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Azadirachta Indica Extracts as Corrosion Inhibitor for Mild Steel in Acid Medium

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The inhibitive action of leaves (LV), root (RT) and seeds (SD) extracts of *Azadirachta indica* on mild steel corrosion in H_2SO_4 solutions was studied using weight loss and gasometric techniques. The results obtained indicate that the extracts functioned as good inhibitors in H_2SO_4 solutions. Inhibition efficiency was found to increase with extracts concentration and temperature, and followed the trend: SD > RT > LV. A mechanism of chemical adsorption of the phytochemical components of the plant extracts on the surface of the metal is proposed for the inhibition behaviour. The experimental data fit into the Freundlich adsorption isotherm.

Keywords: Azadirachta indica, mild steel, weight loss, gasometric method, acid inhibition, acid corrosion

1. INTRODUCTION

The exploration of natural products origin as corrosion inhibitors is becoming the subject of extensive investigation due principally to the low cost and eco-friendliness of these products, and is fast replacing the synthetic and expensive hazardous organic inhibitors. Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant [1-5] and its location [6]. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media [4, 5, 7-17]. A summary of plants extracts used as corrosion inhibitors have recently been given in Okafor *et al.* [5] and Raja and Sethuraman [18].

Azadirachta indica (commonly known as “Neem tree”) is remarkable both for its chemical and for its biological activities. It is one of the richest sources of secondary metabolites in nature [2]. To date more than 300 natural products have been isolated from different parts of the tree, with new compounds added to the list every year [1, 2, 19]. A number of them have been shown to have insect antifeedant, insect growth regulatory, antifungal, antimalarial and antiviral properties [20-22]. The leaves extracts of *Azadirachta indica* have been reported to effectively inhibit the acidic corrosion of metals [9, 23 – 26]. However, the corrosion inhibition effectiveness of other parts of the plant, reported to compose of numerous organic compounds, is yet to be reported.

As a contribution to the current interest on environmentally friendly corrosion inhibitors, the present study aims at broadening the application of plant extracts for metallic corrosion inhibition by investigating the inhibitive properties of leaves (LV), seeds (SD) and root (RT) extracts of *Azadirachta indica* on mild steel corrosion in H_2SO_4 using weight loss and gasometric techniques.

2. EXPERIMENTAL METHODS

2.1. Materials

The mild steel sheets used in this work were obtained from Ejison Resources (Nigeria) and has the composition given in Table 1.

Table 1. Chemical composition of the mild steel

Element	C	Si	Mn	S	P	Ni	Cr	Mo	Cu
Wt%	0.19	0.26	0.64	0.05	0.06	0.09	0.08	0.02	0.27

Gasometric experiments were conducted on mild steel coupons of dimension 0.08 x 2 x 5 cm (surface area 21.22 cm^2) and weight loss experiments on coupons of dimension 0.08 x 4 x 5 cm (surface area 41.44 cm^2). Before use for the corrosion test, the coupon samples were polished using emery papers of up to 800-grit, degreased with absolute ethanol and dried using acetone. All chemicals used were of Analar grade.

2.2. Preparation of plant extracts

Azadirachta indica parts (matured leaves, seeds and roots) were collected as required from the plant in the Botanical garden of the University of Calabar, Nigeria. These were dried in an N53C-Genlab Laboratory oven at 50^{o}C, and ground to powder form. 4.0 g of the powder was digested in 1.0 litre of 2.0 M and 5.0 M H_2SO_4 solution (for weight loss and gasometric measurements, respectively). The resultant solution was kept for 24 hours, filtered and stored. From the stock solution (4.0 g/l), plant extracts (PE) test solutions were prepared at concentrations of 0.1, 0.2, 0.5, 1.0 and 2.0 g/l.

2.3. Weight loss and gasometric measurements

The weight loss and gasometric measurements were carried out as previously described [27, 28]. However, experiments were conducted at 30°C for weight loss, and 30 and 60°C for gasometric measurements. For the weight loss measurements, the mild steel coupons were each suspended and completely immersed in the test solutions (2.0 M H_2SO_4 with and without different concentrations of the PE) with the help of glass hooks and rods for 5 days at 30 ± 1°C. However, the coupons were retrieved at 24 hrs intervals, washed several times in 20 % sodium hydroxide solution containing 200 g/l of zinc dust until clean, dried using acetone and reweighed [27, 28]. From the weight loss data, the corrosion rates (CR) were calculated from equation (1):

$$CR = \frac{WL}{At} \tag{1}$$

where WL is weight loss in mg, A is the specimen surface area and t the immersion period in hours (120 h). From the corrosion rate, the surface coverage (θ) as a result of adsorption of inhibitor molecules, and inhibition efficiencies of the molecules ($\eta\%$) were determined using equations (2) and (3), respectively.

$$\theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \tag{2}$$

$$\eta\% = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) x100 \tag{3}$$

where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of the inhibiting molecules, respectively.

Gasometric technique is based on the principle that corrosion reactions in aqueous media is characterised by the evolution of gas resulting from the cathodic reaction of the corrosion process, which is proportional to the rate of corrosion [11]. The rate of evolution of the gas (RV_H) is determined from the slope of the graph of volume of gas evolved (V) versus time (t), according to equation (4);

$$RV_H = \frac{\Delta V}{\Delta t} \tag{4}$$

and the inhibitor surface coverage (θ) and efficiencies ($\eta\%$) determined using equations (5) and (6), respectively.

$$\theta = \frac{RV_{H\,blank} - RV_{H\,inh}}{RV_{H\,blank}} \tag{5}$$

$$\eta\% = \left(\frac{RV_{H\,blank} - RV_{H\,inh}}{RV_{H\,blank}}\right)x100 \qquad (6)$$

where RV_{Hblank} and RV_{Hinh} are the rate of hydrogen evolution in the absence and presence of the inhibiting molecules, respectively. This gasometric technique has been corroborated by other well established corrosion rate determination techniques, including weight loss, thermometric and electrochemical techniques [17, 29-30]. The data presented here represents the average of two to three measurements from the weight loss and gasometric techniques.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The weight loss measurements for the mild steel in 2.0 M H_2SO_4 containing different concentrations of the plant extracts (PE) as a function of time (in days) are presented in Fig. 1(a) – (c).

