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RESEARCH PAPER

INHIBITION EFFECT OF ETHANOLIC EXTRACT OF *IPOMOEA BATATAS* PEEL ON THE CORROSION OF MILD STEEL IN HYDROCHLORIC ACID MEDIUM

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Abstract

The corrosion inhibition of mild steel in HCl solution in the presence of *Ipomoea batatas* peel extract (IBPE) at a temperature range of 30°C to 60°C was studied using the chemical weight loss method. The IBPE acts as an inhibitor in the acid environment. The inhibition efficiency (IE) increases with increase in inhibitor concentration but decreases with an increase in temperature and concentration of acid. 93.96%, 89.99% and 85.61% IE were obtained at 6.67 g/L extract in 0.5, 1.5 and 2.5M acid media respectively at temperature of 30°C. 84.86%, 83.99% and 81.13% IE were obtained at 6.67 g/L extract in 0.5, 1.5 and 2.5M acid media respectively at temperature of 40°C. Also 78.92%, 76.21% and 75.73% IE were obtained at 6.67 g/L extract in 0.5, 1.5 and 2.5M acid media respectively at temperature of 50°C, while 71.45%, 69.87% and 66.00% IE were obtained at 6.67g/L extract in 0.5, 1.5 and 2.5M acid media respectively at temperature of 60°C. The inhibitive effect of the IBPE could be attributed to the presence of some compound in the peel which is adsorbed on the surface of the mild steel. The peel extract was found to conform to the Langmuir adsorption isotherm and Freundlich adsorption isotherm at all the concentration levels and temperature studied.

Key words: Corrosion, inhibition, adsorption isotherm, *Ipomoea batata*, peel.

INTRODUCTION

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment (Andreani, 2015; Ofuyekpone, 2015; Desai, 2017). Metals corrosion is a major industrial problem that has recently attracted many investigations and researches (Rajendran, 2012). It is worth investigating in oil field applications because corrosion problems represent a large portion of the total costs for oil and gas producing companies every year worldwide. Moreover, appropriate corrosion control can help in avoiding many potential disasters that can cause serious issues including loss of life, negative social impacts, and water resource and environmental pollution (Finsgar, 2014). Low carbon steel is being used extensively, under different conditions in industries and the corrosive nature of acid solution on the steel material causes considerable cost (Desai, 2017). Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulphuric acids have been widely used in the pickling processes of metals as reported by Gherraf, 2010. This consequently makes the metal prone to corrosion (Rajendran, 2012). In order to reduce the corrosion of metal, several techniques have been applied, one of them is utilization of organic compounds, and more specifically, cationic surfactants that are gaining high use as corrosion inhibitors (Asefi, 2011).

Inhibitors are one of the most convenient methods for protection against corrosion, particularly in acid solutions to prevent unexpected metal dissolution and acid consumption (Desai, 2017). The effective method of preventing corrosion is usually by adding a small number of corrosion inhibitors to reduce or prevent metal surface dissolution thereby protecting the metal in acidic or aggressive environment (Udom et al., 2017). Corrosion inhibition features of several substances are directly associated with the adsorption phenomena, which can follow different types of isotherms such as those of Temkin, Langmuir, Freundlich, and Frumkin that have been employed to show adsorption phenomena over steel electrodes (Gherraf, 2010).

The tubers of *Ipomoea batatas* commonly known as sweet potato are consumed as food. Sweet potatoes are mainly used to produce starch and starchy foods, which generates a considerable quantity of residue. The majority of this residue is discarded which later leads to pollution, while few quantities are utilized to feed domestic animals. The peels are used in the production of pectin, which had increased the potential for the return of the sweet potato processing industry (Zaidel, 2015). It contains gallic acid, catechin, chlorogenic acid, caffeic acid, ellagic acid, epicatechin, rutin, isoqercitrin, quercitrin , amylose and amylopectin (Salawu et al., 2015). These classes of compounds are known to act as free radical scavenging serving as primary antioxidants (Panda, 2011). This study was conducted to investigate the inhibition ability of sweet potato peels extracts on mild steel in Hydrochloric acid medium at different temperatures.

