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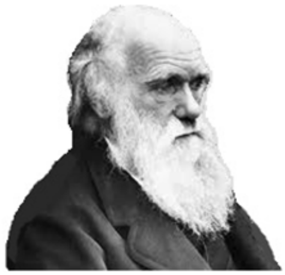

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Kinetics and Thermodynamic Studies of Corrosion Inhibition of Mild Steel Using Methanolic Extract of *Erigeron floribundus* (Kunth) in 2 M HCl Solution

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ABSTRACT

The investigation of kinetics and thermodynamics of the corrosion of mild steel in a 2 M HCl solution using methanolic extract of *Erigeron floribundus* was carried out by means of gravimetric techniques. The results obtained indicate that the extract retarded corrosion. The inhibition efficiency was seen to increase with increase in concentration of the inhibitor, as well as with increase in temperature. The values of activation energy (Ea) obtained indicate a chemisorptions mechanism, whereas the value of Gibb free energy (ΔG^{o}_{ads}) indicates a spontaneous adsorption of the extract components on the metal surface. Kinetic modelling of the experimental data obeys first order reaction. The adsorption of methanolic extract of *Erigeron floribundus* onto the mild steel surface followed the Langmuir adsorption isotherm model. Therefore, the extract functions as good corrosion inhibitor for mild steel in hydrochloric acid.

***Keywords*:** *Erigeron floribundus*, corrosion inhibition, kinetics, Adsorption mechanism

1. INTRODUCTION

Photo 1. *Erigeron floribundus* (Kunth)
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Organic compounds containing polar functional groups such as nitrogen, sulphur and oxygen in conjugated system have been reported to be effective corrosion inhibitors for steel [1]. Some plants extracts contain a mixture of polar functional group and thus possess multiple active centre's. The study of corrosion inhibition of plants extracts has been on the increase in recent times. Generally the inhibitive effect of plants extract is attributed to the adsorption of organic substances on the metal surface by blocking active sites or forming a protective barrier on steel surfaces [2, 3].

The effectiveness of inhibition by the adsorbed inhibitor system will be determined by the energy released on forming the metal-inhibitor bond compared to the corresponding changes when the pure acid react with the metal [1, 4]. In recent years, natural compounds such as herbal plants are employed as corrosion inhibitor, in order to develop new cleaning chemicals for green environment, *Erigeron floribundus* is well known reputed medicinal plant traditionally used for the treatment of skin disorders by the rural populace as well as those from the urban area. This species is widespread in Nigeria [5, 6]. The main purpose of this study is to investigate the inhibitive potential of methanolic extract of *Erigeron floribundus* as a ecofriendly corrosion inhibitor on the mild steel in 2 M HCl solution using gravimetric technique. The summary of plants extracts used as corrosion inhibitors have recently been given in [1-5] and [7-16] (Figure 1).

2. EXPERIMENTAL METHODS

2. 1. Preparation of specimen

Mild steel specimens having a composition of 0.6 % Mn; 0.36 % P; 0.15 % C; 0.07 % S and 98.79 % Fe, the specimen used in this work were obtained from physics Department, University of Calabar - Nigeria. The mild steel was mechanically press cut to coupons of dimension 4.00 x 1.20 x 0.08cm with surface area 10.10 cm^2.

2. 2. Preparation of the plant extract

The fresh part of *Erigeron floribundus* were obtained within the premises of Faculty of Agriculture Cross River University of technology, Calabar. The fresh plant was washed with water, air, dried, powder and extracted with methanol for 24 hours. The methanolic solution was filtered and refluxed further to obtain a concentrated solution. The clear dark brown methanolic concentrated solution was dried under vacuum to get a semi solid liquid [14]. 8 g of semisolid liquid that is methanolic extract was dissolved in 2 M HCl solution and kept for 24 hours. The resultant solution were filtered and stored. From the stock solution (8 g /L) inhibitor test solutions of concentration; 0.1, 0.5, 1.0, 2.0 and 4.0 g /L were prepared using serial dilution method. These solutions were then used for the corrosion test. [15].