Table 2. Calculated values of corrosion rate, inhibition efficiency, rate constant and half-life for mild steel coupons (of cross sectional area of 41.44 cm^2) in 2.0 M H_2SO_4 solutions containing different parts of *Azadirachta indica* (using the weight loss technique)

Plant's part	PE concentration (g/l)	Corrosion rate (mg cm^{-2} hr^{-1})	Inhibition efficiency (%)	Rate constant (day^{-1})	Half life (days)
	Blank	3.14	-	0.21	3.2
LV	0.2	3.12	0.5	0.17	3.1
	0.5	2.12	32.5	0.12	5.8
	1.0	1.81	42.4	0.09	7.2
	2.0	1.41	55.0	0.07	9.5
	4.0	1.24	60.4	0.05	11.4
RT	0.1	2.76	12.0	0.23	3.7
	0.2	2.66	15.1	0.15	4.0
	0.5	2.10	33.2	0.10	5.6
	1.0	1.69	46.2	0.09	7.7
	2.0	1.34	57.2	0.07	10.3
	4.0	1.04	66.8	0.02	14.7
SD	0.2	2.47	21.2	0.22	4.5
	0.5	1.78	43.4	0.12	6.8
	1.0	1.61	48.6	0.10	7.5
	2.0	1.24	60.6	0.07	10.5
	4.0	0.57	81.8	0.06	28.9

The results show that the weight loss values increased with increase in time but decreased with increase in concentration of the PE for all the plant's part used. The decrease is due to the inhibitive effects of the PE and these effects increased with increase in the PE concentration.

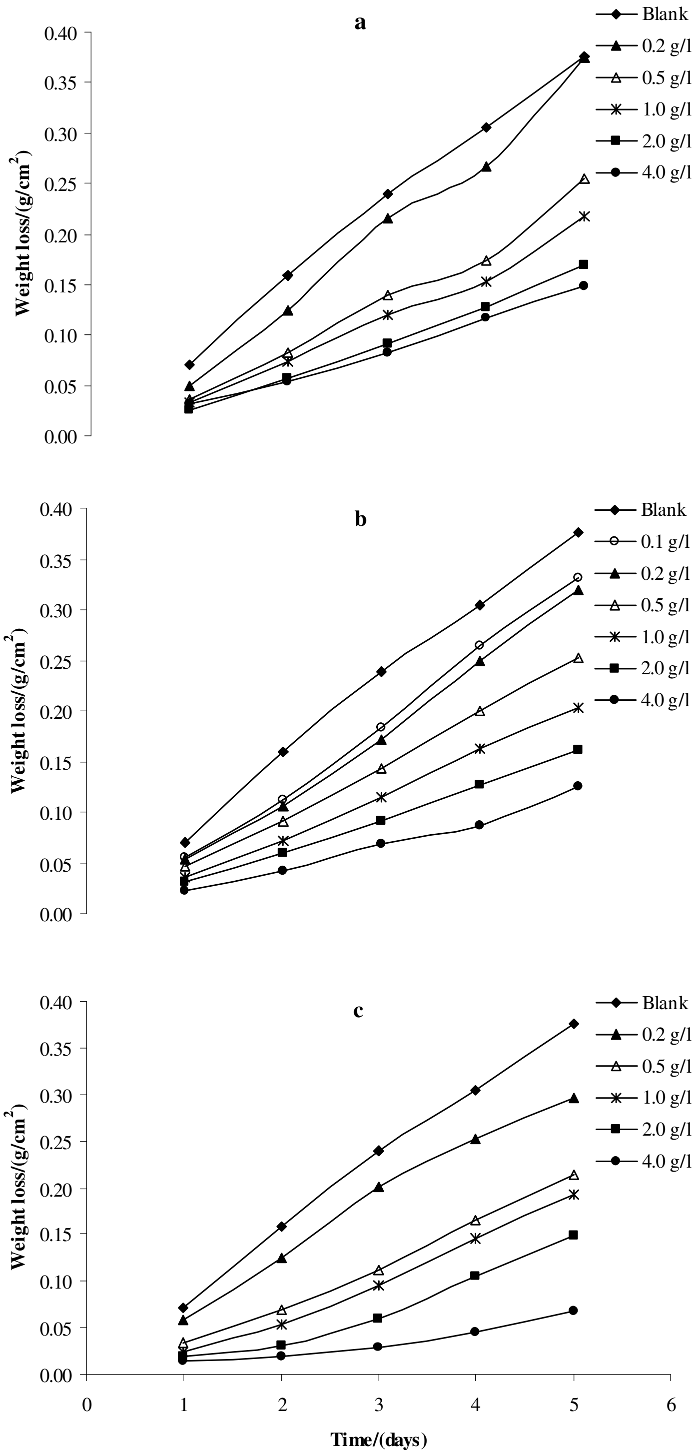


Figure 1. Variation of weight loss with time for mild steel (of cross sectional area of 41.44 cm^2) in 2.0 M H_2SO_4 solutions containing (a) LV, (b) RT and (c) SD extracts of *Azadirachta indica*

Table 2 shows the rate of corrosion of mild steel in 2.0 M H_2SO_4 solutions devoid of and containing different concentrations of PE. Inspection of Table 2 reveals that the corrosion rates of the mild steel decreased with increase in the PE concentration indicating that the PE inhibits the corrosion of mild steel in 2.0 M H_2SO_4 solutions. Inspection of Fig. 1 and Table 2 reveals that the weight loss values as well as the corrosion rates for all concentration used followed the trend: SD < RT < LV. The values of inhibition efficiencies of different PE concentrations are also given in Table 2.

