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Green corrosion inhibitor for mild steel in 2 M HCl solution: Flavonoid extract of *Erigeron floribundus*

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ABSTRACT

The potential of flavonoid extract of *Erigeron floribundus* as green inhibitor for the corrosion of mild steel in 2 M HCl solution was studied using gasometric method. The results obtained, indicated that the extract is an adsorption inhibitor for the corrosion of mild steel. The inhibition efficiency of the inhibitor was found to increased with increase in concentration of the inhibitor. From the observed trend for the variation of inhibition efficiency with temperature and the range of value obtained from activation energy (16.16-3.02 $KJmol^{-1}$), enthalpy (13.5-38.84 $KJmol^{-1}$), entropy (-22.67 to 88.44 $KJmol^{-1}$) and free energy (-4.23 to -2.61 $KJmol^{-1}$), a chemical and physical adsorption mechanism is propose for the adsorption of the inhibitor on the mild steel surface. In addition, the adsorption is endothermic, spontaneous and is best described by Langmuir adsorption isotherm.

***Keywords*:** Green inhibitor, Flavonoid, corrosion, mild steel, *Erigeron floribundus*

1. INTRODUCTION

Corrosion is the physicochemical interaction between a metal and its environment, which results in changes in the metal's properties and which may lead to significant functional impairment of the metal and the environment. We only talk about corrosion when

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there is a change in the metal's properties which may lead to an undesirable outcome. This can range simply from visual impairment to complete failure of technical systems that causes great economic damage and even present a hazard to people. The metals commonly used in industries include carbon steel, stainless steel, mild steel, zinc, copper and aluminum etc. Acid solution are often used in drilling operations in oil and gas exploration as well for cleaning and descaling and pickling of steel structure which are normally accompanied by dissolution of the metal. Therefore it is very important to add corrosion inhibitors to decrease the dissolution rate in such situations. Organic heterogeneous compounds containing nitrogen, oxygen, sulphur and aromatic ring in their molecular structures have been reported to be efficient corrosion inhibitors [1-2]. The used of natural products of plant origin as corrosion inhibitors has been widely reported by several authors [3-9]. Such interest derives from their inexpensive and eco-friendly nature and easy availability. *Erigeron floribundus* is known as a natural weed widely distributed throughout urban, rural area of cross river state, Nigeria. The leaves of *Erigeron floribundus* are used for the treatment of skin disorders [10]. Studied have been carried out to identified more useful application of certain active compounds such as alkaloid, phenol, Triterpenes, Tannins and Flavonoids [11]. The methanolic extracts of leaves of *Erigeron floribundus* have been reported to effectively inhibit the acidic corrosion of metals (Abeng *et al*., 2017). However the corrosion inhibition effectiveness of flavonoid extracts of *Erigeron floribundus* is yet to be reported. The current study investigate the inhibitive effects of flavonoid extract on mild steel corrosion in HCl solution using gasometric technique.

2. EXPERIMENTAL METHODS

2. 1. Material

The mild steel specimens used in the study have a composition of; 0.6 % Mn, 0.36 % P, 0.15 % C, 0.07 % S and 98.79 % Fe. The specimens used were obtained from physics department workshop, university of Calabar, Nigeria. The mild steel was mechanically press cut to coupons of dimension 4.00 × 1.20 × 0.08 cm with surface area $20.20 cm^2$ and were mechanically polished with series of emery paper of variable grades starting with the most coarse and proceeding in stepts to the finest (600) grade. The polished coupons were degreased with ethanol, dried with acetone and weighed. All the experimental solutions were prepared with distilled water. The chemicals used were of Analar grade and all weighing were done with AEADAM PGW 253 electronic digital balance.

