



Corrosion Inhibition Of Oil Well Steel In Hydrochloric Acid Pickling Solution By The Extract Of *Ficus Abutilifolia* And Propargyl Alcohol

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ABSTRACT

The corrosion inhibition of oil well tubular steel (N-80 steel) in 15% Hydrochloric acid pickling solution by extract of *Ficus abutilifolia* (FA) was studied using weight loss technique. Maximum inhibition efficiency was obtained at an optimum concentration. However, increase in temperature decreased the inhibition efficiency at the temperature range studied. The inhibition efficiencies were compared to that of a known corrosion inhibitor, Propargyl Alcohol. Optimum inhibition efficiency for the tubular steel in the presence of *Ficus Abutilifolia* was 59.12% at 30°C, 55.06% at 60°C while those for Propargyl Alcohol were 96.79% at 30°C and 90.98% at 105°C. The phenomenon of physical adsorption has been proposed from the heat adsorption values of all inhibitors studied. Activation energy values indicate a surface reaction. The ΔG values are negative and suggestive of adsorption on metal surface. The data obtained from this study fits well into the Temkin adsorption isotherm for *Ficus Abutilifolia* and Freundlich for Propargyl Alcohol.

KEY WORDS: Corrosion inhibition, oil well steel, weight loss, *Ficus Abutilifolia*, hydrochloric acid.

INTRODUCTION

Acid solutions are often used in industry for cleaning, descaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution of the metal ^[1]. The addition of inhibitors effectively secures the metal against an acid attack ^[2,3]. The applicability of organic compounds as corrosion inhibitors for metals in acidic media has been recognized for a long time ^[4,5]. The existing data show that most organic inhibitors act by adsorption on the metal surface. The adsorption of inhibitors occurs through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. These compounds which are adsorbed on the metallic surface block the active corrosion sites.

Though many synthetic organic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and the environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system viz, kidney, liver, or disturb a biochemical process and enzyme system at some site in the body ^[6]. The toxicity may manifest either during the synthesis of the compound or during its application.

Recent awareness of the corrosion inhibiting abilities of tannins, alkaloids, organic and amino acids as well as organic dyes has resulted in sustained interest on the corrosion inhibiting properties of natural products of plant origin ^[7]. Such investigation is of much importance because in addition to being environmentally friendly and ecologically acceptable, plants products are inexpensive, readily available and renewable sources of materials. The use of natural products as corrosion inhibitors have been widely reported by several authors ^[8-10]. The aim of this work is to study the suitability of *Ficus Abutilifolia* extract as a corrosion inhibitor in 15% HCl Pickling solution.

EXPERIMENTAL METHODS

Materials

The steel sample used for this research work, as – received was obtained from S. C. C Nigeria Ltd Abuja, Nigeria. The alloy composition of the steel is given in Table 1.

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Table 1: The high strength low alloy steel is commercial micro alloyed steel (in hot-rolled condition) with the following percentage alloy

Element	C	Mn	Si	P	S	Mo	V	Ti	AL	Fe	Total
Composition,%	0.22	1.2	0.25	0.025	0.025	0.001	0.004	0.002	0.051	98.22	100

Inhibitors

The corrosion inhibitor used for this research work are Propargyl alcohol and methanolic extract of *Ficus Abutilifolia*. obtained from Zaria, Kaduna in Northern Nigeria. The extract of *Ficus Abutilifolia* was obtained using a soxhlet according to the conventional methods [11].

Phytochemical Screening of *Ficus Abutilifolia*

The phytochemical screening of *ficus Abutilifolia* was carried out according to the conventional methods used elsewhere. These include: Flavonoids [12], Saponins [13], Tannins [12], Phlobotannins [12], Alkaloids [14], Steroids and Terpenoids [15].

Table 2 Phytochemical analysis of *Ficus Abutilifolia* (FA)

Chemical Constituent	FA
Alkaloids	=
Anthraquinone	+
Saponins	=
Tannins	+
Steroids & terpenoids	+
Flavonoids	+
Nitrogen	+
Sulphur	+

Note: + = Present, - = Absent

Procedure

Prior to the experiment, the as – received steel (6cm x 5cm x 1.5cm) bars were sectioned into coupon of sizes 2cm x 1cm x 0.35cm and polished with emery papers (220-800 grades). The specimens were the washed with distilled water followed by degreasing in absolute ethanol, dried in acetone, weighed and stored in a moisture free desiccators prior to use [16].