MATERIAL AND METHODS

Preparation of Sweet Potato (*Ipomoea batatas*) peel Extracts

Fresh tubers of sweet potato were purchased from the Gwagwalada market, Abuja, Nigeria. The peels of sweet potato tubers were removed cleaned with water, air-dried for 36 hours and then ground to powder using mortar and pestle. The dried powder peel was then weighed and extracted with ethanol at room temperature for 24 hours. The extracted peel was recovered from the solvent by evaporating the solution slowly at room temperature. The solvent-free extract was preserved in a desiccator prior to use.

Preparation of Metal Specimen

The mild steel model of 1mm thick was acquired from the mechanic workshop unit of the general service center (GSC) of Sheda Science and Technology Complex (SHESTCO). It has 98.70% purity with traces of elements such as carbon, Silicon, Aluminum, Manganese, Copper and Chromium. The mild steel model was cut into a rectangular shape of 5.1 x 2.6 cm and a small hole was punched for thread attachment. The surface of the mild steel coupons was sandpapered to give a freshly polished appearance.

Weight Loss Determination

The loss in weight measurements was conducted using the total immersion method in a 100 ml capacity beakers. The mild steel coupons were weighed up and suspended in separate beakers with 75mL of 0.5 M, 1.5 M, and 2.5 M hydrochloric acid solution respectively with the aid of a black thin thread. The coupons were retrieved after 2 hours' immersion period, washed carefully with soft brush to remove the corrosion product (Rust Stain). Dipped in distilled water and dried in acetone as hitherto reported by Awe, (2015). The mild steel coupons weight loss (ΔW), in gram was determined from the change in weight before (W_i) and after (W_f) reaction (Udom, 2017).

$$\Delta W = W_i - W_f \quad (1)$$

The corrosion rates (g/cm^2h) in with and without the inhibitors were determined using the equation.

$$CR = \frac{\Delta W}{At} \quad (2)$$

The degree of surface coverage (θ) for each concentration of Ipomoea batatas peel extract was calculated by relating the corrosion loss in presence (Wu) and absence of inhibitor (Wi) by means of the formula:

$$\theta = \frac{w_u + w_i}{w_i} \quad (3)$$

RESULTS AND DISCUSSIONS

Effect of corrosion rate on the concentration of acid and increased temperature

The rate of corrosion was observed to increase as the temperature increases from 30°C to 60°C at a particular concentration and as well as concentration increases from 0.5M to 2.5M at a particular temperature. This is generally expected as an increase in concentration and temperature are two common factors that affect rate of reaction. Increasing IBPE lowers the values of corrosion rate significantly at each temperature as compared to values of corrosion rate without the extract. While increasing temperature from 30°C to 60°C effectively showed a rise in corrosion rate, because electrochemical reaction occurs faster at higher temperature (Zivica, 2002; Qi et al., 2014), the increasing IBPE concentration was able to inhibit the corrosion even at higher acid concentration and temperature. A plot of corrosion rate vs inhibitor concentration is shown in Figure 1.

Effect of Inhibition efficiency on the concentration of acid and increased temperature

The efficiency of inhibition of IBPE was higher in 0.5M HCl solution compared to 1.5M and 2.5M HCl solutions. As the temperature increases from 30°C to 60°C there was a general decrease in the efficiency of the IBPE as shown by the lowering of % values depicted in Table 1 and Figure 2. From the result, maximum inhibition efficiency of 93.96%, 89.99%, and 85.61% was obtained at 6.67g/L extract in 0.5, 1.5 and 2.5M acid media respectively at the temperature of 30°C. At 40°C temperature, 84.86%, 83.99% and 81.13% inhibition efficiency were obtained at 6.67g/L extract in 0.5, 1.5 and 2.5M acid media. There was a general drop in percentage inhibition of 9.1 for 0.5M concentration, 6% for 1.5M concentration and 4.48% for 2.5M concentration as temperature increases from 30°C to 40°C. The decrease in inhibition efficiency might be a result of increase rate of dissolution process of mild steel and incomplete adsorption of the inhibitor to the metal surface, since electrochemical reaction occurs faster at higher temperature (Zivica, 2002; Yameng et al., 2014). A similar, occurrence was reported by kairi and Kassim (2013), for *Curcuma longa* extract on mild steel using 1M HCl, while Suleiman et al., 2016 also reported the behavior of *Acacia tortilis* extract.