2. 2. Extraction of flavonoid from *Erigeron floribundus*

The source and the processing of the plant leaves were reported in [1]. but during the extraction of flavonoid; exactly 7g of the dried powdered sample was weighed into a beaker and extracted with 70 cm^3 of 80 % methanol at room temperature for one hour. The solution was filtered through filter paper. The filterate was evaporated to dryness over water bath. The sample of the dried extract was taken for phytochemical screening and confirmed with greater concentration of flavonoid. Exactly 5g of flavonoid extract of *Erigeron floribundus* was digested in 250 ml of 2 M HCl solution [12-21]. The resultant solution was kept for 24 hours and filtered. The stock solution (25 g/L) obtained was used in preparing test solution of different concentration of the inhibitor: 0.1, 0.5, 1.0, 2.0 and 4.0 g/L. The test solution of the inhibitor were prepared by serial dilution of the stock solution

2. 3. Gasometric method

Gasometric technique is based on the principle that corrosion reactions in aqueous media is characterized by the evolution of gas resulting from the cathodic reactions of the corrosion process, which is proportional to the rate of corrosion [5]. The experiment were conducted at 303, 313, 323 and 333 K. The rate of evolution of the gas (R_H) is determined from the slope of the graph of volume of gas evolved (V) versus Time (t) and the degree of surface coverage (θ) and hence inhibition efficiency IE (%) was determined using equation 1 and 2 respectively.

$$\theta = 1 - RHin/_{RHo} \quad (1)$$

$$IE\,(\%) = 1 - RHin/_{RHo} \times 100 \quad (2)$$

where: R_{Ho} and R_{Hin} are the rates of hydrogen evolution in the absence and presence of the inhibiting molecules.

3. RESULTS AND DISCUSSION

3. 1. Gasometric measurement

Table 1. Values of inhibition efficiency (IE %) and corrosion rate (CR) at 303, 313, 323 and 333 K

	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	9.0	0.09	34.4	0.097	40.0	0.099
0.5g/L	47.4	0.052	45.4	0.054	58.1	0.062	60.0	0.066
1.0g/L	70.7	0.029	68.6	0.031	79.0	0.031	80.0	0.033
2.0g/L	93.1	0.006	90.3	0.008	94.4	0.0082	92.0	0.013
4.0g/L	93.9	0.006	91.9	0.008	96.6	0.0049	95.0	0.008