In the weight loss experiment, 250ml beakers was containing 15% HCl solutions were placed in a thermostated water bath maintained at 30°C-60°C. The steel coupons were suspended in the beakers with the aid of glass hooks. The coupons were retrieved from their corrodent solutions at 30minutes interval for 150 minutes. Further measurements were carried out after introduction of the additives (*Ficus Abutilifolia* and propargyl Alcohol) in the beaker maintained at 30°C-60°C for the same duration. Coupons were dipped into saturated ammonium acetate solution at room temperature, to terminate the corrosion reaction. They were washed by scrubbing with a light brush and dried in acetone and finally in an oven maintained at 80°C. The loss of weight of coupons is evaluated in grams as the difference in weight of the coupons before and after the test [17].

$$W = W_i - W_f \text{ ----- 1}$$

Where

- W = weight loss of coupon,
- W_i = Initial weight of coupon,
- W_f = Final weight of coupon.

Each reading reported is an average of three experimental reading recorded to the nearest 0.000lg on an Adam 184 electronic weighing balance.

The value of corrosion rate, ρ (in $\text{g.cm}^{-2}.\text{min}^{-1}$) was calculated from the following equation [18]:

$$\rho = W / At \text{ ----- 2}$$

- Where W = weight loss (g)
- A = Area of specimen (cm^2)
- t = Exposure time (minutes)

RESULTS AND DISCUSSION

Effect of temperature on corrosion rates and inhibition efficiency of steel

Table 3 shows the values weight loss (in grams), corrosion rate(in g.cm⁻².min⁻¹), inhibition efficiency (I.E %), surface coverage (θ) and obtained at different concentration of the inhibitors in 15% Hydrochloric acid solution for an immersion period of 150 minutes. The corrosion inhibition efficiency (I.E) of the inhibitors is calculated using the formula^[18].

$$I.E = [1 - \rho_1 / \rho_2] \times 100\% \text{ ----- } 3$$

$$\theta = [1 - \rho_1 / \rho_2] \text{ ----- } 4$$

Where ρ₁ = Corrosion rate in the presence of inhibitors

ρ₂ = Corrosion rate in the absence of inhibitor at the same temperature.

θ = Surface coverage

Table 3 Values of weight loss, corrosion rate, inhibition efficiency at various temperatures for propargyl alcohol and extract of *Ficus Abutilifolia*.

Temp(K)	FA					PA			
	Conc (v/v %)	Wt Loss (g)	Corr.Rate x10 ⁵ (g.cm ⁻² .min ⁻¹)	Inh.Eff(%)	Surface Coverage(θ)	Wt Loss (g)	Corr.Rate x10 ⁵ (g.cm ⁻² .min ⁻¹)	Inh.Eff(%)	Surface Coverage(θ)
303	Blank	0.0914	9.9897	-	-	0.0914	9.9897	-	-
	0.1	0.0522	5.7013	42.9277	0.4293	0.0095	1.0395	89.5940	0.8959
	0.3	0.0421	4.6015	53.9371	0.5394	0.0069	0.7488	92.5042	0.9250
	0.5	0.0379	4.1426	58.5313	0.5853	0.0052	0.5693	94.3016	0.9430
	0.7	0.0376	4.1114	58.8431	0.5884	0.0034	0.3694	96.3021	0.9630
	0.9	0.0374	4.0837	59.1211	0.5912	0.0029	0.3207	96.7894	0.9679
313	Blank	0.1097	11.9894	-	-	0.1097	11.9894	-	-
	0.1	0.0653	7.1382	40.4623	0.4046	0.0132	1.4465	87.9351	0.8794
	0.3	0.0530	5.7899	51.7083	0.5171	0.0101	1.1086	90.7535	0.9075
	0.5	0.0473	5.1700	56.8781	0.5688	0.0082	0.8930	92.5518	0.9255
	0.7	0.0470	5.1350	57.1703	0.5717	0.0060	0.6532	94.5519	0.9455
	0.9	0.0467	5.1069	57.4048	0.5740	0.0053	0.5843	95.1269	0.9513
323	Blank	0.1393	15.2203	-	-	0.1393	15.2203	-	-
	0.1	0.0882	9.6369	36.6839	0.3668	0.0205	2.2440	85.2564	0.8526
	0.3	0.0709	7.7519	49.0688	0.4907	0.0167	1.8223	88.0269	0.8803
	0.5	0.0635	6.9404	54.4006	0.5440	0.0154	1.6787	88.9704	0.8897
	0.7	0.0621	6.7862	55.4133	0.5541	0.0115	1.2620	91.7082	0.9171
	0.9	0.0619	6.7617	55.5744	0.5557	0.0107	1.1662	92.3378	0.9234
333	Blank	0.1505	16.4515	-	-	0.1505	16.4515	-	-
	0.1	0.0979	10.6988	34.9681	0.3497	0.0241	2.6345	83.9861	0.8399
	0.3	0.0780	8.5256	48.1777	0.4818	0.0199	2.1763	86.7715	0.8677
	0.5	0.0703	7.6832	53.2977	0.5330	0.0196	2.1407	86.9876	0.8699
	0.7	0.0678	7.4139	54.9351	0.5494	0.0145	1.5871	90.3529	0.9035
	0.9	0.0676	7.3933	55.0602	0.5506	0.0136	1.4847	90.9756	0.9098