Table 1. Result for rate of corrosion, degree of surface coverage and inhibition efficiency of IBTE at different temperature

	CR x 10^{-5} ($gcm^{-2}min^{-1}$)				**Θ**				**IE (%)**			
I conc	**30**	**40**	**50**	**60**	**30**	**40**	**50**	**60**	**30**	**40**	**50**	**60**
	0.5M HCl											
0	14.22	28.29	21.22	34.17								
1.33	3.80	8.50	7.63	18.96	0.7330	0.6995	0.6406	0.4452	73.30	69.95	64.06	44.52
2.67	3.15	7.51	7.03	13.95	0.7787	0.7346	0.6686	0.5916	77.87	73.46	66.86	59.16
4.00	2.44	6.34	5.95	13.10	0.8281	0.7761	0.7196	0.6166	82.81	77.61	71.96	61.66
5.33	2.10	5.52	4.93	11.34	0.8522	0.8049	0.7675	0.6681	85.22	80.49	76.75	66.81
6.67	0.86	4.28	4.47	9.78	0.9396	0.8486	0.7892	0.7145	93.96	84.86	78.92	71.45
	1.5M HCl											
0	25.74	33.48	36.27	39.87								
1.33	8.58	10.95	14.69	22.88	0.6666	0.6729	0.5949	0.4261	66.66	67.29	59.49	42.61
2.67	6.33	9.91	13.12	21.07	0.7540	0.7040	0.6383	0.4715	75.40	70.40	63.83	47.15
4.00	5.16	8.02	11.14	18.32	0.7997	0.7604	0.6930	0.5404	79.97	76.04	69.30	54.04
5.33	4.41	6.93	10.16	14.81	0.8289	0.7931	0.7198	0.6285	82.89	79.31	71.98	62.85
6.67	2.72	5.36	8.63	12.02	0.8945	0.8399	0.7621	0.6987	89.45	83.99	76.21	69.87
	2.5M HCl											
0	40.94	45.56	46.04	52.48								
1.33	15.24	15.79	20.73	32.39	0.6276	0.6534	0.5496	0.3827	62.76	65.34	54.96	38.27
2.67	12.81	14.39	17.41	27.93	0.6871	0.6841	0.6218	0.4678	68.71	68.41	62.18	46.78
4.00	10.34	11.18	15.34	24.96	0.7475	0.7547	0.6668	0.5245	74.75	75.46	66.68	52.45
5.33	9.31	10.39	13.99	20.01	0.7725	0.7719	0.6962	0.6187	77.25	77.19	69.62	61.87
6.67	5.89	8.60	11.18	17.84	0.8561	0.8113	0.7573	0.6600	85.61	81.13	75.73	66.00