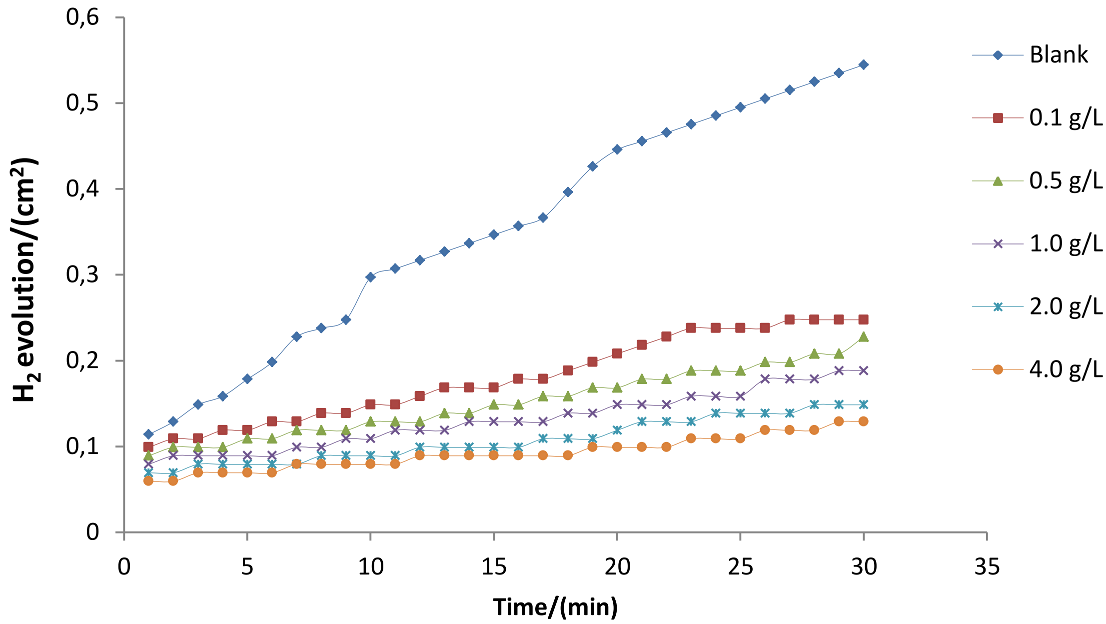

Figure 1. Variation of volume of hydrogen gas (V_H) with time for mild steel coupons of cross sectional area of (20.20 cm^2) in 2 M HCl solutions containing the various concentration of flavonoid extract of *Erigeron floribundus* at 303 K

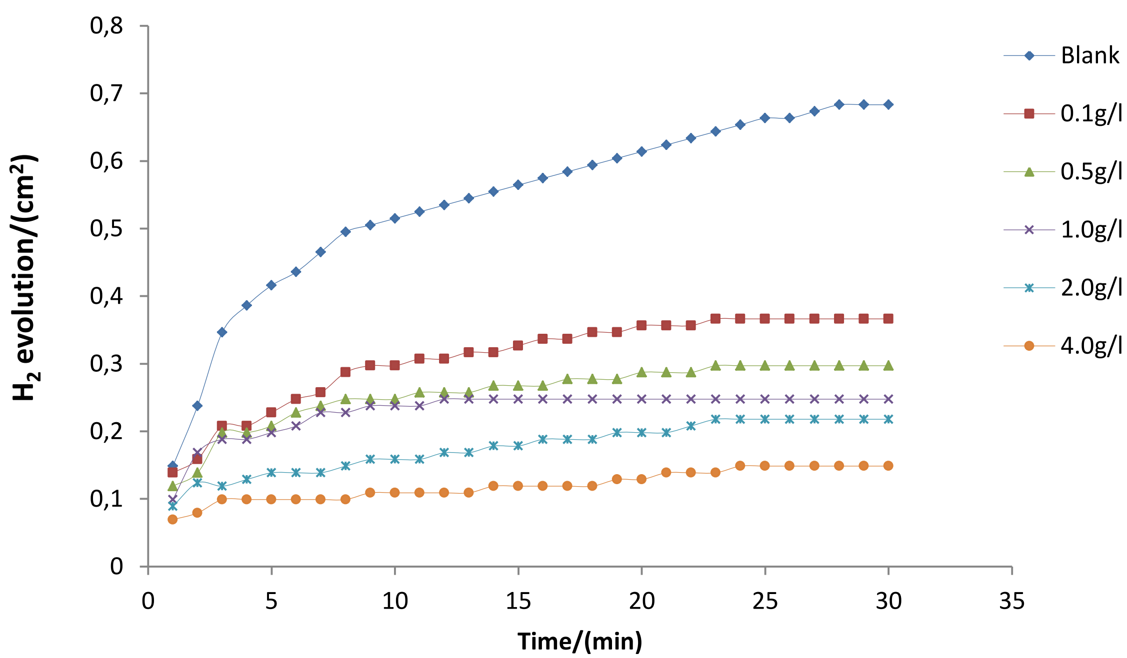

Figure 2. Variation of volume of hydrogen gas (V_H) with time for mild steel coupons of cross sectional area of (20.20 cm^2) in 2 M HCl solutions containing the various concentration flavonoid extract of *Erigeron floribundus* at 313 K.