As observed from Table 3, corrosion rates generally increase with rising solution temperature. This increase in corrosion rate with rising solution temperature is typical of Arrhenius type reactions^[18]. However, addition of the inhibitor reduces the corrosion rates. The table shows that at 30°C, addition of 0.1 v/v % of the inhibitor caused a decrease in corrosion rate from 9.9897x10⁻⁵ g.cm⁻².min⁻¹ to 5.7013x10⁻⁵ g.cm⁻².min⁻¹ for FA and from 9.9897x10⁻⁵ g.cm⁻².min⁻¹ to 1.0395x10⁻⁵ g.cm⁻².min⁻¹ for PA. Similar observations were made at 40°C, 50°C and 60°C.

These decreases in corrosion rates may be due to the known fact that organic inhibitors decrease metal dissolution by forming a protective adsorption film that blocks the metal surface, separating it from the corrosive medium^[19]. This implies that corrosion rate is indicative of the number of free corroding sites remaining after some sites have been effectively blocked by inhibitor adsorption^[20]. It is observed that corrosion rate reduction in the presence of PA is much higher than that due to FA. This reduction in corrosion rate caused by PA may be because of the formation of protective film by polymerization of PA on active metallic surface due to its polymeric nature^[21,22].

It was observed that inhibition efficiencies increase with increase in inhibitor concentrations. The inhibitor species are adsorbed on the mild steel/solution interface where the adsorbed species mechanically screen the coated part

of the metal surface from the action of the corrosive medium [18]. This adsorption could be attributed to the presence of tannins, saponins, flavonoids, sulphur and nitrogen in the structure of the extract [23].

Efficiencies decreased with temperature increase. On addition of maximum concentration of 0.9 v/v %, inhibition efficiencies decrease from 59.12 % at 30°C to 55.06 % at 60°C for FA. Similar decrease from 96.79 % to 90.98 % for PA. Decrease of IE with increasing temperature suggests that the corrosion inhibition of the inhibitors for the steel material might be caused by the adsorption of the inhibitor onto the steel surface from the acidic solution. This trend is also in agreement with what is known about the dependence of adsorption on temperature that as temperature rises, the quantity adsorbed decreases [24]. This decrease in inhibition efficiency with increase in temperature can be attributed to the decrease in the protective nature of the inhibitive film formed on the metal surface (or desorption of the inhibitor molecules from the metal surface) at higher temperatures. This depicts physical adsorption mechanism. Physical (electrostatic) adsorption takes place when inhibition efficiency decreases with rise in temperature while chemisorptions take place when inhibition efficiency increases with increase in temperature [25].

Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between the two processes at a particular temperature. With increase of temperature, the equilibrium between adsorption and desorption processes is shifted to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature [26]. Thus, it is appropriate to say that decreasing temperature favours the inhibition efficiency of FA and PA on steel in hydrochloric acid.

Kinetic Considerations

Kinetic treatment of weight loss results

The corrosion reaction is a heterogeneous one, composed of anodic and cathodic reactions with the same or different rate [27]. It is on this basis that kinetic analysis of the data is considered necessary. In this present study, the initial weight of steel coupon at time, *t* is designated *W_i*, the weight loss is ΔW and the weight change at time *t*,

(*W_i* - ΔW) or *W_f*.