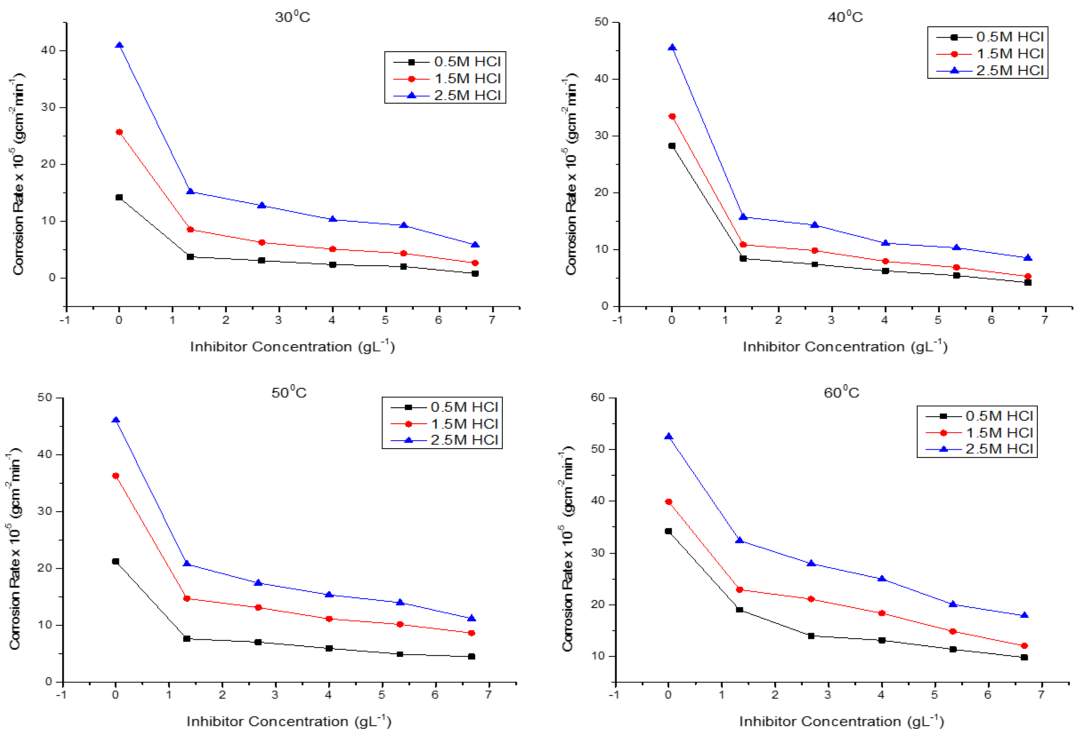

Figure 1. Corrosion rate Vs concentration of IBPE at different temperatures

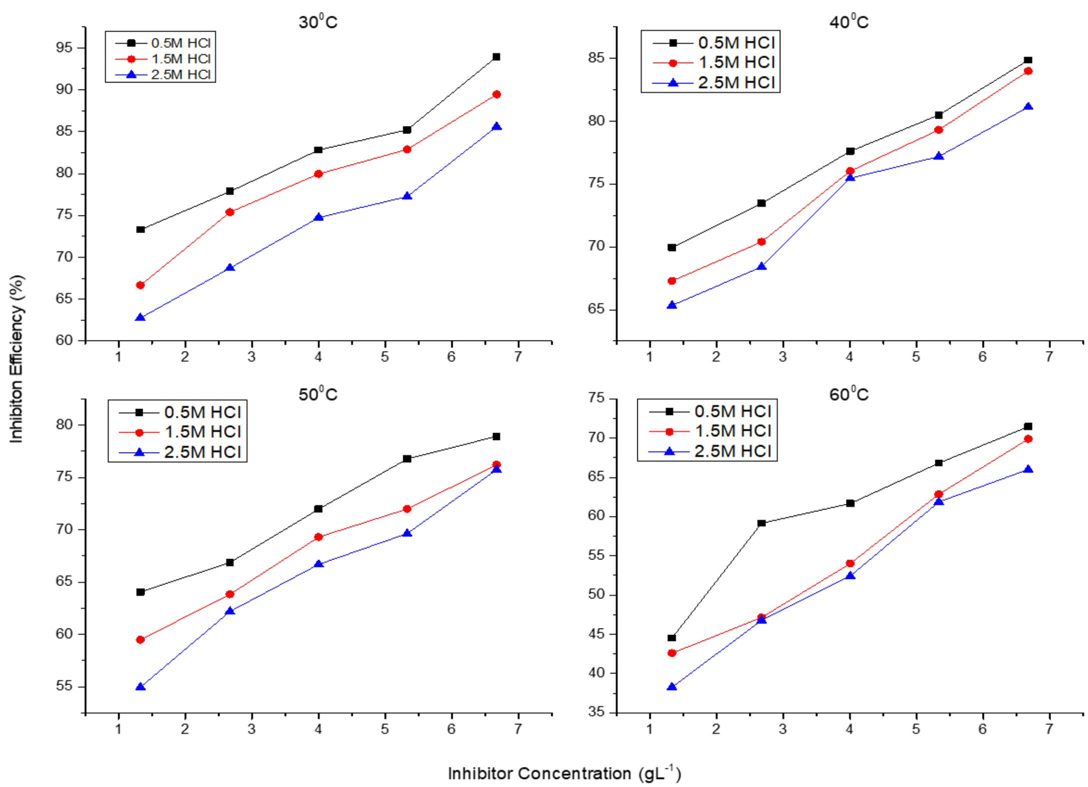

Figure 2. Effect of IBPE concentration on efficiency at different temperatures

Adsorption isotherm

The degree of corrosion inhibition largely depends on the surface conditions and method of adsorption of the inhibitor. It was assumed that the uncovered parts of the metal surface are most affected as this is where the corrosion process takes place (Kairi and Kassim, 2013; Awe et al., 2015). The degree of surface coverage (θ) thus has a direct relationship with inhibition efficiency as shown Equations 4 and 5.

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}} \quad (4)$$

$$\log\theta = \log K_{ads} + \frac{1}{n}\log C \quad (5)$$

where K_{ads} is the adsorption-desorption equilibrium constant. The inhibition was found to follow the Langmuir (equation 4) and Freundlich adsorption isotherms (equation 5). The high values of the adjusted correlation of determinant of 0.9482 to 0.9956 for Langmuir isotherm and 0.879 to 0.9773 for Freundlich adsorption isotherm, which were obtained from the linear fitted curve indicates how strong the linear relation is, between the plotted factors. Figures 3 and 4 depict such relationships.