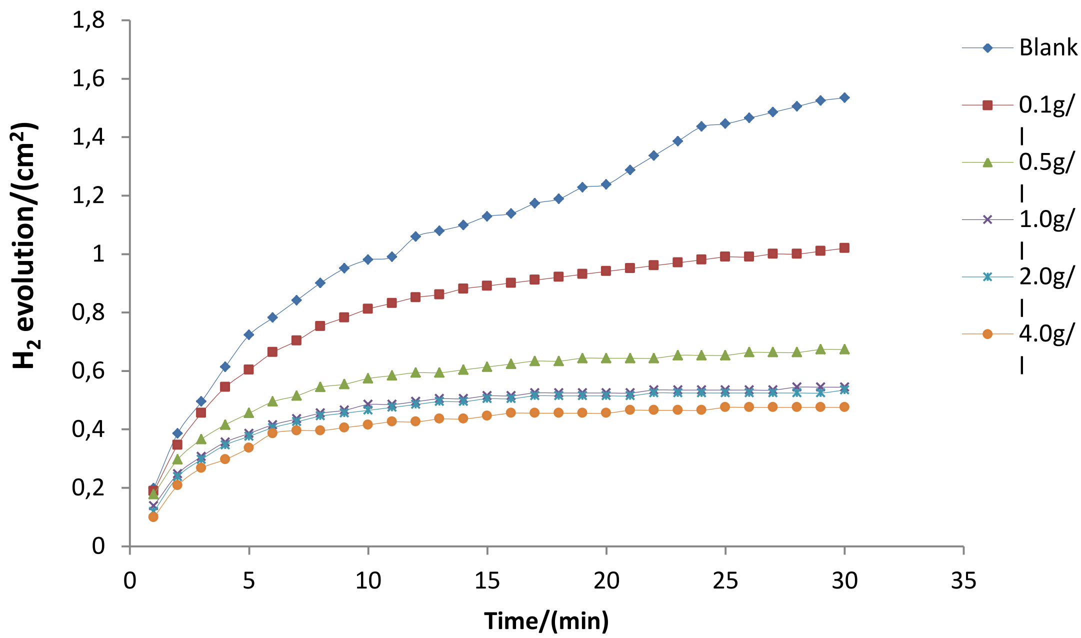

Figure 3. Variation of volume of hydrogen gas (V_H) with time for mild steel coupons of cross sectional area of (20.20 cm^2) in 2 M HCl solutions containing the various concentration flavonoid extract of *Erigeron floribundus* at 323 K.

