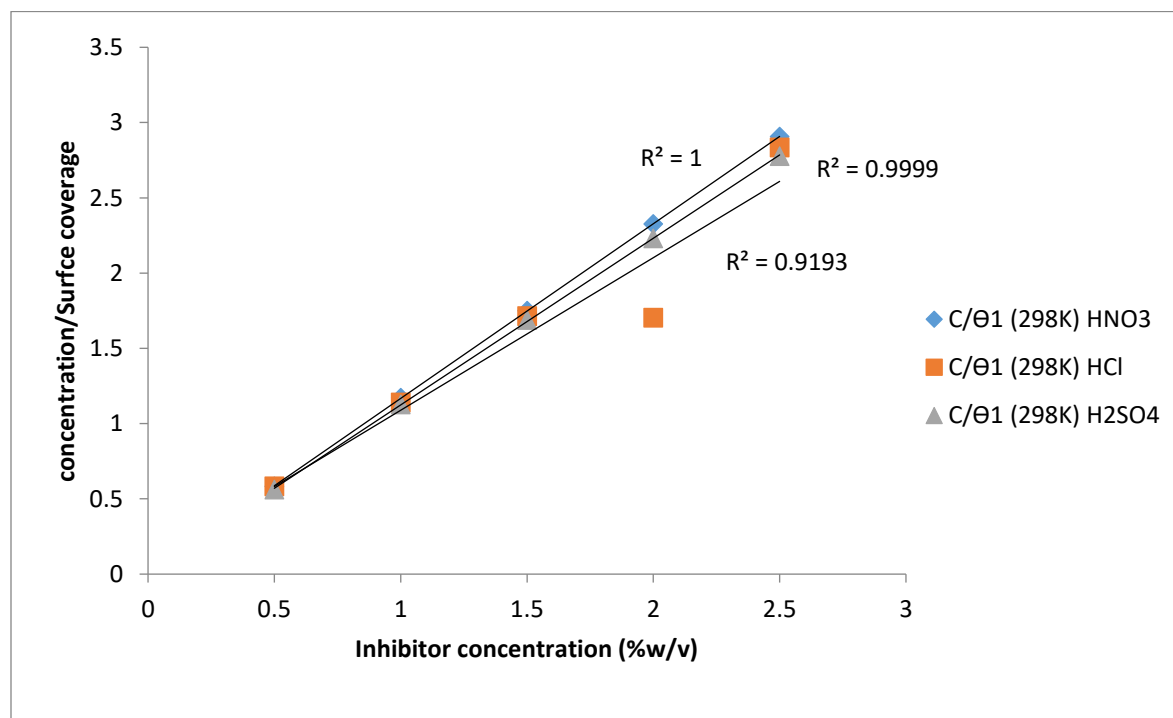


Fig.11. Langmuir isotherm plots of the corrosion of mild steel in 1M (HNO<sub>3</sub>,HCl, H<sub>2</sub>SO<sub>4</sub>) in the presence of *Azadirachta indica* gum extract at 298K

