Corrosion Inhibitive Efficacy of Natural Plant Extracts on Zinc in 0.5 M HCl Solution

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Abstract *Newbouldia leavis* (NL) and Pepper fruit (PF) leaf extracts were investigated for their ability to impede corrosion of zinc in 0.5 M HCl by gravimetric and thermometric techniques. The results obtained showed that different concentrations of the (NL and PF) extracts hinder the corrosion of zinc in 0.5 M HCl. Inhibition efficiency of each extract varies with concentration, time of immersion and temperature. The values of activated energies were higher in the suppressed corrosion reaction of zinc than the values calculated for the blank. The thermodynamic study shows that the NL and PF leaf extracts adsorbed on the surface of zinc was spontaneous and follows Frumkin adsorption isotherm. Physical adsorption mechanism has been proposed for adsorption of these inhibitors on the surface of zinc metal.

Introduction

The most effective way to mitigate materials from corrosion is through the use of inhibitors.

There are many inhibitors that can be used to protect materials from corrosion but some are of these are toxic and harmful to the environment. These prompted the search for natural inhibitors that are eco-friendly and biodegradable. Several works of literature have reported on the efficacy and efficient use this inhibitors [1- 3]. The efficiency of biomass extracts in mitigating corrosion has been correctly linked with the organic constituents therein including alkaloids, tannins, saponins, flavonoids, carbohydrates, fats and oil, and proteins as well as their hydrolyzed products. In addition, biomass resources are low-cost, readily available, and renewable.

Generally, inhibitor molecules may physically or chemically adsorb on a corroding metal surface. In any case, adsorption is generally over the metal surface forming an adsorption layer that functions as a barrier protecting the metal from corrosion [4, 5]. It has been commonly recognized that an organic inhibitor usually promotes the formation of a chelate on a metal surface, by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption [6]. In this way, the metal acts as an electrophile; and the nucleophile centers of inhibitor molecule are normally heteroatoms with free electron pairs that are readily available for sharing, to form a bond [7].

The power of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, containing functional electronegative groups and πelectron in triple or conjugated double bonds, are usually good inhibitors. Heteroatoms, such as sulfur, phosphorus, nitrogen, and oxygen, together with aromatic rings in their structure are the major adsorption centers. The planarity and the lone electron pairs in the heteroatoms are important features that determine the adsorption of molecules on the metallic surface [8].

The current paper is centered on the evaluation of the corrosion inhibition properties of non-toxic leaf extract namely, NL and PF. NL and PF had been used in the area of medicine and cosmetics, applicable to hair, skin, and nail. This paper reports the study of the effect of NL and PF to extract on the corrosion inhibition of zinc in 0.5M HCl solution, by gravimetric and thermometric methods.

Materials and Method

Preparation of the extracts

The leaves of *Newbouldia leavis* and Pepper fruit were collected around the Faculty of Engineering, Nnamdi Azikiwe University, Awka, and shade dried for three days. 200g of dried powder were soaked completely with ethanol and left for 48 hrs. The resulting paste was filtered and the filtrate boiled to remove excess ethanol and the pure leaf extracts were collected respectively.

Specimen preparation

Rectangular specimen of zinc was mechanically pressed cut to form different coupons, each of dimension exactly 5.0 x 3.0 x 0.6cm. The specimens were mechanically polished; a hole drilled at one end for free suspension and numbered by punching. The specimens were decreased with acetone, washed with distilled water and abraded with 200 grade emery paper, cleaned and dried then stored in desiccators for further study.

Mass Loss method

In the mass loss measurements, zinc coupon in triplicate was completely immersed in 100ml of the test solution of 0.5 M HCl in the presence and absence of the inhibitors. The metal specimens were withdrawn from the test solutions after an hour interval for 8 hours at 303K to 343K. The mass loss was taken as the difference in weight of the specimens before and after immersion determined using Electronic analytical balance (JA303P) with sensitivity of ± 0.001g. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported. From the mass loss measurements, Corrosion rate was expressed in mg cm^{-2} hr^{-1} of the samples [10]: The inhibition efficiency ($\eta\%$) was calculated from weight loss using the following equation:

$$CR = \frac{m_1 - m_2}{At} \tag{1}$$

Where m_1 and m_2 are the weight loss in (mg) of Zinc before and after immersion, respectively, in test solutions, *A* is the area of specimen (cm^2) and *t* is the exposure time (hr). The inhibition efficiency ($\eta\%$) was evaluated from corrosion rate as: [11],

$$\eta\% = 1 - \frac{CR_{(inh)}}{CR_{(unin\ h)}} \times 100 \tag{2}$$

Where *CR (uninh)* and *CR (inh.)* are the corrosion rates in the absence and presence of the inhibitor, respectively at same temperature.