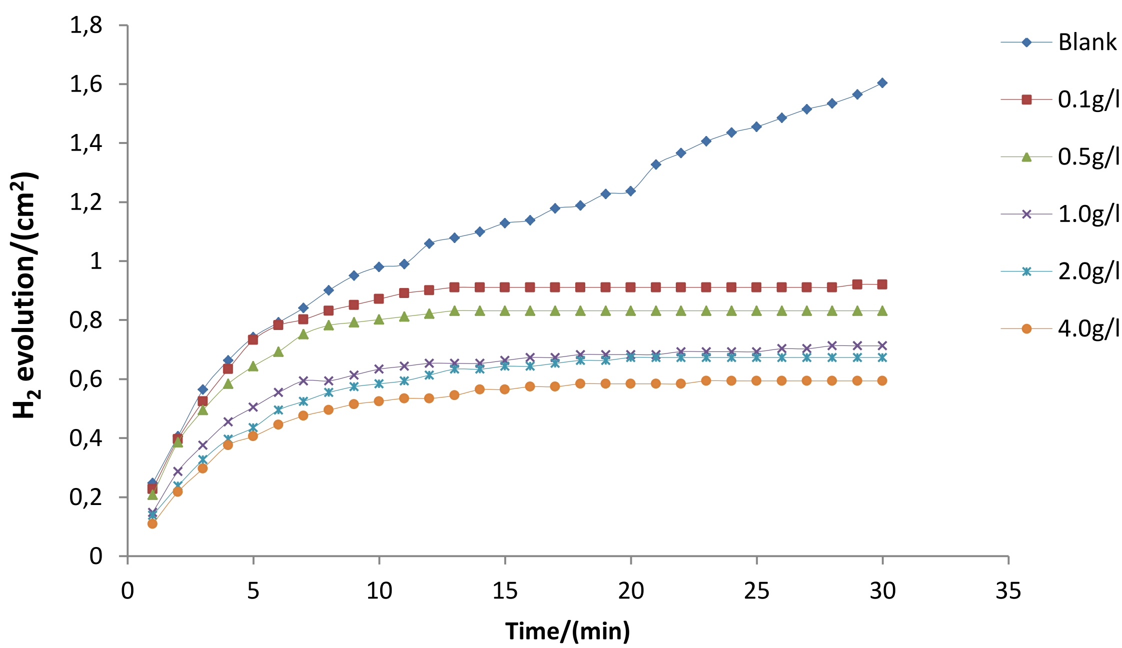

Figure 4. Variation of volume of hydrogen gas (V_H) with time for mild steel coupons of cross sectional area of (20.20 cm^2) in 2 M HCl solutions containing the various concentration flavonoid extract of *Erigeron floribundus at 333 K.*

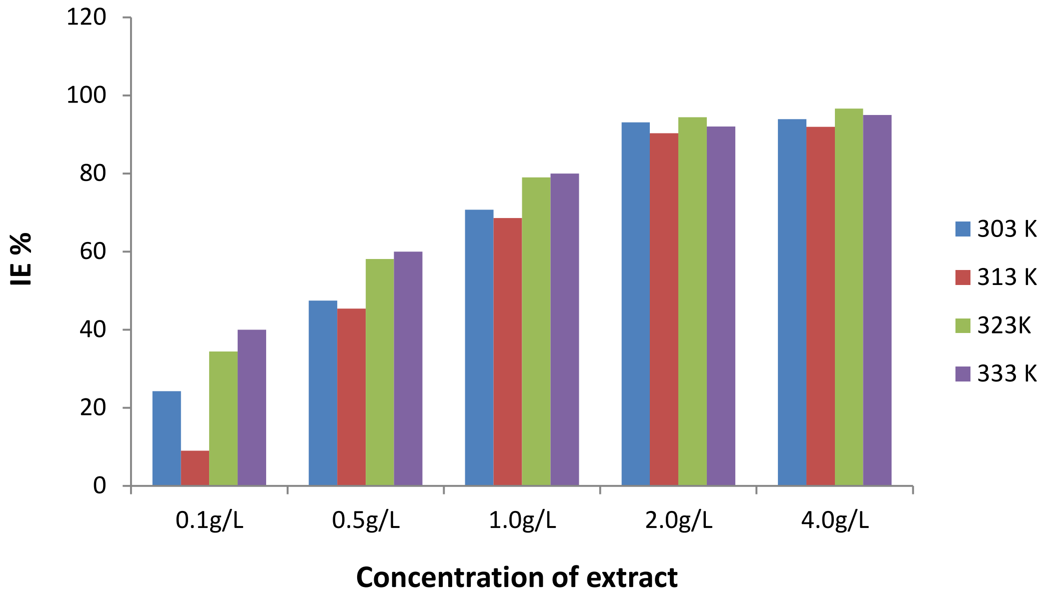

Figure 5. Variation of inhibition efficiency with flavonoid extract concentration for mild steel in 2 M HCl solutions at different temperature .

Figure 1-4 shows the representation of hydrogen evolution plots for mild steel in uninhibited and inhibited solution at 303, 313, 323 and 333 K. The rate of hydrogen evolution, obtained from the slope of the graphs is shown in Table 1. It is observed that the presence of the flavonoid decreased the volume of hydrogen evolved as well as the rate of hydrogen evolution and consequently the corrosion rate of the mild steel in 2 M HCl solution compared to the blank. Inspection of Table 1 also show that the inhibition efficiency increases with increase in the concentration of the extract and increases with increase in temperature. This imply that the flavonoid component of *Erigeron floribundus* (EF) are adsorbed on the mild steel-solution interface. The trend in temperature suggests chemical adsorption of the inhibiting components of the (EF). From the rate of hydrogen evolution, the inhibition efficiency was determined using equation 2. The results obtained are shown in Figure 5

3. 2. Effect of temperature

The effect of temperature on the inhibition of Flavonoid fraction of *Erigeron floribundus* was investigated, the Arrhenius-type relationship between the corrosion rate (K) of mild steel in acidic media and temperature (T) as often expressed by the Arrhenius equation used to determine the activation energies (E_a)

$$K = A \exp(-E_a/RT) \qquad (3)$$

where: A is the pre-exponential factor and R is the universal gas constant. The variation of logarithm of corrosion rate with the reciprocal of absolute temperature is shown in Figure 6.