The PE shows a significant inhibitive effect on mild steel in H_2SO_4 solutions that reaches up to 81.8 % for seed extracts (SD) concentration of 4.0 g/l. Fig. 2 shows the variation of inhibition efficiency with extracts concentration for mild steel in 2.0 M H_2SO_4 solutions containing different parts of the PE and indicates that the inhibition efficiencies increased with increase in the PE concentration. Comparing the inhibition efficiencies of the PE shows that the efficiencies followed the trend: SD > RT > LV.

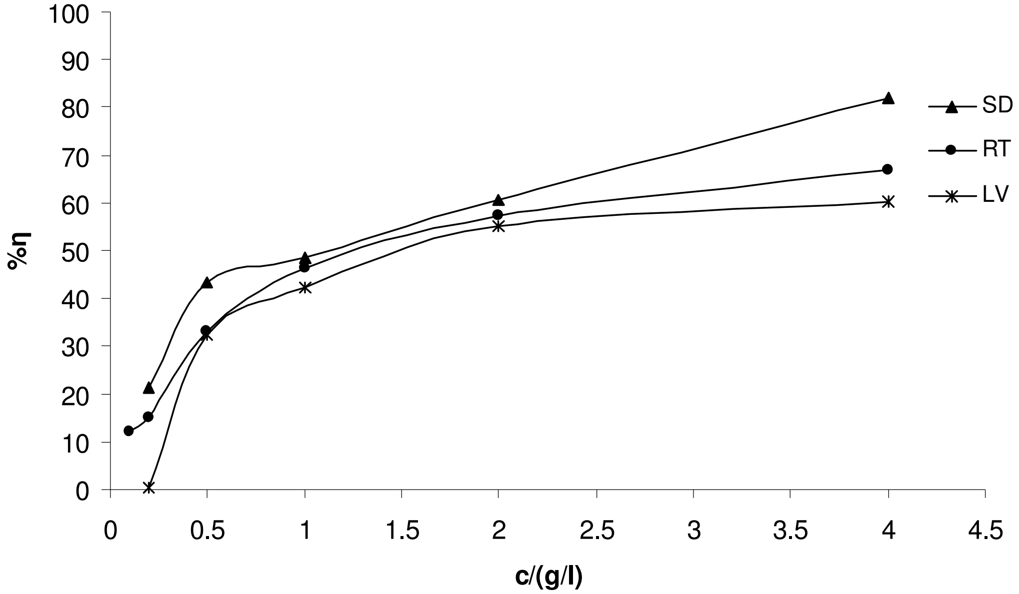


Figure 2. Variation of inhibition efficiency with PE concentration for mild steel coupons (of cross sectional area of 41.44 cm^2) in 2.0 M H_2SO_4 solutions containing different parts of *Azadirachta indica.*

In the present study of corrosion of mild steel in H_2SO_4 solutions, weight at time *t* (after post-treatment of coupons) is designated W_f. When log W_f was plotted against time (in days), a linear variation was observed, which confirms a first-order reaction kinetics with respect to mild steel in H_2SO_4 solutions, formulated as :

$$\log w_f = \log w_o - kt \tag{7}$$

where W_o is the initial weight before immersion, *k* is the rate constant and *t* is time. The values of the rate constants, *k*, obtained from the slopes of the plots in Fig. 3 are presented in Table 2.