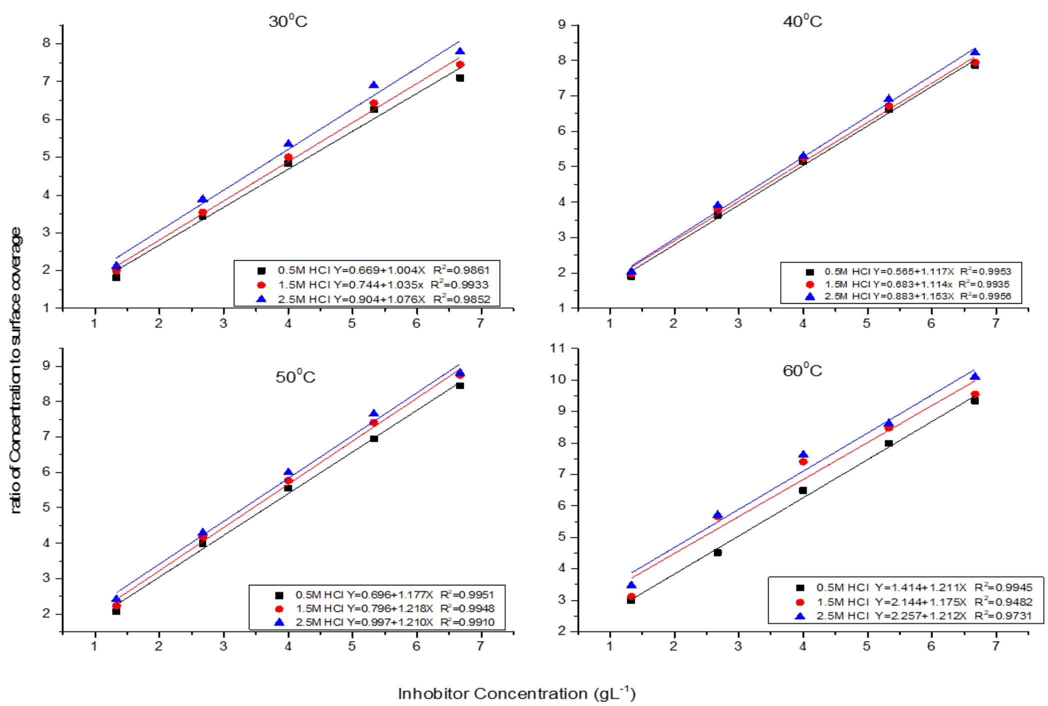

Figure 3. Langmuir adsorption isotherm of IBPE at different temperatures

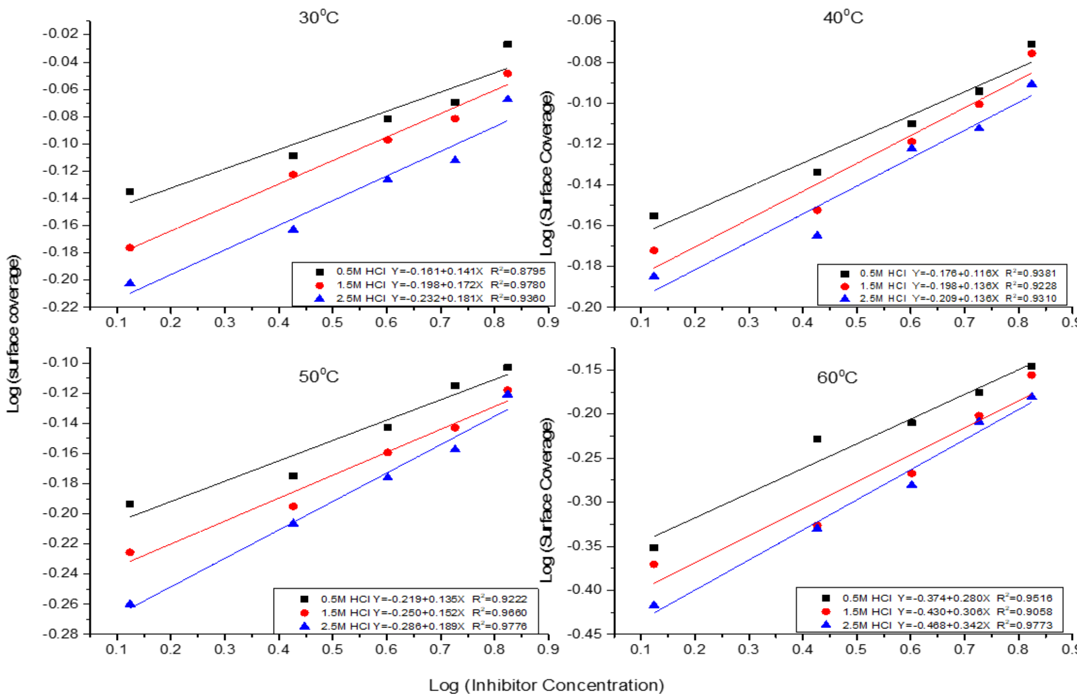

Figure 4. Freundlich adsorption isotherm of IBPE at different temperatures

Thermodynamic parameters

The feasibility of the adsorption process was also determined by calculating, the standard free energy of adsorption (ΔG_{ads}) using the equation below.

$$\Delta G_{ads} = -RTLn(55.5\, K_{ads}) \quad \textbf{(6)}$$

where 55.5 is the molar concentration of water in the solution, R is universal constant and T is absolute temperature. From the results obtained, ΔG ranges from -16.03 to -18.733 according to the Langmuir isotherm, while the Freundlich isotherm gave ΔG value of -8.1361 to -9.4313. It can be said that the inhibitor adsorption on mild steel surface is spontaneous. This also suggests a physical adsorption mechanism for the peel extracts of *Ipomoea batabas*, since the values obtained are below -20KJ/mol (Eddy, 2010; Kairi and Kassim, 2013; Udowo et al., 2017). Details of the calculation parameters are given in Table 2.

Table 2. Result of rate of corrosion, surface coverage and inhibition efficiency at different temperatures.

	Langmuir Isotherm				**Freundlich Adsorption Isotherm**			
0.5M								
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
ΔG_{ads}(KJ/mol)	-17.66	-18.70	-18.73	-17.33	-9.1831	-9.3971	-9.4313	-8.7356
