Original Research Article

Effect of *Triumfetta rhomboidea* Leaves extract on the Corrosion Resistance of Carbon Steel in Acidic environment

ABSTRACT

The inhibition capability of *Triumfetta rhomboidea* (TR) leaves extract on the corrosion of carbon steel in I M HCl was evaluated using weight loss technique. Scanning electron microscopy (SEM) and analysis were also performed. Results showed that the extract acts as good inhibitor for carbon steel and its efficiency increases with increase in its concentration and exposure time. The SEM observations confirmed the existence of a protective film of inhibitor on carbon steel surface. The inhibiting action of TR extract was attributed to the phytochemical species present in the extract and its adsorption on the carbon steel surface. The adsorption of TR extract on carbon steel surface obeys Langmuir adsorption isotherm with physical adsorption on the metal surface.

Keywords: Triumfetta rhomboidea, Carbon Steel, Weight Loss, Scanning electron microscopy, Adsorption

INTRODUCTION

The use of corrosion inhibitors is one of the most efficient methods of resisting the corrosion of metals from aggressive species. Large numbers of inorganic and organic compounds have been studied to investigate their corrosion inhibition capacity and they have proven to be good corrosion inhibitors for metals [1-4]. The inhibitory mechanism usually proposed is the adsorption of the inhibitor molecules onto the metal surface, creating a barrier between the metal and the electrolyte, blocking active sites and reducing the metal dissolution and/or reduction reactions [5].

Most synthetic corrosion inhibitors are toxic and pose environmental hazards. Their use however has been severely criticized and green corrosion inhibitors are encouraged because they are eco-friendly, non-toxic and inexpensive. Recent researches have shown the corrosion inhibitive effect of some extracts from plants such as *Vernonia amygdalina* [6], *Carica papaya* and *Camellia sinensis* [7], *Annona Muricata. L* [8], *Gundelia tournefortii* [9], *Ocimum sanctum* (Holy Basil) [10] and *Palicourea guianensis* [11], to mention but a few, exhibiting good inhibitor efficiencies on the corrosion of different metals. The activity of corrosion inhibition of plant extracts could be due to the presence of heterocyclic constituents such as, alkaloids, flavonoids, tannins, cellulose and polycyclic compounds. In this study, the inhibitive properties of *Triumfetta rhomboidea* leaves extract on the corrosion of carbon steel in I M HCl have been investigated using weight loss and scanning electron microscopy (SEM) analysis.

2. MATERIALS AND METHODS

2.1. Material Preparation

Carbon steel material of composition C = 0.015%; Si = 0.027%; Mn = 0.250%; S = 0.027%; P = 0.010%; Ni = 0.014%; Cr = 0.016% and the balance Fe were cut into coupons of dimension 4 cm x 2 cm and used for this study. The coupons were prepared and cleaned as described elsewhere [12]. The blank corrodent was 1.0 M HCl solution.

The leaves of *Triumfetta rhomboidea* procured from the herbarium of the Department of Botany, University of Port Harcourt, were crushed into small pieces, dried and powdered. Weighed amount of the powdered materials was refluxed for 1 h using doubled distilled water. After cooling, the solutions were filtered and dried in an oven for one night. Stock solution of the inhibitor was prepared by refluxing weighed amounts of the extract for 3 h in 500 mL of 1 M HCl [13]. The solution was cooled, filtered and stored. From the stock solution, inhibitor test solutions were prepared in concentrations of 50, 100, 150, 200, and 300 ppm in 1 M HCl.

2.2. Weight loss measurement

Pre-weighed carbon steel coupons were completely immersed in test solutions containing blank 1 M HCl and various concentration of the inhibitor for 24 hours at 303, 313 and 323K. The weight loss with respect to time was determined by retrieving the coupons from test solutions at the duration of 24 h, cleaned appropriately, dried, and reweighed [14]. The weight loss was taken to be the difference between the weights of the coupons at a given time and its initial weight. The process continued for a period of 120 h. All tests were performed in triplicate to ensure the reproducibility of results, and the mean value of the weight loss reported.

From the weight loss data, the corrosion rate (CR) was determined from the equation below:

$$\mathrm{CR} = \frac{W_1 - W_2}{\mathrm{At}} \qquad (1)$$

Where W_1 and W_2 are the weights of the metal specimen (mg) before and after immersion in the test solutions, A is the total area of the specimens (cm^2) and t is the immersion time (h).

The surface coverage(θ) and inhibition efficiency (%IE) were calculated from the corrosion rate data according to equations 2 and 3, respectively:

$$\theta = \left(1 - \frac{\mathrm{CR_{inh}}}{\mathrm{CR_{blank}}}\right) \qquad (2)$$

$$\%\mathrm{IE} = \left(1 - \frac{\mathrm{CR_{inh}}}{\mathrm{CR_{blank}}}\right) \mathrm{X}\ 100 \qquad (3)$$

Where CR_{blank} and CR_{inh} are the corrosion rates in the absence and presence of the inhibitor respectively

2. 3. Scanning Electron Microscopy

The XL-30FEG Scanning Electron Microscope (SEM) was used to picture the changes of the surface morphology of the metal coupons in the absence and presence of the optimum concentration of *Triumfetta rhomboidea* leaves extract after immersion in the test solution at 303 K. Carbon steel coupons of dimensions 4 cm × 2 cm were prepared as shown in Section 2.1 and immersed for 24 h in the test solutions, in the absence and presence of 300 ppm TR. The coupons were taken out and washed with distilled water, dried in cool air and used for SEM inspection.