2. 3. Gravimetric measurement

Weighed test specimens were fully immersed separately for 5 hours in each of the beakers containing the extract for the five sets, the same process as above was done for the beaker containing only 2 M HCl solution. Each of the test specimen was taken out every one hours washed with distilled water, raised with ethanol dried in acetone and re-weighed [7]. From the weight loss data the corrosion rate (CR) were calculated from equ. 1.

$$\mathrm{CR} = \frac{WL}{At} \times 1000 \ (\mathrm{mg\ cm^{-2}\ hr^{-1}}) \qquad 1$$

where WL is the weight loss data, A the specimen surface area and t the immersion period.

Thus from corrosion rate the inhibition efficiency IE % was evaluated using equ. 2.

$$\mathrm{IE}\ \% = \frac{CR(blank) - CR(inh)}{CR(blank)} \times 100 \qquad 2$$

where IE % is the inhibition efficiency, CR_{blank} is the corrosion rate for the blank while CR_{inh} is the corrosion rate for inhibited solution. [8].

3. RESULTS AND DISCUSSION

3. 1. Effect of temperature on corrosion inhibition of mild steel 2 M HCl solution

The variation of weight loss, corrosion rate and inhibition efficiency obtained from experimental measurement of mild steel in 2 M HCl solution at the Temperature of 303 K, 313 K, 323 K and 333 K as function of concentration in presence methanolic extract of *Erigeron floribundus* is shown in Fig. 1, 2 and 3.

The results show that weight loss and corrosion rate values decreases from uninhibited to inhibited solution at all temperature. The decrease is payable to the inhibitive effect of the plant extract and this effects increased with increase in the concentration of the plant extract. Inspection of Fig. 3 revealed that inhibition efficiency increases with increase in the concentration of the methanolic extract and increases with increase in temperature.

This could be attributed that the phytochemical components present in the plant extract are adsorbed on the mild steel-solution interface [6] Inhibition efficiency and corrosion rate of mild steel in various concentration of methanolic extract with temperature are summarized in Table 1.

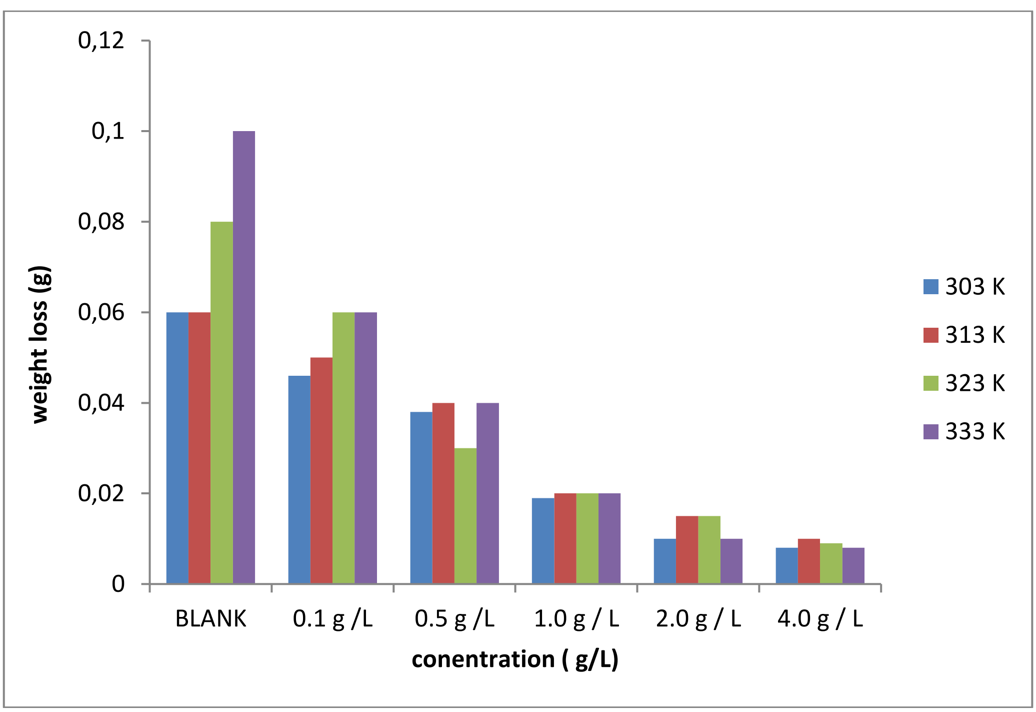

Fig. 1. Variation of weight loss of Mild steel in 2 M HCl solution as function of as function of concentration in presence of methanolic of *Erigeron floribundus* extract