Slope	1.0030	1.1170	1.1770	1.2110	0.1410	0.1160	0.1350	0.2800
K_{ads}(g/l)	20.000	23.810	19.231	9.434	0.690	0.6668	0.6039	0.4227
R^2	0.9861	0.9953	0.9951	0.9945	0.8795	0.9381	0.9222	0.9616
1.5M								
ΔG_{ads}(KJ/mol)	-17.42	-18.20	-18.34	-16.18	-8.969	-9.2655	-9.2396	-8.3782
Slope	1.0350	1.1140	1.2180	1.1740	0.1720	0.1360	0.1520	0.3060
K_{ads}(g/l)	18.182	19.608	16.667	6.211	0.6339	0.6339	0.5623	0.3715

R^2	0.9933	0.9936	0.9948	0.9484	0.9780	0.9228	0.9660	0.9058
2.5M								
ΔG_{ads}(KJ/mol)	-16.89	-18.25	-17.74	-16.03	-8.7712	-9.1994	-9.0172	-8.1361
Slope	1.0760	1.1520	1.2100	0.1700	0.1810	0.1360	0.1890	0.3420
K_{ads}(g/l)	14.706	20.000	13.333	5.882	0.5861	0.6180	0.5176	0.3404
R^2	0.9852	0.9956	0.9910	0.9732	0.9360	0.9310	0.9776	0.9773

The dependence of the rate of corrosion on temperature, are given by the Arrhenius and transition state equation of Equations; (4) and (5), respectively:

$$\log CR = \log A - \frac{Ea}{2.303RT}$$
(4)

$$Log \frac{CR}{T} = \left[\log \frac{R}{Nh} + \frac{\Delta S}{2.303R}\right] - \frac{\Delta H}{2.303R}$$
(5)

where: CR is rate of corrosion, *Ea* is apparent activation energy, *R* is universal gas constant (8.314 J mol-1 K-1), *T* is temperature, A is Arrhenius pre-exponential factor, *h* is Plank's constant (6.626176 x 1034 Js), *N* is Avogadro's number (6.02252 x 1023 mol-1), Δ*S* is the entropy of activation and Δ*H* is the enthalpy of activation.