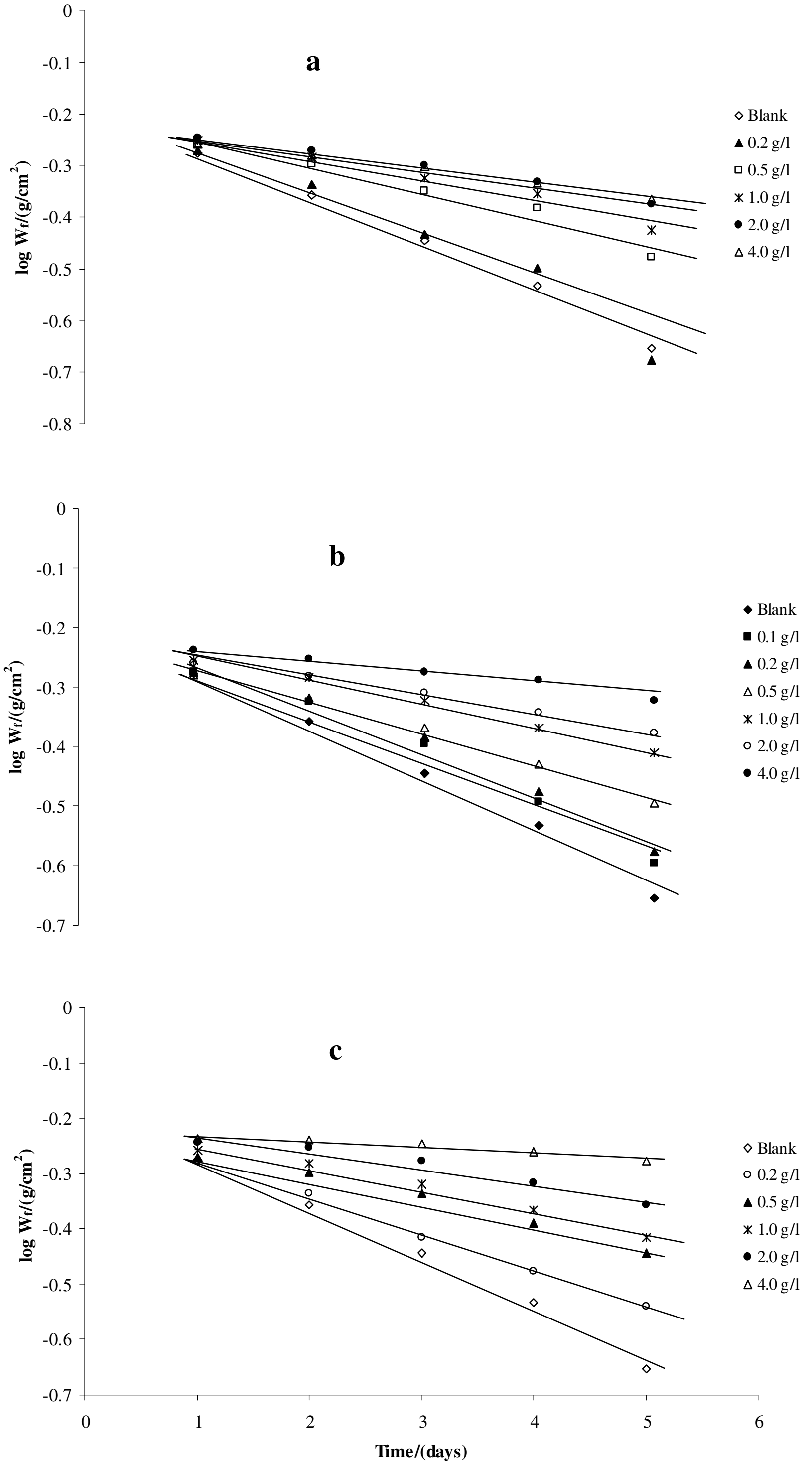


Figure 3. Plot of log W_f against time for mild steel coupons (of cross sectional area of 41.44 cm^2) in 2.0 M H_2SO_4 solutions containing (a) LV, (b) RT and (c) SD extracts of *Azadirachta indica.*

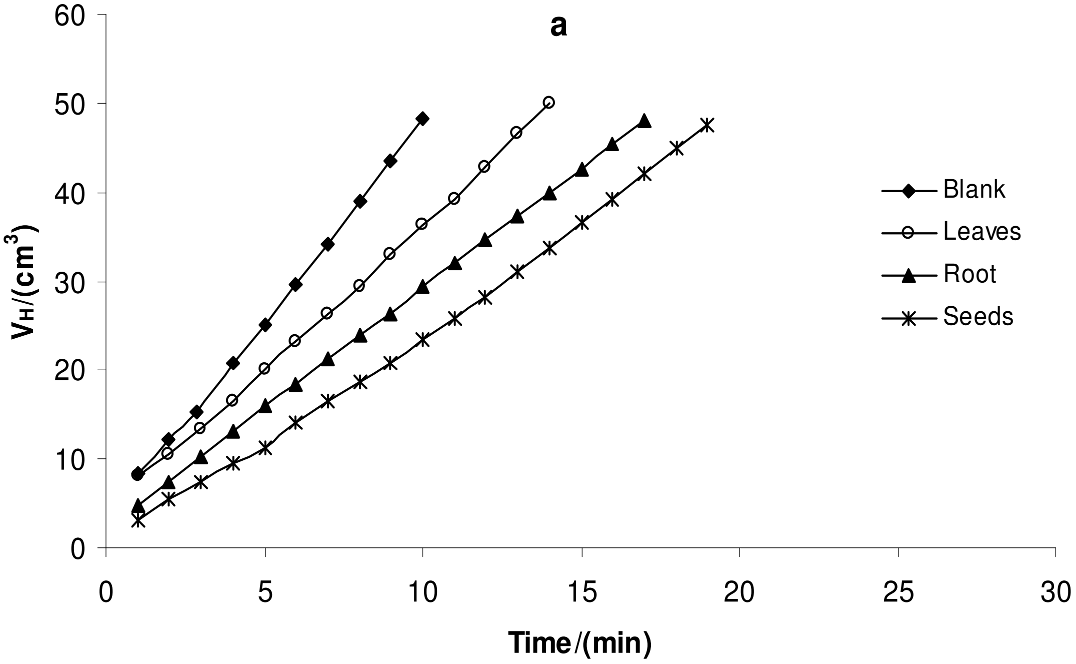
The results obtained reveal that the rate constant decreases with increase in PE concentration. From the rate constant values, the half-life values, $t_{½}$, of the metal in the test solutions were calculated using the equation:

$$t_{1/2} = \frac{0.693}{k} \qquad (8)$$

and the deduced data also presented in Table 2. The half-life values were observed to increase with increase in concentration of the PE, indicating decrease in the dissolution rate of the metal in the solutions with increase in the PE concentration.

3.2. Gasometric results

The corrosion of mild steel in H_2SO_4 solution is characterised by the evolution of hydrogen and the rate of corrosion is proportional to the amount of hydrogen evolved [11]. The volume of hydrogen evolved, V_H, during the corrosion of mild steel in 5.0 M H_2SO_4 solutions in the absence and presence of the PE at 30 and 60°C was measured as a function of time. The result obtained (at 60°C) for 2.0 g/l and 4.0 g/l PE are as shown in Fig. 4 (a) and (b), respectively. Similar results were obtained at other concentrations and at 30°C. The rate of hydrogen evolution, obtained from the slopes of the graphs is presented in Table 3. It is observed that the presence of the PE decreased the volume of hydrogen evolved as well as the rate of hydrogen evolution, and consequently the corrosion rate of the mild steel in 5.0 M H_2SO_4 solutions compared to the blank.