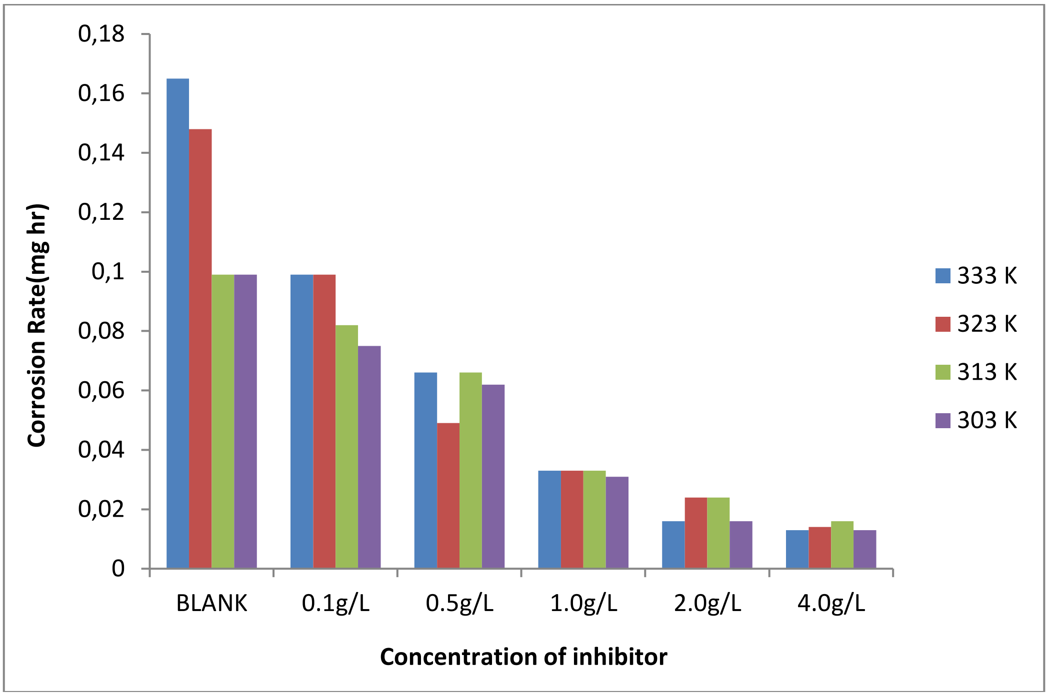

Fig. 2. Variation of corrosion rate of Mild steel in 2 M HCl solution as function of as function of concentration in presence of methanolic of *Erigeron floribundus* extract