The plot of log CR against 1/*T* is presented in Fig. 7, with a slope of -*Ea/*2.303 *RT* and intercept of log *A*. Examination of the temperature dependency on inhibition efficiency as well as assessment of activation energy of corrosion in the absence and presence of inhibitors give an understanding of the possible mechanism of inhibitor adsorption. A reduction in inhibition efficiency with rise in temperature and an increase in *Ea* in the presence of inhibitor compared to its absence, is frequently being interpreted as the formation of an adsorptive film of physisorption (Awe et al., 2015). The derived values of activation energy, enthalpy and entropy of corrosion are shown in Table 3.

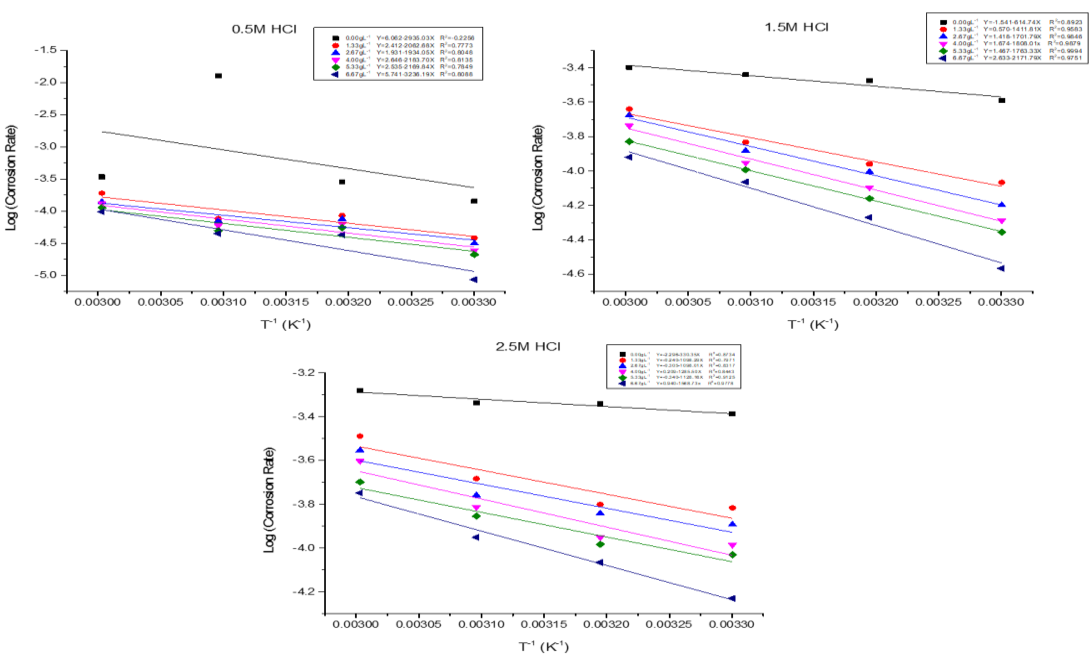

Figure 5. Relationship between the logs of corrosion rate with inverse temperature as a function of the energy of activation.