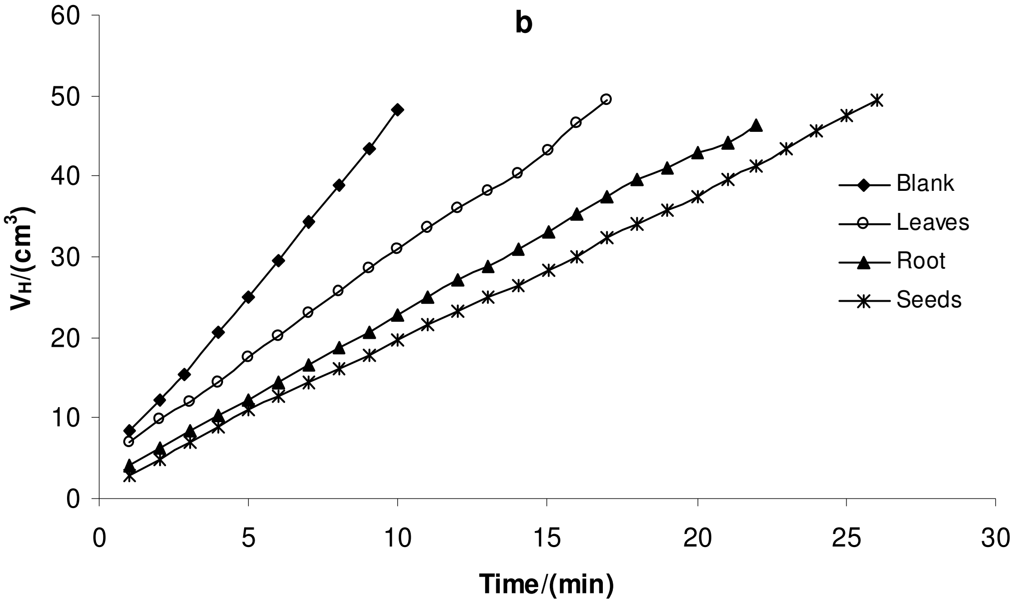


Figure 4. Variation of volume of evolved hydrogen (V_H) with time for mild steel coupons (of cross sectional area of 21.22 cm^2) in 5.0 M H_2SO_4 solutions containing (a) 2.0 g/l and (b) 4.0 g/l extracts of different parts of *Azadirachta indica* at 60°C.

The decrease is also dependent on the concentration of the PE and temperature. Inspection of Table 3 also shows that the rate of hydrogen evolution followed the trend: LV > RT >SD. From the rate of hydrogen evolution, the inhibition efficiency was determined using equation (6). The results obtained are as shown in Fig. 5 (a) and (b) at 30 and 60°C, respectively. It is observed that the inhibition efficiency increases with increase in the PE concentration and increases with increase in temperature. This suggests that the phytochemical components of the PE are adsorbed on the mild steel – solution interface. The trend in temperature suggests chemical adsorption of the inhibiting components of the PE. Comparing the inhibition efficiencies of the PE (Fig. 6) shows that the efficiencies followed the trend: SD > RT > LV for all systems. Similar trend was observed in 2.0 M H_2SO_4 from the weight loss measurements.

3.3. Adsorption behaviour

The observed inhibition of the corrosion of mild steel in the H_2SO_4 solutions with increase in the PE concentration can be explained by the adsorption of the components of the PE on the metal surface. From a theoretical standpoint, the inhibition action of organic molecules has been regarded as a simple substitution process, in which an inhibitor molecule (*I*) in the aqueous phase substitutes an *x* number of water molecules adsorbed on the surface [32-36]:

$$I_{(aq)} + xH_2O_{(ads)} \Leftrightarrow I_{(ads)} + xH_2O_{(aq)} \qquad (9)$$

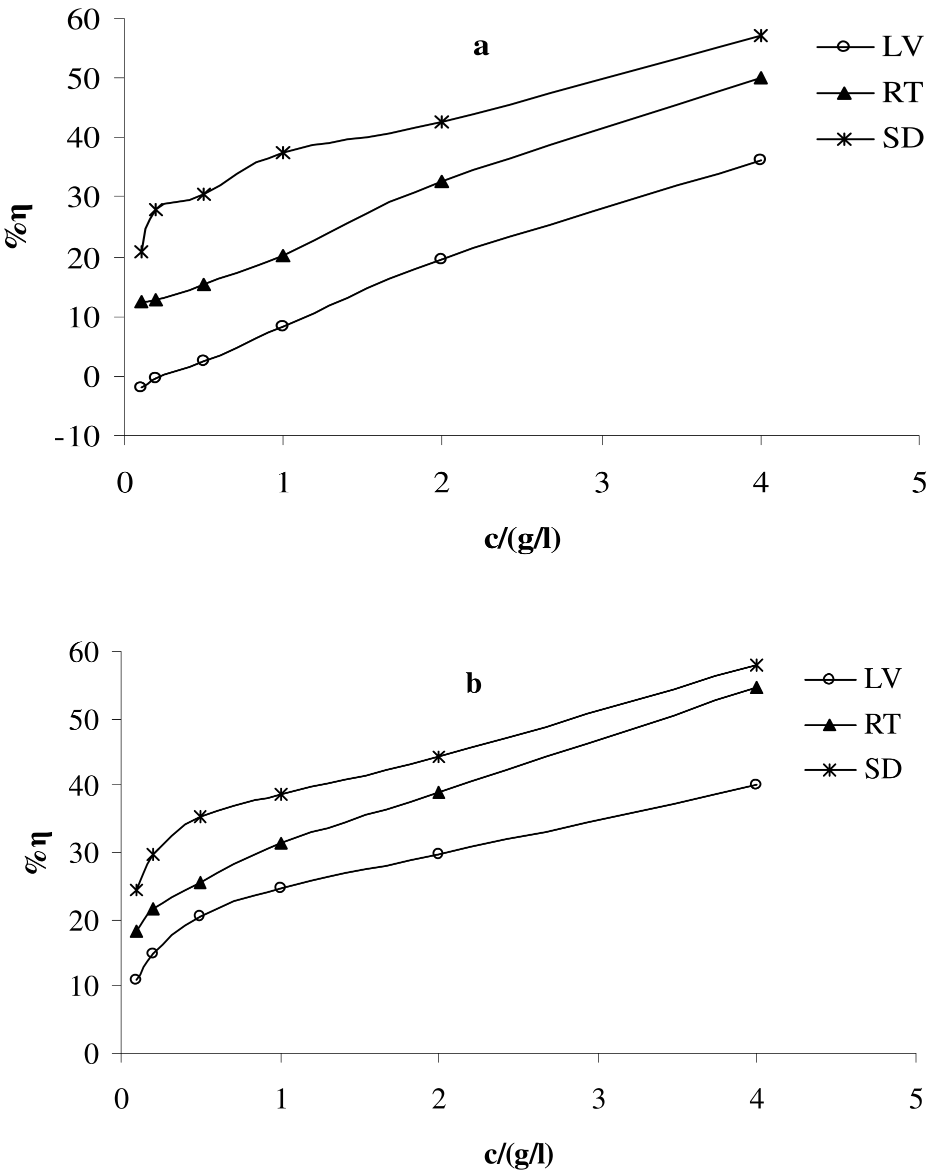


Figure 5. Variation of inhibition efficiency with PE concentration for mild steel coupons (of cross sectional area of 21.22 cm^2) in 5.0 M H_2SO_4 solutions containing different parts of *Azadirachta indica* at (a) 30°C and (b) 60°C.

The inhibitor molecules may then combine with Fe^{2+} ions on the metal surface, forming metal-inhibitor complex. The resulting complex, depending on its relative solubility could either inhibit or catalyse further metal dissolution. Plant extracts are viewed as an incredible rich source of naturally synthesized chemical compounds. These large numbers of different chemical compounds may form adsorbed intermediates (organo-metallic complexes) such as [Fe-PE] [10, 12, 15] which may either inhibit or catalyse further metal dissolution. From the observed results it can be inferred that the insoluble Fe-PE complexes dominates the adsorbed intermediates and thus the resultant inhibitive effects. This conclusion is in line with those of Jaen *et al.* [37].

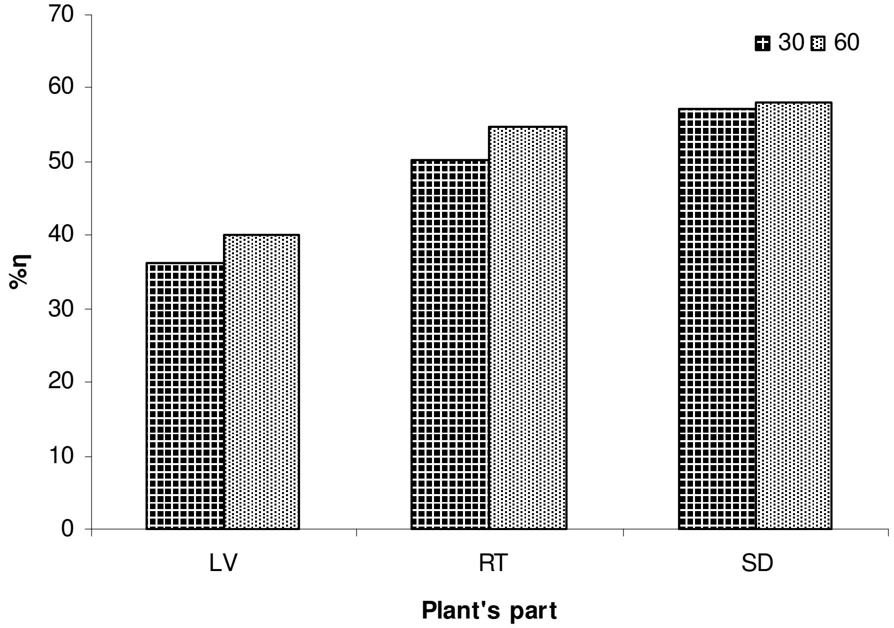


Figure 6. Maximum inhibition efficiency for mild steel coupons (of cross sectional area of 21.22 cm^2) in 5.0 M H_2SO_4 containing 4.0 g/l of different parts of *Azadirachta indica* extracts