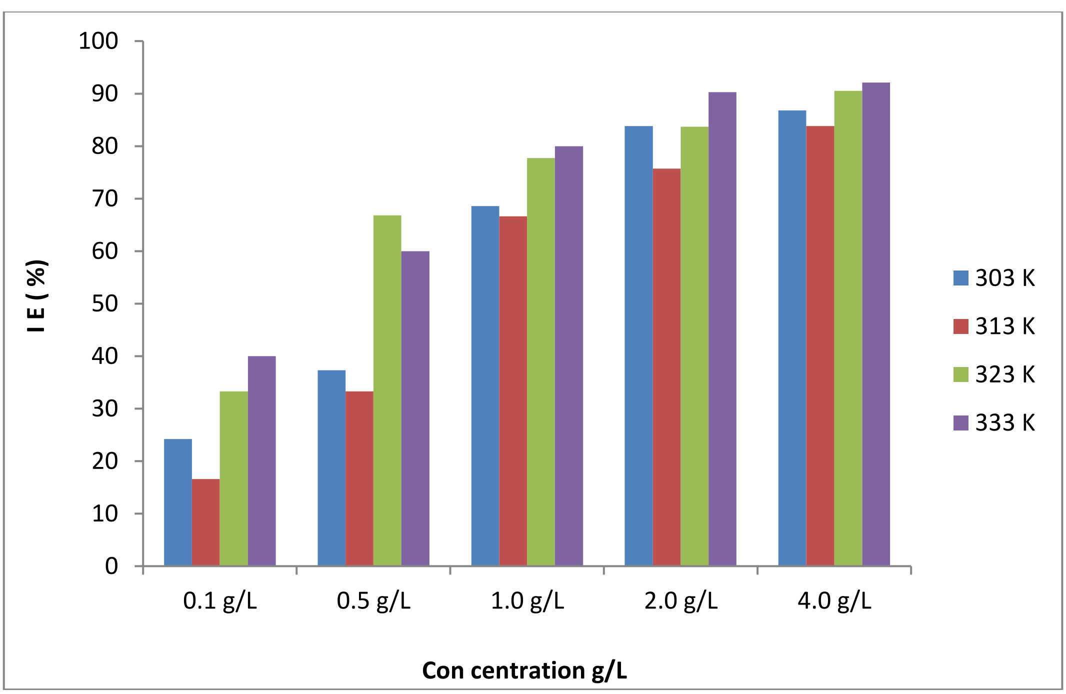

Fig. 3. Variation of inhibition efficiency of Mild steel in 2 M HCl solution as function of as function of concentration in presence of methanolic of *Erigeron floribundus* extract

Table 1. Effect of various temperature on mild steel corrosion in 2 M HCl solution containing various concentration of methanolic extract of *Erigeron floribundus.*

	303 k		313 K		323 K		333 K	
Con (g/L)	IE %	CR(mg/hr)	IE%	CR(mg/hr)	IE%	CR(mg/hr)	IE%	CR(mg/hr)
BLANK		0.099		0.099		0.148		0.165
0.1g/L	24.2	0.075	16.6	0.082	33.3	0.099	40.0	0.099
0.5g/L	37.3	0.062	33.3	0.066	66.8	0.049	60.0	0.066
1.0g/L	68.6	0.031	66.6	0.033	77.7	0.033	80.0	0.033
2.0g/L	83.8	0.016	75.7	0.024	83.7	0.024	90.3	0.016
4.0g/L	86.8	0.013	83.8	0.016	90.5	0.014	92.1	0.013

3. 2. Kinetics and thermodynamic of the corrosion inhibition of mild steel in 2 M HCl solution

The corrosion rate of most reactions increases as temperature increased, like the corrosion rate displayed in Table 1. It is found experimentally that a plot of In k against 1/T gives a straight line. This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the expression as equ. 3

$$\text{In } k = \text{In } A - \frac{Ea}{RT} \qquad 3$$

where is the pre exponential factor, Ea is the activation energy, collectively this two quantities are called Arrhenius parameters while R is gas constant, T is absolute temperature, k represent the rate constant or corrosion rate [17].

The Arrhenius plot obtained from equ.3 gave a straight line graph as shown in Fig. 4 with the slope of -Ea / 2.303 R. Analysis of temperature dependence of inhibition efficiency as well as comparison of the corrosion activation energies in absence and presence of inhibitor give 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, whereas 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 recognized as physical adsorption mechanism [6,11]. The inhibition efficiency with temperature obtained in Table 1 and Fig. 3 suggests chemisorption of the phytochemical constituents of the plant extract on the surface of the metal. In order to confirm this, corrosion activation energies, E_a for the mild steel dissolution in 2 M HCl solution in the absence and presence of the methanolic extract were obtained from the plot of In CR versus 1/T and are listed in Table 2. In the corrosion of mild steel in 2 M HCl solution weight at time after post treatment of coupons is chosen as w_f, when Inw_f /w_o was plotted against time in hours, a linear variation was observed, which confirms a first order reaction kinetics with respect to mild steel in 2 M HCl solution, formulated as

$$\text{In}\,\frac{wf}{wo} = -\,kt \qquad 4$$

where w_o is the initial weight before immersion, k is the rate constant and t is time. The values of the rate constants obtained from the slopes of the plot in Fig. 5 are obtainable in Table 2.