When log *W_f* was plotted against time (Figures 1 and 2), a linear variation was observed, which confirms a first-order reaction kinetics with respect to tubular steel in HCl solutions, formulated as [28] :

$$\log W_f - \log W_i - kt \text{ ----- } 5$$

where *W_i* is the initial weight before immersion,
k is the rate constant and
t is time.

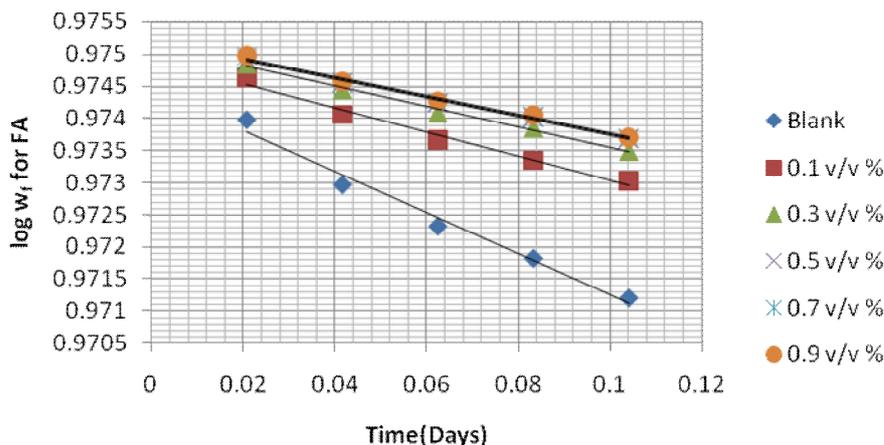


Figure 1: Variation of log *W_f* with time (days) for tubular steel coupon in 15% HCl solution containing FA

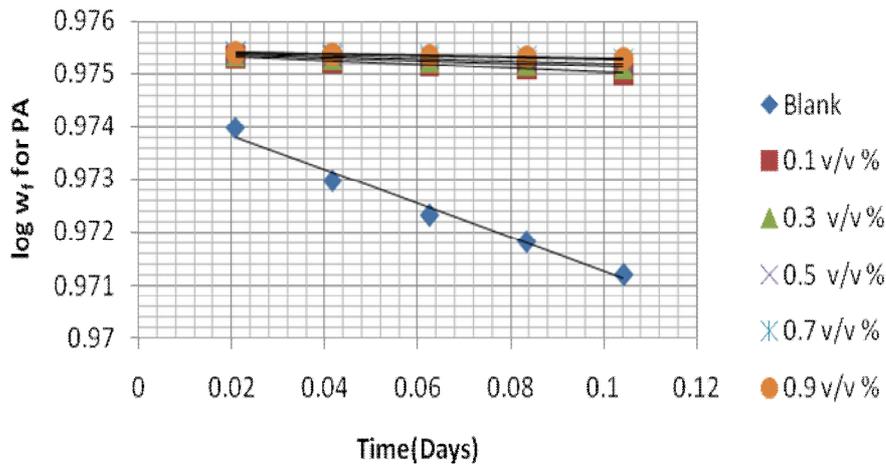


Figure: 2 Variation of log W_f with time (days) for tubular steel coupons in 15% HCl solution containing PA

From the rate constant values obtained from the graphs, the half-life values, $t_{1/2}$, of the metal in the test solutions were calculated using the equation [28]:

$$t_{1/2} = 0.693/k \text{ ----- 6}$$

The values of rate constant, k and half-life, $t_{1/2}$, for FA and PA are presented in Tables 4 and 5

Activation Energy

The apparent activation energy, E_a , can be calculated from the Arrhenius equation [7,24,29].

$$\log \frac{\rho_1}{\rho_2} = \frac{E_a}{2.303} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \text{ 7}$$

Where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2 respectively. The values of activation energy for FA and PA are presented in Table 4 and 5.