The fraction of zinc surface covered by the adsorbed extract molecules (θ) was calculated as,

$$\theta = 1 - \frac{CR_{(inh)}}{CR_{(unin\ h)}} \tag{3}$$

Thermometric

Thermometric was carried out according to [12]. The reaction number (RN) was calculated from the rise in temperature of the system per minute, using equation 4:

$$RN\left(^{\circ}C/min\right) = \frac{T_m - T_1}{t} \tag{4}$$

Where Tm is the maximum temperature of the system, T1 is the initial temperature and t is the time. The inhibition efficiency ($\eta\%$) was evaluated by:

$$\eta\% = \frac{RN_{aq} - RN_w}{RN_{aq}} \pi r^2 \tag{5}$$

Where RN$_{aq}$ is the reaction number of the aqueous acid in the absence of the inhibitors and RN$_w$ is the reaction number of the aqueous acid in the presence of the inhibitors.

Results and Discussions
Gravimetric measurements

The weight loss of zinc in 0.5M HCl having different concentrations of NL and PF extracts respectively was investigated for eight days and presented in Fig 1. Fig 1 shows that the weight loss values obtained from the two extracts (NL and PF) increase as the time increases and reduce as the concentration increases. This is an indication that the extracts; NL and PF suppressed the corrosion of zinc in 0.5M HCl solution.
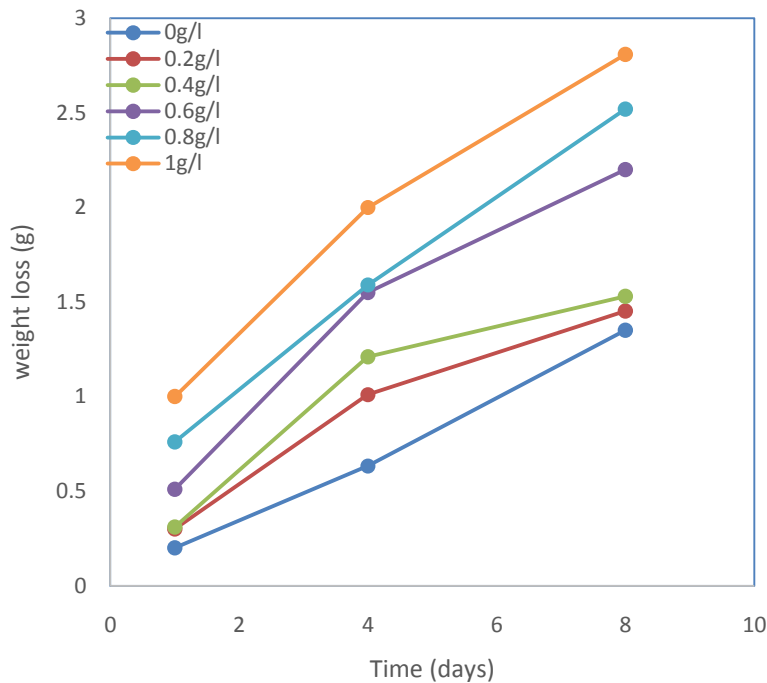
(a)
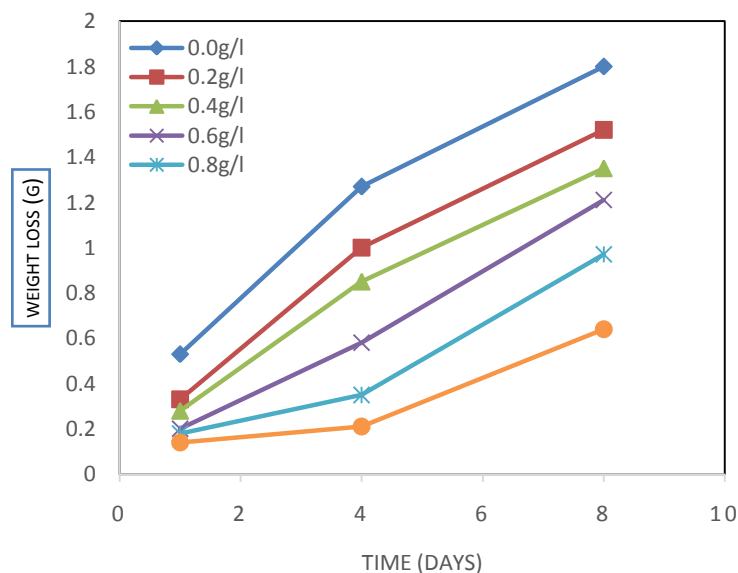
(b)