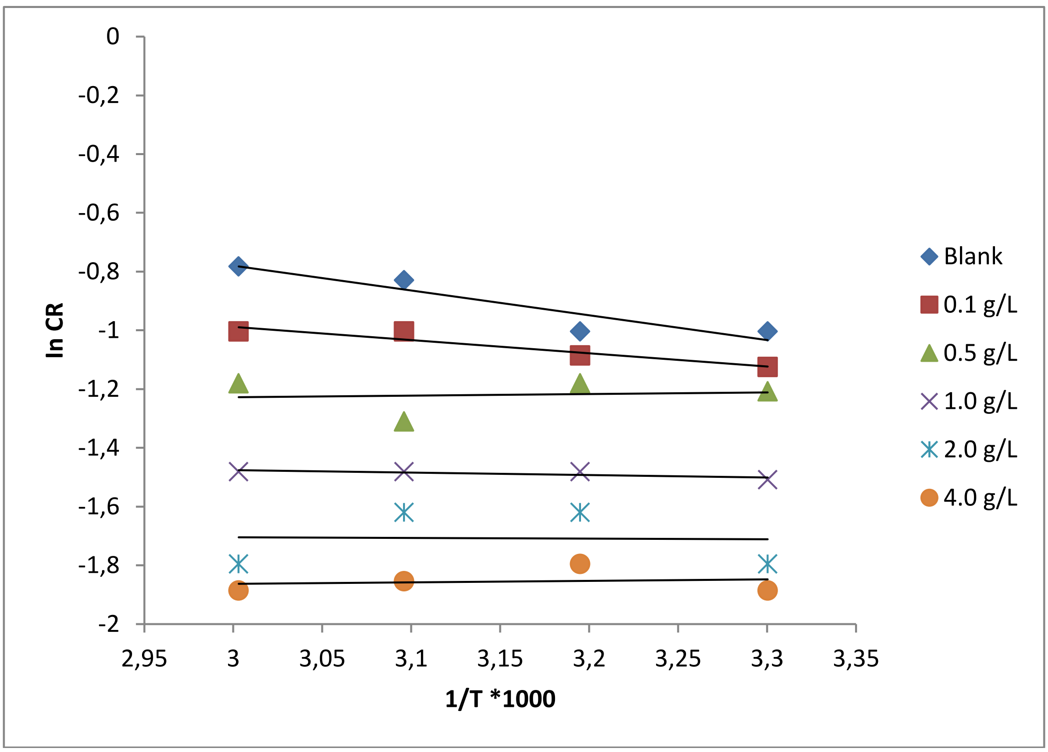

Fig. 4. Arrhenius plot for the mild steel in 2 M HCl solution in different concentration of methanolic extract of *Erigeron floribundus.*

Table 2. Calculated values of activation energy, enthalpy, entropy, rate constant and half life for mild steel coupon in 2 M HCl solution containing methanolic extract of *Erigeron floribundus.*

Con (g/L)	Ea KJ/mol	ΔH KJ/mol	ΔS KJ/mol	Rate Con.	Half Life	R^2
BLANK	16.16	13.51	-22.67	4.12	0.422	0.999
0.1g/L	8.59	59.54	-49.3	3.04	0.495	0.999

0.5g/L	10.33	-36.76	-82.84	2.20	0.552	0.998
1.0g/L	15.89	-10.33	-79.65	1.58	0.625	0.999
2.0g/L	4.21	-22.01	-87.55	1.32	0.681	0.999
4.0g/L	9.57	-16.84	-94.79	0.57	2.722	1.000