Table 4 Values of rate constant, half life and activation energy for FA at various concentrations

Concentration (v/v %)	Rate Constant ,k (DAY ⁻¹) x10 ⁻³ at temp in K				Half-life, t _{1/2} (DAYS) x 10 ² at temp in K				Activation Energy, kJ mol ⁻¹		
	303	313	323	333	303	313	323	333	303K-313K	313K-323K	323K-333K
Blank	32.0288	38.5984	48.8468	52.5148	0.2164	0.1795	0.1419	0.1320	13.8487	20.4218	7.6790
0.1	18.8425	23.5277	31.2816	34.3460	0.3678	0.2945	0.2215	0.2018	17.0026	23.8392	8.6214
0.3	15.9487	20.0319	26.4325	28.7463	0.4345	0.3459	0.2622	0.2411	18.2105	26.2750	9.9691
0.5	14.5244	18.0063	23.8746	26.2587	0.4771	0.3849	0.2903	0.2639	18.2950	27.1023	10.6087
0.7	14.7614	18.3518	24.0887	26.2327	0.4695	0.3776	0.2877	0.2642	17.3445	26.6505	10.7896
0.9	14.6077	18.2478	24.0336	26.1766	0.4744	0.3798	0.2883	0.2647	17.7360	26.8238	10.7033
								Average	17.7178	26.1382	10.1384

Table 5. Values of rate constant, half life and activation energy for PA at various concentrations

Concentration (v/v %)	Rate Constant ,k (DAY ⁻¹) x10 ⁻³ at temp in K				Half-life, t _{1/2} (DAYS) x 10 ² at temp in K				Activation Energy, kJ mol ⁻¹		
	303	313	323	333	303	313	323	333	303K-313K	313K-323K	323K-333K
Blank	32.0288	38.5984	48.8468	44.9873	0.2164	0.1795	0.1419	0.1540	13.8487	20.4218	7.6790
0.1	3.7693	5.1803	8.2804	9.4875	1.8385	1.3378	0.8369	0.7304	27.1730	49.0390	22.0547
0.3	2.7785	3.9995	6.3586	7.0242	2.4941	1.7327	1.0899	0.9866	31.0384	43.2243	16.8866
0.5	2.2315	3.3377	6.0534	5.9927	3.1055	2.0763	1.1448	1.1564	37.6599	58.1249	24.1037
0.7	1.6251	2.6074	4.6242	5.3742	4.2645	2.6578	1.4986	1.2895	49.0493	56.2887	20.0538
0.9	1.3975	2.2770	4.1297	4.5123	4.9588	3.0435	1.6781	1.5358	50.9266	58.0364	20.6999
								Average	39.1694	52.9426	20.7597

From Tables 4 and 5, there is a general decrease in the rate constants from 303K - 333K with increasing concentrations of FA and PA (Tables 4 and 5). The increase in half-life ($t_{1/2}$) with increase in concentration shown when

FA and PA are present further supports the inhibition of the steel in 15% HCl by the additives. The increase in half life indicates more protection of the metals by the FA and PA [27].

On the basis of the experimentally determined activation energy value (17.72 kJ/mol at 303K - 313K, 10.14 kJ/mol at 323K-333K for FA and 39.17 kJ/mol at 303K - 313 K, 20.76 kJ/mol at 323K-333K for PA), the additive is physically adsorbed on the coupons. These values are higher than the value of 13.85 kJ/mol and 7.68 kJ/mol obtained for the blank indicating that the corrosion reaction of steel is retarded by FA and PA [30]. Similar observations have been reported [27]. The higher values of apparent activation energy in the inhibited systems compared to the uninhibited system suggests higher energy barrier for the corrosion process in the inhibited solutions associated with physical adsorption between the inhibitor species and the steel surface [31,32]. The apparent activation energy values are also lower than the threshold value (80 kJ/mol) required for chemical adsorption indicating that FA and PA inhibit the tubular steel corrosion via physical adsorption mechanism [33].

Thermodynamic Considerations

Heat of Adsorption

One of the thermodynamic tools used in the determination of inhibition mechanism is the standard heat of adsorption, Q_{ads} . Q_{ads} in kJ mol⁻¹ could be calculated using the following equation [17].

$$Q_{ads} = 2.303R \log \left[\frac{\theta_2}{1 - \theta_2} \right] - \log \left[\frac{\theta_1}{1 - \theta_1} \right] \frac{T_1 T_2}{T_2 - T_1} \dots\dots\dots 8$$

Where θ_1 and θ_2 are degrees of surface coverage at temperature T_1 and T_2 by different inhibitor. Values of Q calculated from Equation 8 are recorded in Table 6. The values ranged from -1.86 kJ/mol to -13.43 kJ/mol for FA and -8.74 kJ/mol to -40.59 kJ/mol for PA indicating that the adsorption of the inhibitors on the surface of the steel is exothermic [33].