Figure 1: Weight loss against time for corrosion inhibition of zinc in 0.5 M HCl solution with different concentrations of (a) NL (b) PF extracts

The values of inhibition efficiencies, rate constant, half-life and corrosion rate are presented in Table 1. The in inhibitive action of NL and PF on zinc in 0.5 M HCl solution reached maximum at 86.17% for PF and 77.78% for NL at the same concentration of 1.0g/l. Fig 2 reveals that the inhibition efficiencies of both extracts increases as the concentration increases progressively. The inhibition efficiencies of the extracts followed the order PF<NL.
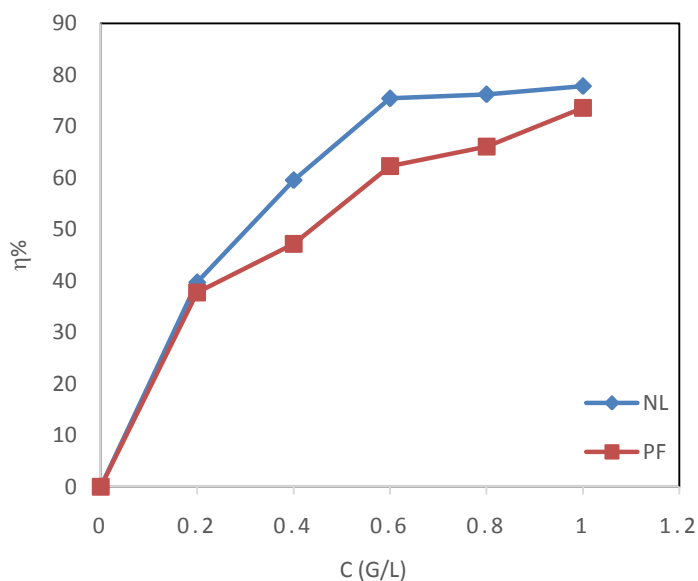

Figure 2: Relationship between inhibition efficiency and concentration of NL and PF for zinc in 0.5 M HCl solution

First -order reaction kinetics was investigated in this work, bearing in mind zinc in 0.5 M HCl solution by denoting weight at time t m_1 and a linear relationship was obtained by plotting log m_1 versus time in days[13], .

$$logm_1 = logm - kt \qquad (6)$$

Where m is the initial weight before immersion, k is the rate constant and t is time. There value of rate constant, k, was obtained from the slopes of Fig 3 and listed in Table 1.

Table 1: Corrosion rate, Inhibition efficiency, Rate constant and Half-life of zinc in the absence and presence of different concentrations of the extracts (NL and PF)

|	NL				PF			
Inhibitor conc.	**Cr mg/cm²/hr)**	**η%**	**Rate constant (day⁻¹)**	**Half-life (day)**	**Cr (mg/cm²/hr)**	**η%**	**Rate constant (day⁻¹)**	**Half-life (day)**
0	26	-	0.54	1.28	29	-	0.04	17.3
0.2	16	39.68	0.49	1.41	20	49.32	0.03	23.1
0.4	14	59.52	0.38	1.82	18	56.21	0.03	24.1
0.6	10	75.40-	0.34	2.04	14	79.67	0.02	40.8
0.8	9	76.19	0.32	1.17	13	84.68	0.01	63.1
1	7	77.78	0.14	4.99	11	86.17	0.00	-