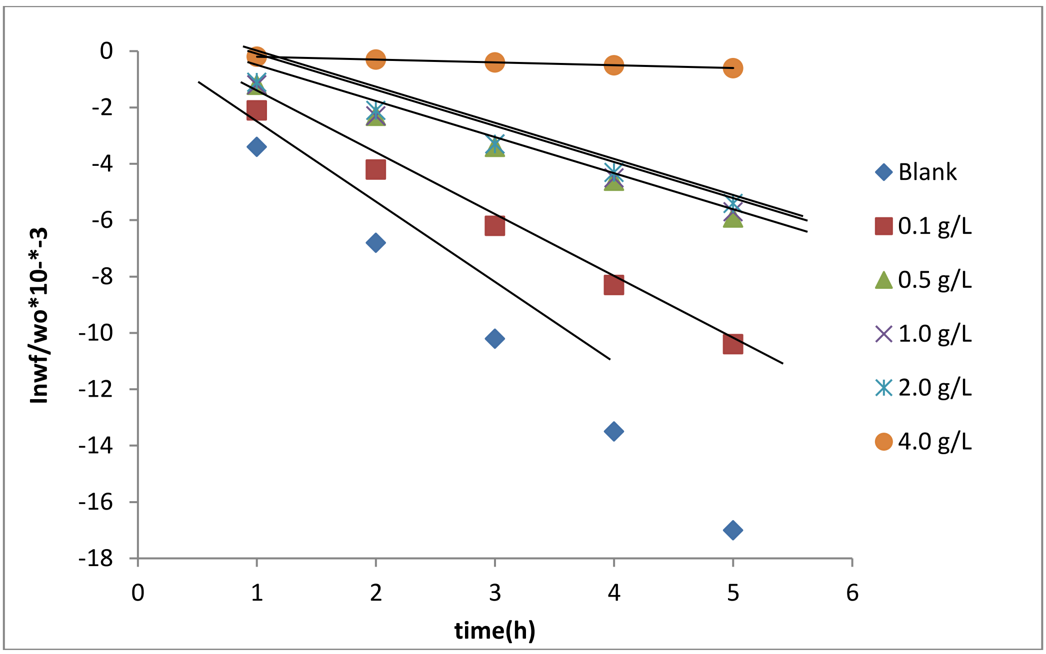

Fig. 5. Plot of In $\frac{wf}{wo}$ against time for mild steel coupons in 2 M HCl solution containing the concentration of methanolic extract of *Erigeron floribundus*.

The results obtained reveal that the rate constant decreases with increase in concentaration of methanolic extract of *Erigeron floribundus*. From the rate constant values, the half life values, $t_{1/2}$ of the metal in the test solutions were calculated from the equation:

$$t_{1/2} = \frac{0.693}{k} \qquad 5$$

and the deduced data are also listed in Table 2. The half life values where observed to increase with increase in concentration of the methanolic extract of *Erigeron floribundus*, indicating decrease in the dissolution rate of the metal in the solution with increase in concentration of the inhibitor.

The transition state equation was used to calculated some thermodynamic parameters (ΔH_{ads} and ΔS_{ads}) for the adsorption of methanolic extract of *Erigeron floribundus* on the mild steel surface.

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \qquad 6$$

where CR is the corrosion rate for mild steel in 2 M HCl solution, R is gas constant, T is the temperature, N is the Avogadro's number, h is the Planck constant., ΔS_{ads} is the entropy of the adsorption and ΔH_{ads} is the enthalpy of adsorption of the inhibitor on mild steel surface. From the logarithm of both sides of equ. 6, equ. 7 was obtained,

$$\text{Log (CR/T)} = \log R/Nh + \Delta S_{ads}/ 2.303R - \Delta H_{ads}/2.303\ RT \qquad 7$$

The plot of log (CR/T) against 1/T for methanolic extract of *Erigeron floribundus* were linear, the slopes and intercept of the transition state plot (Fig. 6) are equal to $-\Delta H_{ads}$ / 2.303R and (log R/Nh + ΔS_{ads}/ 2.303R), respectively. The value of ΔH_{ads} calculated from the slope of the plot were positive in blank and 0.1 g /L and negative in 0.5, 1.0, 2.0 g/L and 4.0 g/L, ΔH_{ads} values of adsorption of methanolic extract of *Erigeron floribundus* on mild steel surface exhibited both endothermic and exothermic reaction respectively. On the other hand the values of ΔS_{ads} calculated from the intercept of the transition state plot are negative. This show that there is a increasing in degree of disorderliness, indicated that there is a bigger association of the inhibitor's molecules rather than dissociation [2, 3].