Most investigators claim a particular compound in PE as solely responsible for the inhibition ability of the extract. This in the real sense is not true, since most PE are composed of numerous organic compounds capable of either inhibiting or accelerating the corrosion process. The net (antagonistic and synergistic) action of the phytochemical components of the plant is what is actually recorded as the inhibition efficiency of the PE [15, 18, 24, 38, 39]. Like most medicinal plants, *Azadirachta indica* is composed of numerous naturally occurring organic compounds. Over 300 compounds have been isolated and characterized from the plant. Among these are: azadirachtin, azadirone, gedunin, nimbin, nimbandiol, nimbinene, nimbolide, nimonol, nimbolin, salannin, margolone, melianol, vilasanin, flavanoids and structurally related compounds [1, 40-43]. Most of these compounds have complicated molecular structures, large molecular weights and significant number of oxygen, sulphur and nitrogen atoms incorporated in the structure. These compounds can adsorb on the metal surface via the lone pairs of electrons present on their oxygen, sulphur and nitrogen atoms. The adsorption of such compounds on the metal surface creates a barrier for charge and mass transfer leading to a decrease in the interaction between the metal and the corrosive environment. As a result, the corrosion rate of the metal is decreased. According to Patel [44,45], the inhibition properties of plant extracts may be due to the presence of nitrogenous compounds in the extract [23] and tannins [46]. Tannins are complex astringent aromatic glycosides found in various plants. They are made up of polyphenols and their acidic and heterocyclic derivatives. Polar organic compounds containing N, S. O atoms are good corrosion inhibitors [47]. They may have been responsible for the formation of an oriented film layer which essentially blocks discharges of H^+ and dissolution of metal ions. Acid pickling inhibitors containing organic N, amine, S and OH groups behave similarly to inhibit corrosion.

This complex composition of *Azadirachta indica* makes it difficult to assign the observed corrosion inhibitive effect to a particular constituent. However, one-third of the isolated compounds from *Azadirachta indica* are tetranortriterpenoids (limonoids). One of the limonoids is azadirachtin, the most potent, environmental friendly biodegradable pesticide, with growth-inhibiting properties at very low concentration [1]. Azadirachtin has been isolated from all parts of the Neem tree, but is present at highest concentration in the mature seeds [2]. From the trend in inhibition efficiencies (SD > RT > LV), azadirachtin may be assumed to contribute significantly to the adsorbed organic compounds responsible for the inhibitive effects of the PE.

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of inhibitor give some insight into the possible mechanism of inhibitor adsorption. An increase in inhibition efficiency with rise in temperature, with analogous decrease in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of chemically adsorption film, while a decrease in inhibition efficiency with rise in temperature, with corresponding increase in corrosion activation energy in the presence of inhibitor compared to its absence, is ascribed to physical adsorption mechanism [16, 24, 29, 30]. The trend in inhibition efficiency with temperature obtained (Table 3 and Fig. 5) suggests chemisorption of the phytochemical constituents of the PE on the surface of the metal. In order to confirm this, the apparent activation energies, E_a, for the dissolution of mild steel in 5.0 M H_2SO_4 in the absence and presence of the PE were calculated from the condensed Arrhenius equation as follows:

$$\log \frac{RV_{H2}}{RV_{H1}} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{10}$$

where RV_{H1} and RV_{H2} are the rates of hydrogen evolution at temperatures T_1 and T_2, respectively. The calculated activated energy values are listed in Table 3. The results indicated that E_a in the presence of the PE decreases compared to the blank result. This behaviour is an indication of chemical adsorption of the components of the PE on the surface of the metal.

An estimate of the heat of adsorption (Q_{ad}) was obtained from the trend of surface coverage with temperature as follows:

$$Q_{ad} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_2}\right)\right] x \, \frac{T_1T_2}{T_2 - T_1} \tag{11}$$

where θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2, respectively. The calculated values are as shown in Table 3. The positive values of the heat of adsorption are consistent with inhibitor chemical adsorption [16].

Table 3. Calculated values of rate of hydrogen evolution (RV_H), inhibition efficiency, activation energy, heat of adsorption and equilibrium constant for mild steel coupons (of cross sectional area of 21.22 cm^2) in 5.0 M H_2SO_4 solutions containing different parts of *Azadirachta indica* (using the gasometric technique).

Plant's part	PE concentration (g/l)	RV_H (cm^{-3} min^{-1})		Inhibition efficiency (%)		Activation energy (kJ mol^{-1})	Heat of adsorption (kJ mol^{-1})	Equilibrium constant X 10^{-2}	
		30°C	60°C	30°C	60°C			30°C	60°C
	Blank	0.39	4.43	-	-	67.77	-		
LV	0.1	0.40	3.94	-2.0	11.0	63.94	-	4.52	15.95
	0.2	0.39	3.77	-0.3	14.9	63.18	-		
	0.5	0.38	3.53	2.5	20.5	62.08	64.02		
	1.0	0.36	3.34	8.1	24.7	62.22	36.53		
	2.0	0.32	3.12	19.4	29.6	63.97	15.63		
	4.0	0.25	2.66	36.1	40.1	65.96	4.73		
RT	0.1	0.34	3.62	12.5	18.3	65.82	12.73	7.81	20.83
	0.2	0.34	3.47	12.7	21.7	64.72	18.01		
	0.5	0.33	3.30	15.5	25.6	64.23	17.49		
	1.0	0.31	3.04	20.1	31.4	63.49	16.77		
	2.0	0.26	2.71	32.8	39.0	65.09	7.47		
	4.0	0.20	2.01	50.1	54.7	65.10	5.08		
SD	0.1	0.31	3.35	20.9	24.4	66.48	5.70	29.64	35.55
	0.2	0.28	3.11	27.7	29.8	66.94	2.88		
	0.5	0.27	2.87	30.5	35.3	65.80	5.99		
	1.0	0.25	2.72	37.4	38.6	67.21	1.47		
	2.0	0.22	2.47	42.8	44.3	67.00	1.76		
	4.0	0.17	1.86	57.0	58.1	67.02	1.30		

The experimental data were applied to different adsorption isotherm equations. It was found that the experimental data fitted the Freundlich adsorption isotherm (Fig. 7) which may be formulated as [16];

$$\frac{\theta}{1-\theta} = c + B \qquad (12)$$

where θ is the surface coverage, c the extracts concentration and B the adsorption coefficient, which represents the adsorption-desorption equilibrium constant. The adsorption-desorption equilibrium constants for the different parts of the PE were obtained from the intercepts of the Freundlich adsorption isotherm plots and the results obtained are presented in Table 3.