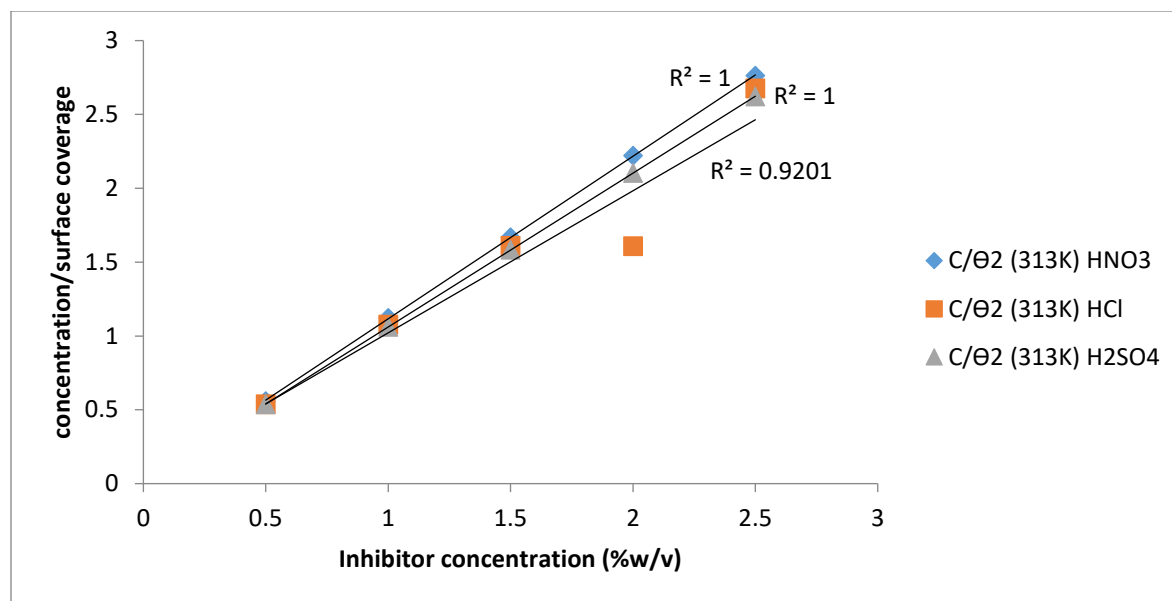


Fig.12. Langmuir isotherm plots of the corrosion of mild steel in 1M (HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>) in the presence of *Azadirachta indica* gum extract at 313K

Solvent	Temperature (k)	K <sub>ads</sub>	R <sup>2</sup>	ΔG° (kJ/mol)
HNO <sub>3</sub>	313	65.79	1	-21.35
	298	142.85	1	-22.24
HCl	313	53.48	1	-20.81
	298	60.60	0.9999	-20.12
H <sub>2</sub> SO <sub>4</sub>	313	16.95	0.9201	-17.82
	298	13.38	0.9193	-16.38

Table 3: Langmuir parameters for mild steel corrosion at 298K and 313K

The table above show the correlation coefficient for all solvents used as well as the free energy of adsorption at 298K and 313K respectively for the Langmuir adsorption isotherm. Other isotherms were also studied, but their correlation values were not significant to be used to predict the kind of adsorption that took place on the metal surface (less than 0.6). R<sup>2</sup> values for Langmuir were well above 0.9 indicating a good fit into the model. Adsorption process is assumed to be spontaneous because the standard free energy is negative all through. Spontaneous adsorption process commonly occurs in the case of organic corrosion inhibitors. HNO<sub>3</sub> was found to have the lowest free energy values of -21.35kJ/mol and -22.24 kJ/mol at 298K and 313K respectively. H<sub>2</sub>SO<sub>4</sub> has the highest of -17.82 kJ/mol and -16.38 kJ/mol at 298K and 313K respectively.

Generally, adsorption is regarded as physisorption if the values of ΔG are up to -20kJ/mol or lower, while those more negative than -40 kJ/mol are regarded as indicative of chemisorption [18]. The assignment of an inhibition mechanism based on purely thermodynamic data is misleading. Also the adsorption of organic molecules on metal surfaces is difficult to be considered as simply physisorption or chemisorption. A variety of experimental conditions control the dominance of one process over the other [19]. Though it could be

implied from the data obtained for Gibbs free energy that the adsorption mechanism could be physical, other parameters such as inhibitor efficiency increasing with temperature and activation energy values support chemisorption. This could therefore be resolved by assuming that there was charge sharing between the gum and the metal surface, and subsequent possible formation of a monolayer adsorption film on the surface.

## CONCLUSION

The results obtained showed that *Azadiracta indica* gum is efficient as inhibitor of corrosion in mild steel. It was found that the inhibitive action is basically controlled by exposure period, temperature, and inhibitor concentration. The study also indicates that both physisorption and chemisorption may have taken place in the inhibition process, but physisorption could be predominant due to the perfect fit of the adsorption data into Langmuir isotherm. Of the three acids used,  $\text{HNO}_3$  was found to have the highest corrosion rate and  $\text{H}_2\text{SO}_4$  the least, and therefore the inhibitor was most effective in  $\text{H}_2\text{SO}_4$  medium.

## COMPETING INTERESTS

We the authors have declared that we have no competing interest in designing, carrying out experiments and interpretation of results.

## AUTHORS' CONTRIBUTIONS

All authors contributed to the success of this publication. Author AIS designed the work. Author AAD performed experiments, and authors BSS and DNS performed literature search and made first draft of the manuscript.

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