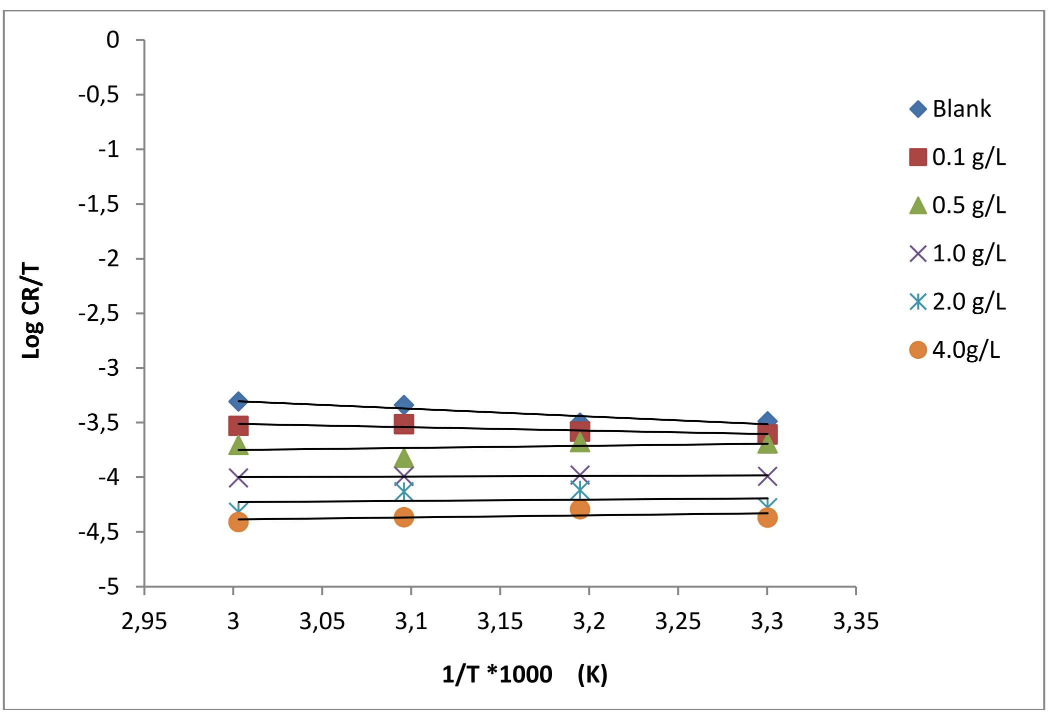

Fig. 6. Variation of log (CR/T) with 1/T for the inhibition of mild steel corrosion in 2 M HCl solution by methanolic extract of *Erigeron floribundus*

We observed a progressive raise in the thermodynamic parameters (ΔH_{ads} and ΔS_{ads}) presented in Table 2. with increasing in the concentration of methanolic extract of *Erigeron* *floribundus* which confirms that methanolic extract of *Erigeron floribundus* is adsorption inhibitors for the corrosion of mild steel in 2 M HCl solution and explain.

3. 3. Adsorption behaviour

The experimental inhibition of the corrosion of mild steel in 2 M HCl solution increases with increase in the concentration of the extract this can be explained by the adsorption of the constituent of the extract on the metal surface. From a hypothetical point of view, the inhibition action of organic molecules has been regarded as a simple substitution process, in which an inhibitor molecule in aqueous phase substitution any number of water molecules adsorbed on the metal surface [7]

$$Inh + yH_2O \leftrightarrow Inh_{(ads)} + yH_2O_{(aq)} \qquad 8$$

The inhibitor molecules may then mingle with Fe^{2+} ions on the metal surface, forming metal-inhibitor complex. The resulting complex, depending on the relative solubility could either inhibit or catalyse further metal dissolution. Methanolic extract of the plant are viewed as an incredible rich source of naturally synthesized chemical compounds. These large numbers of different chemical components may form adsorbed intermediates (organic-metallic complexes) [7]. Most researcher claim that particular compound in plant extract as solely responsible for the inhibition ability. In real sense is not true, since most plant extract 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 Methanolic extract of the plant [4, 7].

Like most medicinal plants, *Erigeron floribundus* is compose of numerous natural occurring compounds, some of this compound have been isolated and characterized from the plant. This include: alkaloid, phenol, triterpenes, sterol, flavonoids, cardiac glycosides and tannins [5, 6]. Most of this compounds have complex molecular structures, large molecular weight and significant number of oxygen, sulphur and nitrogen atoms integrated in the structure. These compounds can adsorb on the metal surface through the lone pairs of the electrons present on their oxygen, sulphur and nitrogen atom. 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 atmosphere. As a result, the corrosion rate of the metal decreased [12, 13].