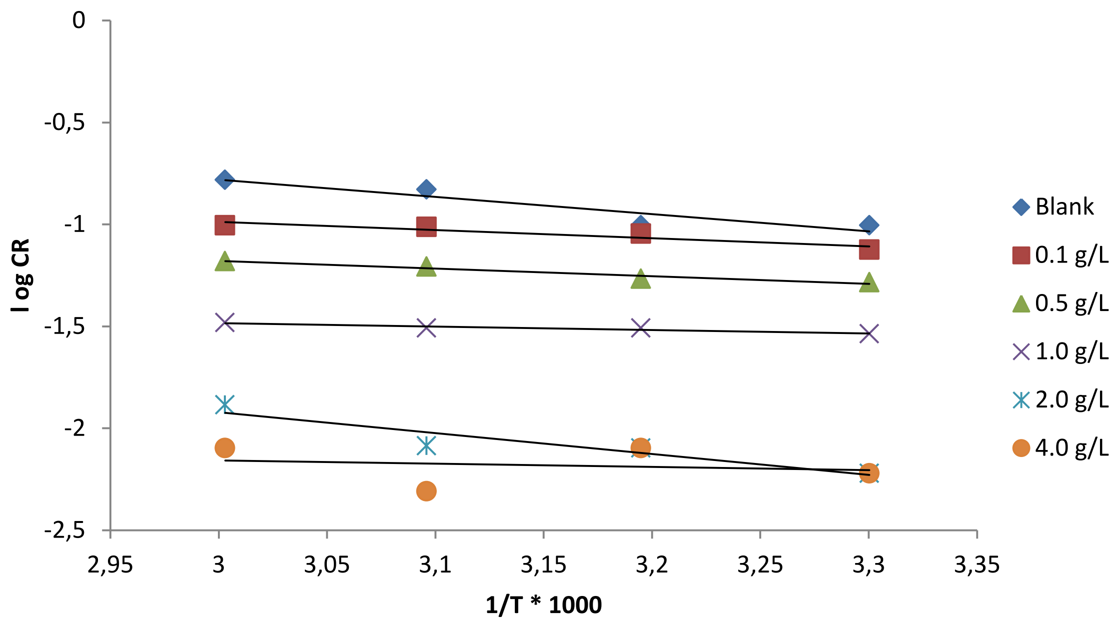

Figure 6. Arrhenius plots for mild steel corrosion in 2 M HCl solution in the absence and presence of different concentration of Flavonoid extract of *Erigeron floribundus*

The calculated values of Ea are given in Table 2. Addition of the extract can be seen to decrease E_a for the corrosion reaction, implying that the extracts would be more effective at higher temperature which correspond to the observed inhibition efficiency with temperature. The trend in activation energy (E_a) proposed chemical adsorption mechanism for the adsorption of the extract.

Table 2. Calculated values of activation energy, activation enthalpy and activation entropy for mild steel in 2 M HCl containing Flavonoid extract of *Erigeron floribundus.*

Con (g/L)	Ea KJ/mol	ΔH^* KJ/mol	ΔS^* KJ/mol
BLANK	16.16	13.51	-22.67
0.1 g/L	7.69	50.56	-52.02
0.5 g/L	7.14	45.01	-57.36
1.0 g/L	3.23	61.34	-74.86
2.0 g/L	3.10	16.92	-34.29
4.0 g/L	3.02	38.84	-88.44

3. 3. Thermodynamic and adsorption parameters

Some other activation parameters such as the enthalpy change of activation (ΔH^*) and entropy change of activation (ΔS^*) were obtained from Erying transition state equation [1].