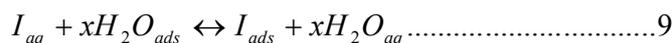
Table 6 Values of heats of adsorption at various concentrations and temperatures for FA and PA

Concentration (v/v %)	Heat of Adsorption (kJ/mol) of FA			Concentration (v/v %)	Heat of Adsorption (kJ/mol) of PA		
	303K-313K	313K-323K	323K-333K		303K-313K	313K-323K	323K-333K
Blank	-	-	-	Blank	-	-	-
0.1	-8.0076	-13.4270	-6.6820	0.1	-13.1527	-19.4753	-8.7430
0.3	-7.0612	-8.8872	-3.1935	0.3	-18.0782	-24.3121	-10.2123
0.5	-5.3476	-8.4486	-3.9730	0.5	-22.6172	-36.3582	-16.8178
0.7	-5.4218	-6.0096	-1.7309	0.7	-32.0373	-37.9116	-14.8855
0.9	-5.5723	-6.2672	-1.8624	0.9	-34.3060	-40.5875	-15.9792

The negative values of Q_{ads} observed for all the inhibitors also show that the adsorption and hence IE decreases with rise in temperature [34]. Generally, decrease of temperature increases the extent of adsorption and thus, heat of adsorption. The decrease of adsorption with increasing temperature implies, by Le Chatelier’s principle, that heat is evolved in the process of adsorption. Since the values of Heats of Adsorption for FA and PA are predominantly less negative than 40kJ/mol; it implies that they are physisorbed on the steel surface [35-37].

Adsorption Mechanism

The observed inhibition of the corrosion of tubular steel in the HCl solutions with increase in the inhibitor concentration can be explained by the adsorption of the components of the inhibitor 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 and x is number of water molecules adsorbed on the surface [38,39].



The inhibitor molecules may then combine with Fe²⁺ 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-I [40,41] which may either inhibit or catalyse further metal dissolution.

Adsorption Isotherms

Values of degree of surface coverage calculated from weight loss measurements have been used to study the adsorption characteristics of the inhibitors on the surface of the steel. The data obtained within the temperature range of 303K and 333K were used to fit curves for different adsorption isotherms including Temkin, Frumkin, Langmuir, Freundlich, Hill de Boer, Parsons, Flory Huggins, Dhar-Flory Huggins, El-Awady and Bockris Swinkles, and the correlation coefficients (R^2) were used to determine the best fits. All of these isotherms are of the general form^[42].

$$f(\theta, x) \exp(-2a\theta) = KC \dots \dots \dots 10$$

where $f(\theta, x)$ is the configurational factor which depends upon the physical model and assumption underlying the derivative of the isotherm^[42]. θ is the surface coverage, C is the inhibitor concentration, x is the size ratio, K is the equilibrium constant of adsorption process and a is the molecular interaction parameter describing the molecular lateral interactions in the adsorbed layer. It can have both positive and negative values. The positive values of a indicates attraction forces between the adsorbed molecules while the negative values indicates repulsive forces between the adsorbed molecules^[18].

The Temkin isotherm is given^[18]:

$$\theta = \frac{1}{f} \ln K_{ads} + \frac{1}{f} \ln C \dots \dots \dots 11$$

The Freundlich isotherm has also been given^[43]:

$$\ln \theta = \ln K_{ads} + \frac{1}{n} \ln C \dots \dots \dots 12$$

where C is the inhibitor bulk concentration in ml L^{-1} , K_{ads} ($\text{ml}^{-1} \text{L}$) is the equilibrium constant of adsorption and f is the Temkin heterogeneity factor which is related to interaction factor a ($f = -2a$). n is Freundlich heterogeneity factor.

The Freundlich and Temkin adsorption isotherms were found to best describe the experimental results for PA as well as FA adsorption on the corroding steel surface at the temperature range studied, with R^2 ranging from 0.89 to 0.98.