Inspection of Table 1 indicates that the values of rate constant decreases as the concentrations of the extracts increases. The half- life increases with increase in the concentrations of the inhibitors (NL and PF) imply a reduction in dissolution rate of zinc in the solution as with increase in concentration of the inhibitors. Half -life $t_{1/2}$ was calculated using Eq. (7)

$$t_{1/2} = \frac{0.693}{k} \qquad (7)$$

(a)

(b)
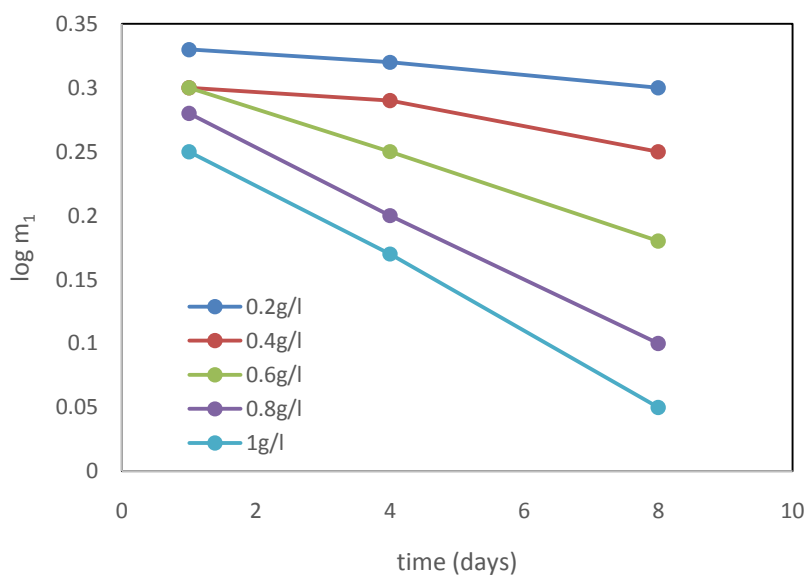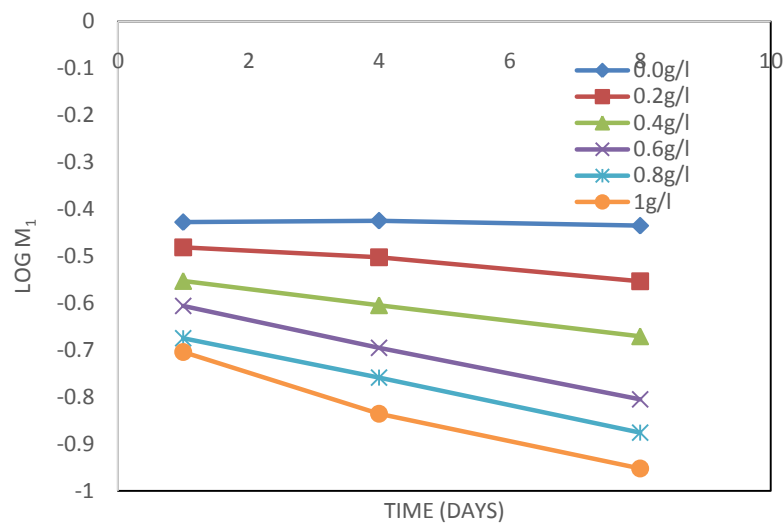
Figure 3: Plot of log m₁ versus time for zinc in 0.5 M HCl solution with different concentrations of (a) NL (b) PF extracts

The activation energies Ea for the corrosion of zinc in the absence and presence of different concentrations of NL and PF were calculated using Arrhenius-type equation.