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S*}{R}\right) \exp\left(-\frac{\Delta H*}{RT}\right) \qquad (4)$$

where: R is molar gas constant; T is absolute temperature, N is Avogadro's constant, h is planck's constant.

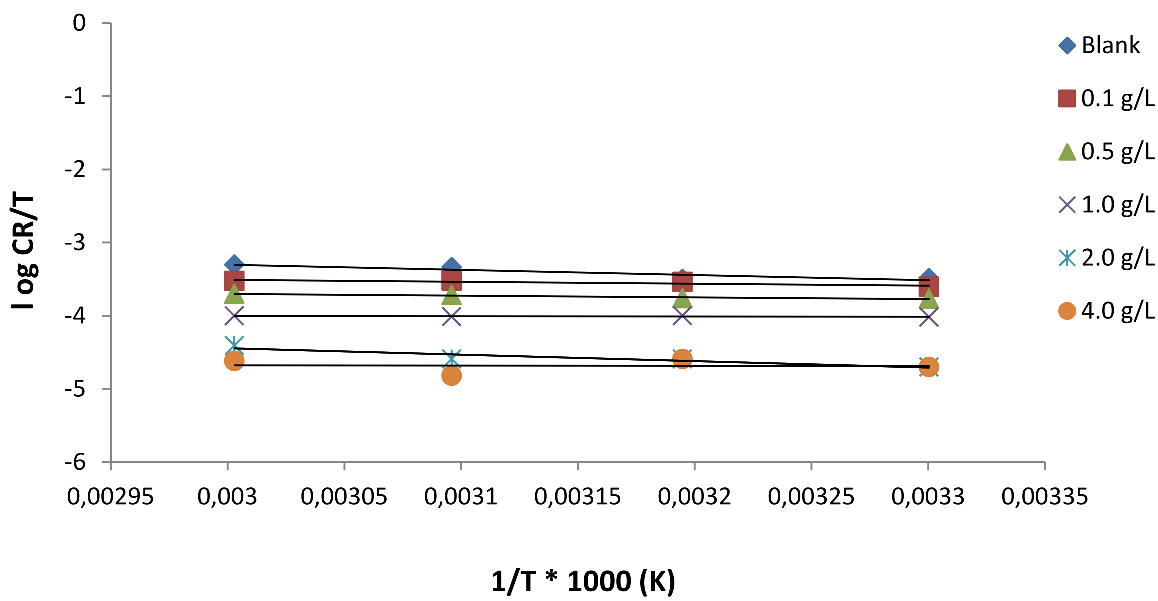

Figure 7. Erying plots for mild steel corrosion in 2 M HCl without and with Flavonoid extract from the EF

Straight lines were obtained from the Eying plots (Figure 7). The calculated values of ΔH^* and ΔS^* obtained from these plots are also given in Table 2. The positive values of ΔH^* both in absence and presence of the extract reveal endothermic reaction. Large and negative values of entropies imply that the activation complex in the rate determining step represents and association rather than a dissociation step, meaning that a decrease in disordering takes place on from reactants to the activated complex. The adsorption behaviour of the plant extract was also studied by fitting data obtained for degree of surface coverage to different adsorption isotherms, the test reveal that adsorption of Flavonoid extract of EF. On mild steel surface is best described by Langmuir adsorption isotherm. The expression of the Langmuir adsorption model can be written as follows:

$$\frac{C}{\theta} = \frac{1}{Kads} + C \qquad (5)$$

where: C is the concentration of the inhibitor, θ is degree of surface coverage of the inhibitor, and K_{ads} is the equilibrium constant of the adsorption using equation 5. The plots of C/θ versus C (Figure 8) was found to be linear, indicating the principle of Langmuir model to the adsorption of the inhibitor, values of Langmuir adsorption parameters deduced from the intercept of the plots are listed in Table 3 in all the temperature studied. From the results obtained, the R^2 values are very closed to unity, indicating that there is a strong adherence of the inhibitor's adsorption of the assumption establishing Langmuir isotherm. The equilibrium constant of the adsorption of the inhibitor is related to the free energy of adsorption (ΔG_{ads}) according the equation 6