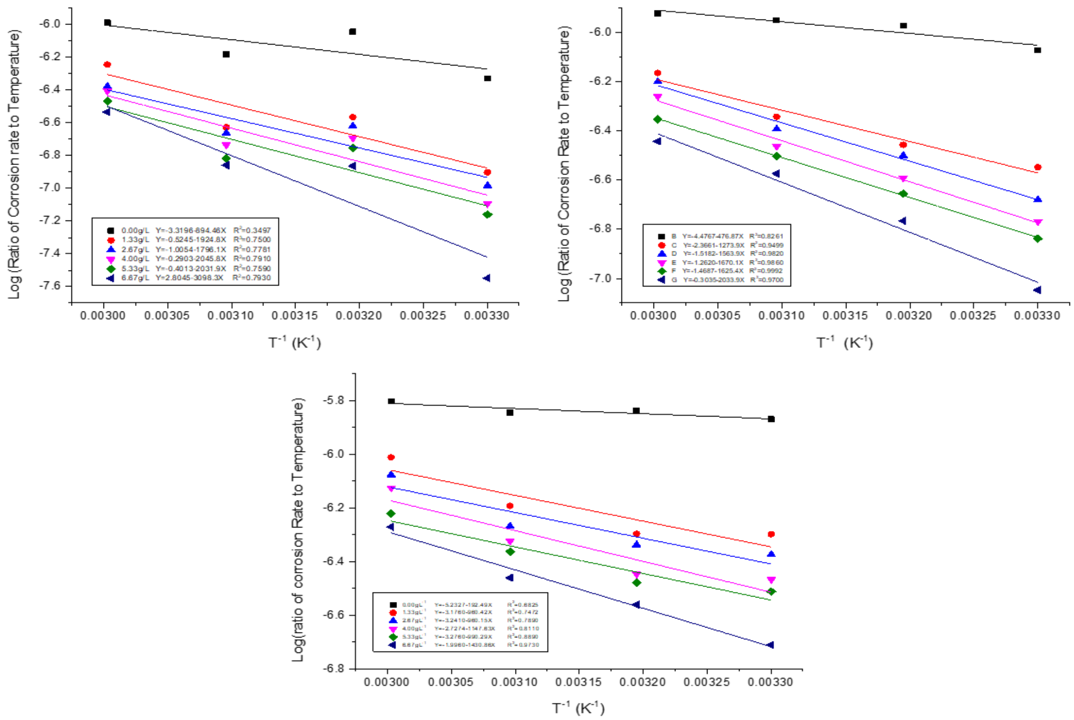

Figure 6. Relationship between the log (ratio of corrosion rate and temperature) with inverse temperature as a function of enthalpy and entropy change.

Table 3. Kinetic parameters for the corrosion of mild steel in 0.5, 1.5 and 2.5 M HCl at different temperatures.

C (gL^{-1})	E_a ($KJMol^{-1}$)			ΔH ($KJMol^{-1}$)			ΔS ($Jmol^{-1}$)		
	0.5M	1.5M	2.5M	0.5M	1.5M	2.5M	0.5M	1.5M	2.5M
Blank	19.77	11.77	6.33	17.13	9.13	3.69	-227.10	-249.28	-263.75
1.33	39.49	27.03	21.03	19.73	15.26	14.70	-144.08	-157.18	-158.21
2.67	37.03	32.58	21.02	-2.46	5.55	-5.36	-206.81	-181.36	-198.84
4.00	41.81	34.62	24.61	4.78	2.03	3.59	-183.91	-192.70	-187.76
5.33	41.55	33.76	21.60	-0.27	-0.86	-3.01	-199.72	-193.64	-208.11
6.67	61.96	41.58	30.04	20.42	7.82	8.44	-136.21	-175.29	-173.09

The results presented in Table 3 show that, Activation energy increases as the IBPE concentration increases, ΔH values were negative for extract concentration of 2.67 and 5.33gL^{-1} while the rest were positive in the presence and absence of *Ipomoea batatas* peel extract. The process of adsorption between the metal surface and the inhibitor can sometimes be an exothermic process where the heat is given off, and in some cases, endothermic process is encountered, where heat is absorbed (Larouj et al., 2017). The positive ΔH suggest slow dissolution of mild steel (AbdulRahiman and Sethumanickam 2014) and chemisorption process resulting from certain amount of destructuring (Fiori-Bimbi et al., 2015). The values of ΔS in both solutions are large and negative, indicating spontaneous and feasible reaction. This shows that going through activated complex is the rate determining step rather than the dissociation steps (Soltani et al., 2010; Kumari, et al., 2014). In the presence of the inhibitor, the value of ΔS increases and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes (Manickam et al., 2016)

CONCLUSION

The ethanolic extracts of *Ipomoea batatas* peel acts as a good and efficient inhibitor for the corrosion of mild steel in hydrochloric acid medium. The corrosion rate increases with increased concentration of acid and temperature. The efficiency of Inhibition increased with inhibitor concentration but decrease slightly with increase in acid concentration and rise in temperature suggesting physisorption. Higher activation energy, enthalpy, and entropy were obtained as the extract concentration increases. The results also show that the inhibition is mostly endothermic, while adsorption process occurs mostly at lower temperatures, lower acid concentration, and larger high magnitude free energy values. The Langmuir and Freundlich adsorption isotherm provides a formal explanation of the adsorptive behaviors of the extract on mild steel surface. The higher values of ΔG and K_{ads} indicate the spontaneity of the adsorption ability to extract at lower temperatures. Even though the numerical values of ΔG obtained from Langmuir and Freundlich adsorption isotherm differ greatly.

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