$$CR = Ae^{-\frac{E_a}{RT}} \tag{8}$$

where Cr is the corrosion rate, Ea is the apparent activation energy of the Aluminum dissolution, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. Fig 4 presents the Arrhenius plot for corrosion rate of zinc in 0.5M HCl. The values of Ea for zinc calculated from the slope of log CR versus 1/T and listed in Table 2.
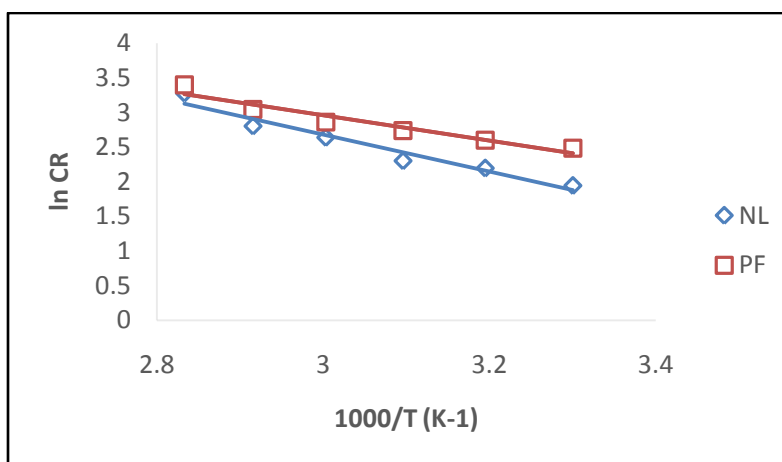
Figure 4: Arrhenius plot of log CR versus 1000/T of zinc in 0.5M HCl at different concentrations of NL and PF

The enthalpy of activation ($\triangle$H*) and the entropy of activation ($\triangle$S*) for corrosion of zinc can be evaluated from using transition state equation.

$$CR = \frac{K_B T}{h} \exp\left(\frac{\Delta S^*}{h}\right) \exp(- \frac{\Delta H^*}{RT}) \tag{9}$$

Where K_B is Boltzmann's constant and h is the plank's constant. Linear relationship are obtained from plot of ln(CR/T) against 1/T Fig 5. The slopes of Fig 5 gives -$\triangle$H* and intercept of lnCR/T axis, $\triangle$S* values were estimated and listed in Table 2.

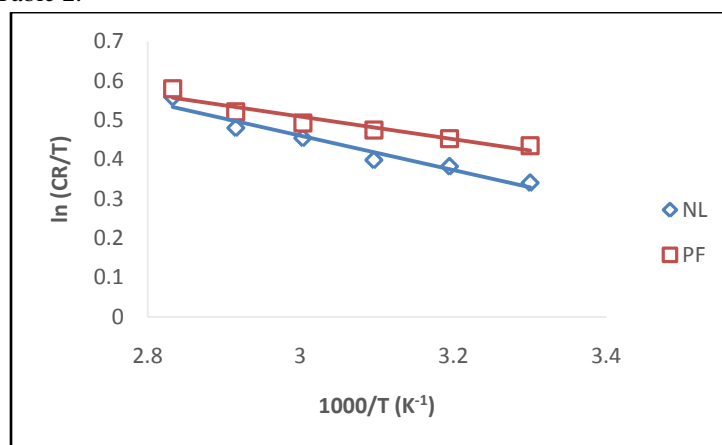*Figure 5: Transition state plot of ln(CR/T) against 1/T of zinc in 0.5M HCl at different concentrations of NL and PF*

Table 2: Activation parameters for corrosion reaction of zinc in 0.5 M HCl in the absence and presence of different concentrations of the extracts

	NL			PF		
Inhibitor conc. (g/l)	Ea (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol/K)	Ea (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol/K)
0.0	50.7	51.7	-0.05	47.8	44.6	-40.6
0.2	52.4	50.5	-0.08	56.2	53.8	-39.5
0.4	56.6	53.4	-0.07	54.4	51.5	-48.4
0.6	56.4	54.0	-0.07	50.1	48.0	-50.6
0.8	59.5	55.7	-0.07	49.2	46.8	-48.7
1.0	56.0	53.0	-0.06	49.6	44.5	-40.1

The calculated values of entropies are high and negative in PF system indicating that the activated complex in the rate determining step signifies an association rather than dissociation step, this implies that a decrease in disordering occurs from reactants to the activated complex.

Adsorption isotherm consideration

Corrosion inhibition process is associated with adsorption species on the surface of the metal. The most commonly used adsorption isotherms are Frumkin, Langmuir, Temkin, Freundlich, Florry Huggins, Bockris-Swinkel and El-Awardy isotherms. These isotherms are the form of equation (10);

$$f(\theta, x)\exp(-2a\theta) = kC \tag{10}$$

Where f(θ,x) is the configuration factor which depends on the physical model and the assumptions underlying the derivation of the isotherm, θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, x is the zero ratio, a is the molecular interaction parameter and k is the equilibrium constant for the adsorption process. Adsorption of NL and PF is best explained by Frumkin adsorption isotherm.