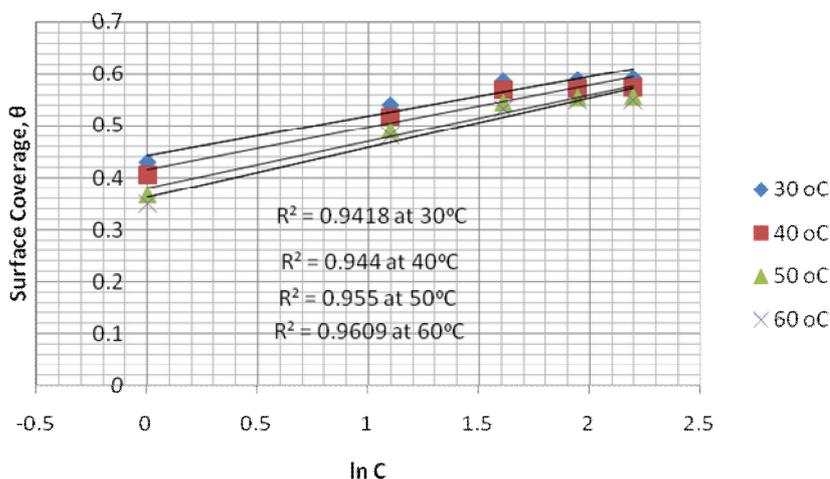


Figure 3 Temkin plot θ vs $\ln C$ For FA

Fig. 3 shows the plot of surface coverage versus logarithmic concentration of FA at different temperatures. Straight lines ($R^2 > 0.94$) were obtained indicating that the adsorption of the FA onto mild steel surface can be approximated by Temkin isotherm.

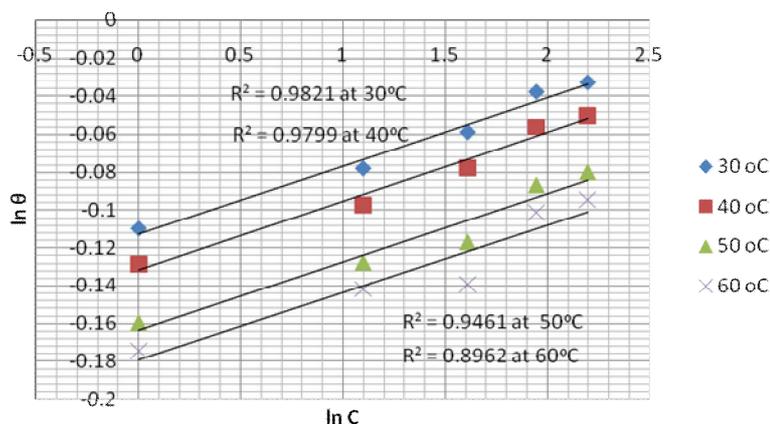


Figure 4 Plots of Freundlich $\ln \theta$ vs $\ln C$ For PA

By plotting values of $\ln \theta$ versus $\ln C$ (Figure. 4), linear plots were obtained ($R^2 > 0.89$) confirming the applicability of Freundlich adsorption isotherm to the adsorption of PA on the surface of the tubular steel at the temperatures studied. The values of constants obtained for the Freundlich adsorption isotherm are tabulated in Table 7.

Gibb’s free energy

From the intercept obtained from the isotherm plots, free energy of adsorption ΔG_{ads} at different temperatures is calculated^[44].

$$\Delta G_{ads} = -RT \ln 55.5 K_{ads} \text{ -----13}$$

Where R = universal gas constant
 T = Temperature(in K)
 K_{ads} = Equilibrium constant

The adsorption parameters deduced from Temkin isotherm are presented in Table 7. As shown in Table 7, the negative values of ΔG_{ads} suggest spontaneous adsorption of the inhibitor and usually characterize their strong interaction with the metal surface¹.