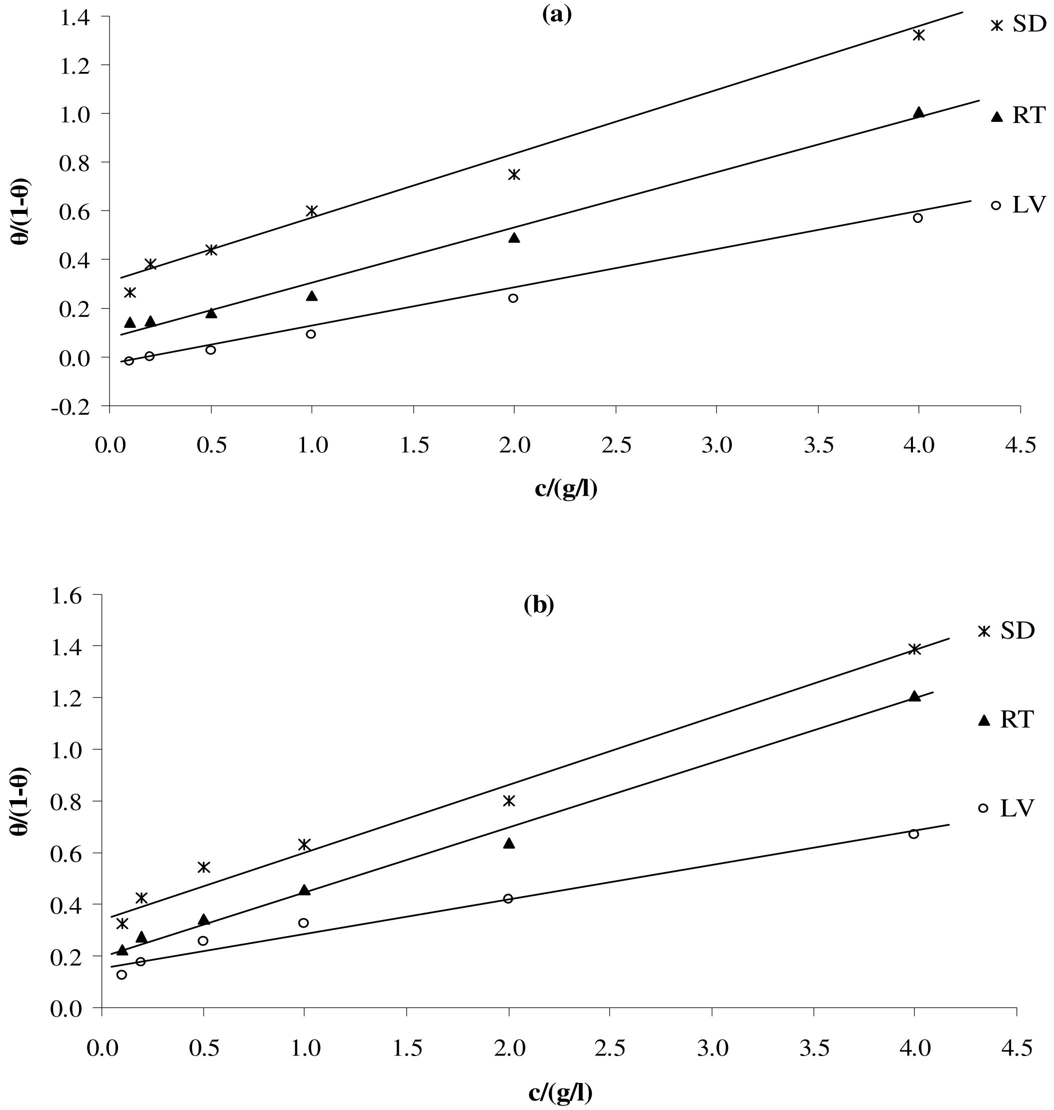


Figure 7: Plot of surface coverage, $\theta/(1-\theta)$, against *c* for mild steel coupons (of cross sectional area of 21.22 cm^2) in 5.0 M H_2SO_4 solutions containing different parts of *Azadirachta indica* at (a) 30°C and (b) 60°C (Freundlich isotherm).

The results show that the values of *B* increase with temperature indicating that more of the phytochemical constituents were adsorbed as temperature increases confirming the proposed chemical adsorption mechanism. It is also observed from Table 3 that *B* values followed the trend: SD > RT > LV confirming that the increase in inhibition efficiency is due to increase in the surface concentration (adsorption) of the most dominating phytochemical constituents in the PE.

4. CONCLUSIONS

The results presented in this paper show that the leaves (LV), root (RT) and seeds (SD) extracts from *Azadirachta indica* inhibit the corrosion of mild steel in H_2SO_4 solutions to reasonable extent. The inhibition efficiencies of the plant extracts (PE) increased with increase in extract concentration and with temperature and followed the trend: SD > RT >LV. From the trend in inhibition efficiencies (SD > RT > LV), azadirachtin, present at highest concentration in the mature seeds, is assumed to contribute significantly to the adsorbed organic compounds responsible for the inhibitive effects of the *Azadirachta indica* extracts. The adsorbed species formed insoluble [Fe-PE] complex due to their interactions with the dissolved iron ions. The acid extract of the PE can be considered as a source of relatively cheap, ecofriendly and effective acid corrosion inhibitor. Based on the trend of inhibition efficiency with temperature and from the obtained values of activation energy and heat of adsorption, the corrosion inhibition is attributed to chemical adsorption of the phytochemical components of the plant on the surface of the mild steel. The experimental data fit into the Freundlich adsorption isotherm.

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