Frumkin isotherm equation (11) is followed by when a plot of log(θ/(1-θ)[C] against θ gives a linear relationship with the slopes equal to 2α/2.303.

$$\log\left(\frac{\theta}{(1-\theta)[C]}\right) = logK + 2\alpha/2.303 \tag{11}$$

Where α is the lateral interaction term describing the molecular interaction in the adsorbed layer, K is the desorption-adsorption equilibrium constant and C is the concentration of the inhibitor.
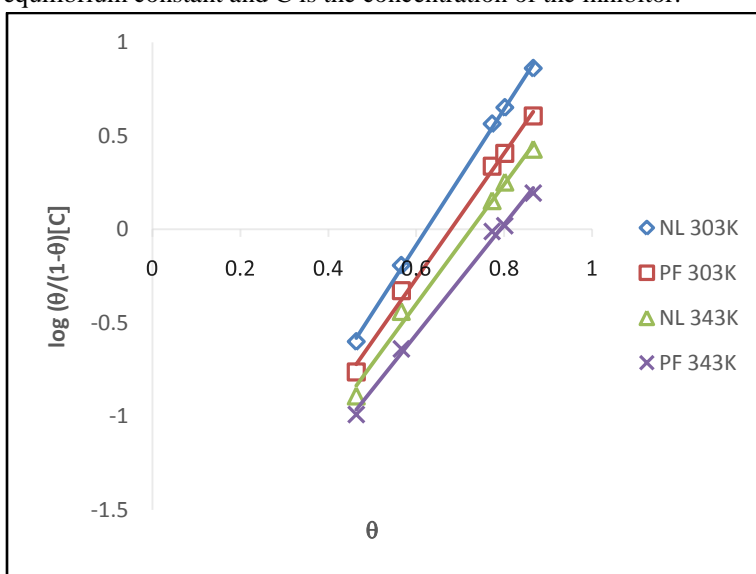

Figure 6: Frumkin isotherm for the adsorption of NL and PF on the surface of zinc

Fig 6 displays the Erumkin plots for the used inhibitor at different temperatures. The values of α obtained from slopes of the lines (listed in Table 3) shows the attractive behaviour of the inhibitors.

Again, the value of α at 343K is higher than the value at 303K implying that the strength of the attractive behaviour of the inhibitor increases with temperature. The values R² from Table 3 shows that both inhibitor performed best at 303K; this approves that the adsorption behaviour is highly affected by temperature.

Table 3: Calculated values of Frumkin isotherm parameters

Inhibitor	T (K)	R^2	Log K	K_{ads} (M⁻¹)	Slope	ΔG_{ads} kJ/mol	Isotherm value
NL	303	0.9775	-0.9252	0.1188	2.3427	-4.752	1.171
	343	0.9623	-1.3193	0.0479	4.3801	-2.789	α 2.191
PF	303	0.9808	-1.0917	0.0810	3.7211	-13.430	1.862
	343	0.9648	-1.1620	0.0689	4.4666	-15.724	α 2.233

The values of corrosion rate, Reaction number and their inhibition efficiencies from weight loss and thermometric methods are presented in Table 1. The table reveals that the corrosion rate, weight loss and reaction number decrease as the inhibitor concentration increases. Inhibition efficiency increases with increase in concentration reaching a maximum of 88.21 % and 77.78 % respectively at 1.0g/L in NL. The increase in the efficiency compounds studied can be explained on the basis of increased adsorption of the compound on the metal surface.

Conclusion

1. It was found from this study, that NL and PF extracts performs comfortably as corrosion inhibition of zinc in 0.5 M HCl solution. The inhibition efficiency increases as the concentration increases to reach a maximum value of 86.17 % at 1.0 g/l as well as temperature but decreases with time of immersion.

2. The inhibitors works by being adsorbed on the surface of zinc metal according Frumkin adsorption model. The adsorption properties of the inhibitors follow the physical adsorption mechanism.

3. The calculated value of Gibbs free energy for the adsorption process were all negative showing that the process is spontaneous**.**

Conflict of Interest

The authors acknowledged no conflict of interests on the publishing of this article.

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