Table 7. Values of ΔG_{ads} (kJ/mol), Temkin heterogeneity factor (f), attraction constant (a), adsorptional constant (K), Freundlich heterogeneity factor and correlation coefficient (R^2) for FA and PA

Temp (K)	TEMKIN FOR FA					FREUNDLICH FOR PA				
	1/f	a	K (mL.L ⁻¹)	ΔG (kJ/mol)	R^2	1/n	n	K (mL.L ⁻¹)	ΔG (kJ/mol)	R^2
303	0.0770	-6.4901	306.8445	-24.5555	0.9418	0.0361	27.7	0.8934	-9.8387	0.9821
313	0.0810	-6.1707	170.1670	-23.8305	0.9440	0.0365	27.4	0.8765	-10.1135	0.9799
323	0.0902	-5.5426	66.5334	-22.0685	0.9550	0.0362	27.6	0.8490	-10.3510	0.9461
333	0.0956	-5.2303	44.0620	-21.6100	0.9609	0.0356	28.1	0.8360	-10.6283	0.8962

The increase in values of ΔG_{ads} with increasing temperature for FA indicates the occurrence of exothermic process at which adsorption was unfavorable with increasing reaction temperature as the result of the inhibitor desorption from the steel surface^[45]. However, decrease in ΔG_{ads} with increasing temperature as found with PA suggests that increasing temperature facilitates inhibitor adsorption^[18].

For a physical adsorption mechanism, the value of the free energy of adsorption should be more negative than -40 kJ/mol therefore the data is consistent with those required for physical adsorption mechanism^[33]. It is also seen from Table 7, that the values of a are negative in all cases, indicating that repulsion exists in the adsorption layer^[46]. It is known that when the n value is greater than 1.0, conditions are favorable to adsorption^[47]. In the present study for PA, values of n are all greater than unity implying favoured adsorption process.

Entropy of adsorption

Another thermodynamic function, namely, entropy of adsorption, ΔS_{ads} , was obtained from the slope of the plot of ΔG_{ads} against T depicted in Figure 4 according to the relationship:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S \text{-----14}$$

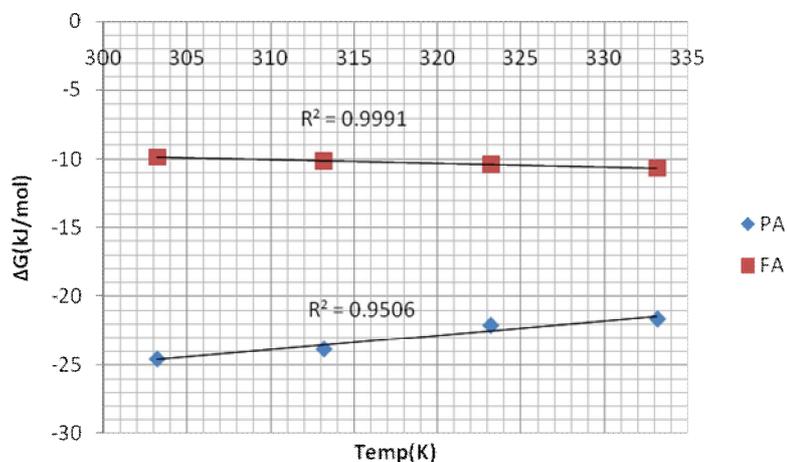


Figure 5: Gibbs free energy versus temperature graph for FA and PA

From the graph (figures 5), the values of entropy (slopes) are $-0.105984 \text{ kJ K}^{-1}\text{mol}^{-1}$ and $0.02607 \text{ kJ K}^{-1}\text{mol}^{-1}$ respectively for FA and PA. These results show orderliness and disorderliness of the corrosion inhibition process respectively for FA and PA [48].

Conclusions

The results presented in this paper show that extracts from the leaves of *Ficus Abutilifolia* (FA) and propargyl alcohol (PA) inhibit the corrosion of N-80 steel in HCl solutions to a reasonable extent. The inhibition efficiencies of the inhibitors (FA and PA) increased with increase in concentration and decreased with increase in temperature and followed the trend: PA>FA. From the trend in inhibition efficiencies, inhibitors, present at highest concentration in the corrodent, is assumed to contribute significantly to the adsorbed organic compounds responsible for the inhibitive effects of the inhibitors.

The adsorbed species formed insoluble [Fe-I] complex due to their interactions with the dissolved iron ions. The methanolic extract can be considered as a source of relatively cheap, eco-friendly and effective acid corrosion inhibitor. Based on the trend of inhibition efficiency with temperature and from the obtained values of activation energy, heat of adsorption and Gibb's free energy, the corrosion inhibition is attributed to physical adsorption of the phytochemical components of the plant on the surface of the tubular steel. The experimental data fit into the Temkin and Freundlich adsorption isotherms for FA and PA respectively.

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