The experimental data were applied to different adsorption isotherm model. It was found that the experimental data fitted the Langmuir adsorption isotherm (Fig. 7) which may be formulated as [9, 10]

$$\frac{Cinh}{\theta} = \frac{1}{bads} + C_{inh} \qquad 9$$

where θ is the surface coverage , C_{inh} is the concentration of the inhibitor and b_{ads} is the adsorption-desorption equilibrium constant. adsorption-desorption equilibrium constant was obtained from the intercept of the Langmuir adsorption isotherm plots and linear regression coefficient were used to determined the best fit. The result obtained for ΔG_{ads} and b_{ads} are shown in Table 3.

Table 3. Calculated values of equilibrium constant and free energy of the adsorption at different temperature.

Tem	b_{ads}	ΔG_{ads} KJ/mol	R^2
313	0.038	-39.72	0.998
333	0.036	-40.03	0.999

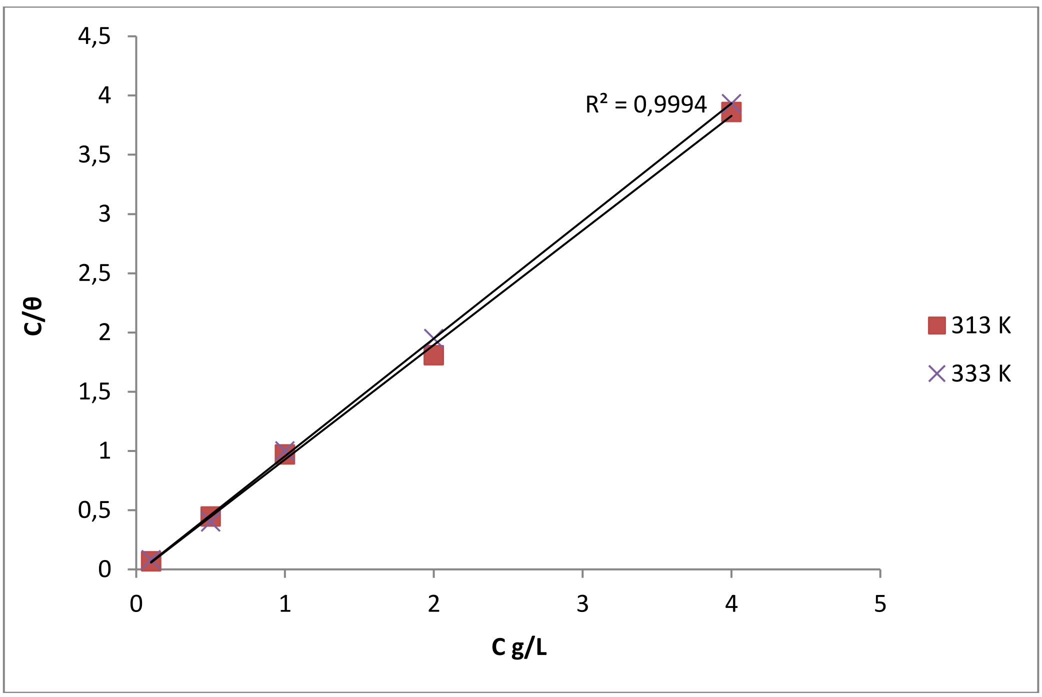

Fig. 7. Langmuir adsorption isotherm of methanolic extract of *Erigeron floribundus.*

The value obtained for ΔG^o_{ads} were negative indicating that the adsorption process is spontaneous. Generally, the values of ΔG^o_{ads} less than -20 KJ mol^{-1} signify physisorption and values more negative than -40 KJ mol^{-1} signifying chemisorptions [7, 9, 10]. The results listed in Table 3 show that ΔG^o_{ads} values are more negative than -20 KJ mol^{-1}. This revealed that the adsorption of the inhibitor on the metal surface is spontaneous and confirms chemisorptions mechanism.

4. CONCLUSIONS

The results presented in this paper show that the methanolic extract from *Erigeron floribundus* inhibit the corrosion of mild steel in 2 M HCl solution to reasonable extent. The inhibition efficiency of the methanolic extract increased with increasing concentration of the inhibitor with temperature. Inhibition process followed first order reaction kinetic. It is observed that the positive and negative values obtained for enthalpy show a mixed reaction process such as endothermic and exothermic reactions. Also the value of entropy is negative indicated association mechanism and negative value of the free energy revealed that the reaction process is spontaneous. Adsorption isotherm mechanism followed Langmuir adsorption.

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