$$\Delta Gads = -2.303\, RT\, Log\; 55.5 Kads \qquad (6)$$

where: R is the gas constant, T is the absolute temperature, K_{ads} is the equilibrium constant of the adsorption, 55.5 is the molar concentration of water in solution. The values of K_{ads} obtained from the intercept of Figure 8. The free energy are negatively less than -40 KJmol^{-1} require for chemical adsorption, therefore the adsorption of the extract on mild steel surface is spontaneous and support physical adsorption mechanism [13, 14].

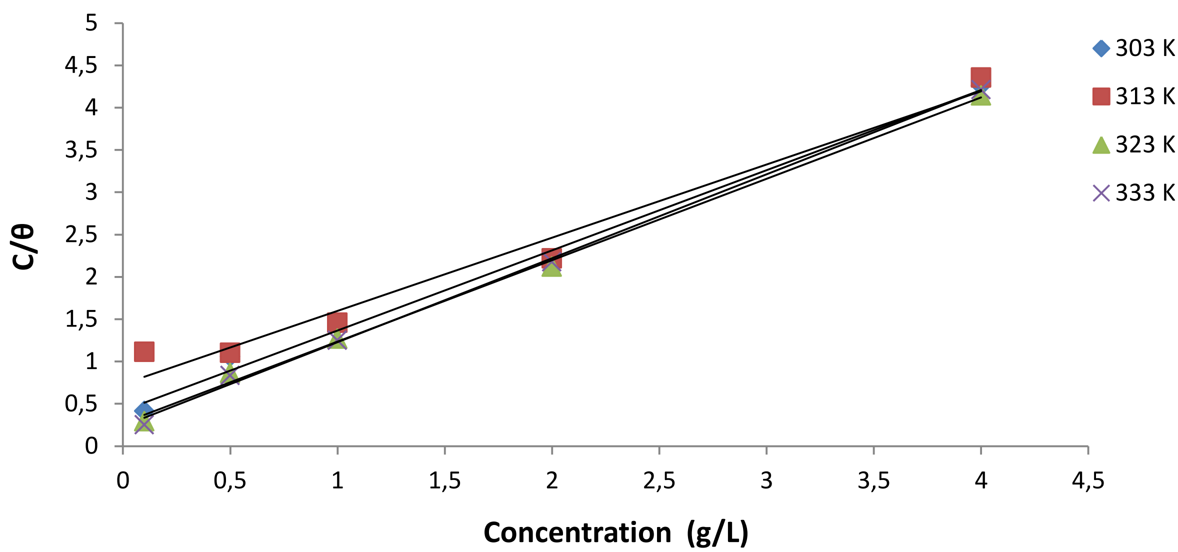

Figure 8. Langmuir isotherm for the adsorption of Flavonoid fraction of the *Erigeron floribundus* on the mild steel surface.

Table 3. Langmuir adsorption parameters for the adsorption of Flavonoid fraction of the *Erigeron floribundus* on the mild sreel surface.

Temp.	Equilibrium constant (K_{ads})	ΔG Kjmol^{-1}	Cofficient of Determination (R^2)
303 K	0.418	-4.23	0.992

313 K	0.732	-7.65	0.973
323 K	0.273	-2.94	0.997
333 K	0.235	-2.61	0.997

4. CONCLUSION

From the study we conclude that Flavonoid extract of the *Erigeron Floribundus* is an adsorption inhibitor for the corrosion of mild steel in 2 M HCl solution. The adsorption of the inhibitor is spontaneous and supported a mechanism of physical adsorption and the adsorption obeyed Langmuir isotherm model. The inhibition efficiency of the inhibitor increased with increasing concentration of the inhibitor.

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