3. RESULTS AND DISCUSSION

3.1. Weight loss Measurement

The data obtained from the weight loss measurements were: corrosion rate (CR), surface coverage (θ) and inhibition efficiency (%IE). The measurements were obtained at different temperatures of 303, 313 and 323 K and different immersion time of 24, 48, 72, 96 and 120 hours in the presence of 50, 100, 150, 200, and 300 ppm by weight of TR in 1 M HCl.

3.1.1. Effect of concentration

Figures 1 indicate the variation of corrosion rate for carbon steel with and without different concentrations of the inhibitor in 1 M HCl solution at different temperatures. The figure clearly shows that, corrosion rate decreases significantly as the concentration of the TR increases from 50 ppm to 300 ppm by weight, which indicates the decrease of the carbon steel dissolution in the acidic medium. The decrease in corrosion rate with increase in concentration of TR is due to the fact that the adsorption of inhibitor molecules on the surface of the metal increases the surface coverage of the metal.

The surface coverage and inhibition efficiency calculated for carbon steel from the weight loss study are presented in Table 1. The calculated surface coverage revealed that the increase of the inhibitors concentration from 50 ppm to 300 ppm by weight increased the surface coverage considerably. From the Table, it's also observed that the inhibition efficiency increases with increasing concentration of TR. The maximum inhibition efficiency of 87 % was obtained at 300 ppm of TR at 303 K. Similar results for eco-friendly inhibitors have been reported by several researchers [15-18]. From the result obtained it was seen that the inhibitor was very efficient in preventing carbon steel corrosion in 1 M HCl.

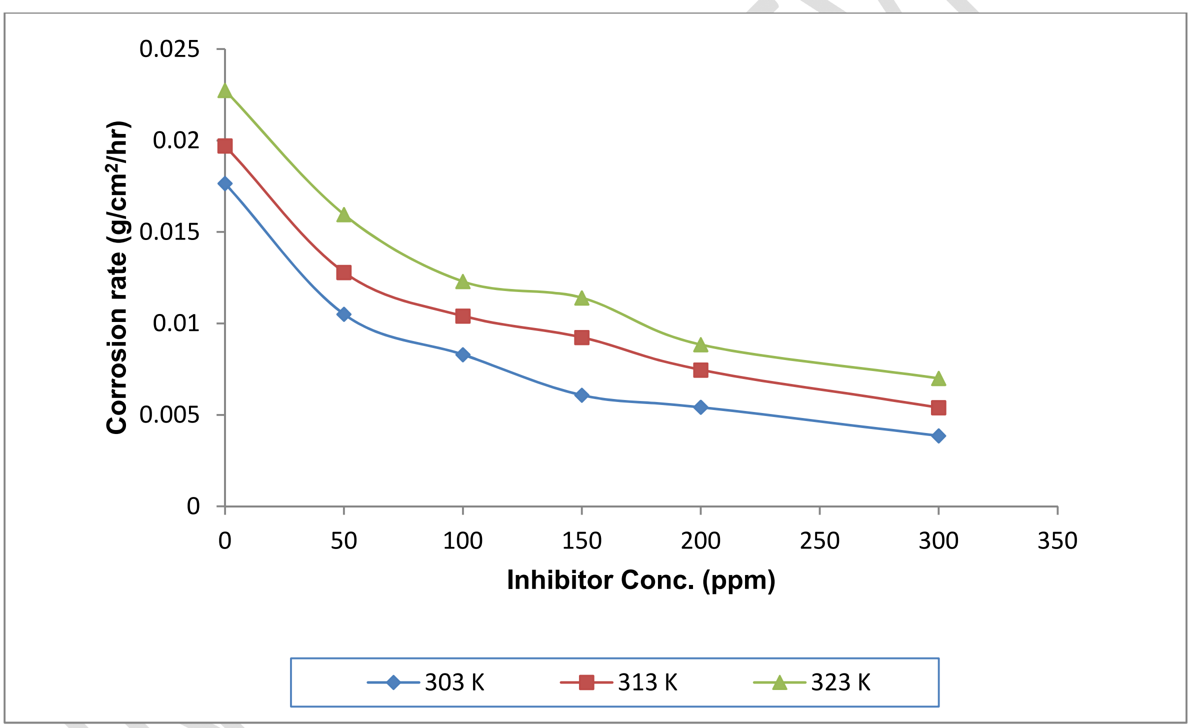

Fig. 1. Variation of corrosion rate for carbon steel with and without different concentrations of *Triumfetta rhomboidea* leaves extract in 1 M HCl solution at different temperatures

Table 1. Surface Coverage (θ) and Inhibition Efficiency (%IE) for carbon steel in 1M HCl solutions containing *Triumfetta rhomboidea* at different temperatures

TR conc. (ppm)	Surface coverage, θ			Inhibition Efficiency, %IE		
	303 K	313 K	323 K	303 K	313 K	323 K
Blank	-	-	-	-	-	-

50	0.68	0.62	0.60	68.2	62.3	59.6
100	0.74	0.69	0.65	73.8	68.9	65.3
150	0.79	0.74	0.71	78.6	74.2	70.9
200	0.83	0.78	0.76	83.1	78.3	76.2
300	0.87	0.83	0.80	87.4	82.5	79.7

3.1.2. Effect of temperature

The effect of temperature on the corrosion inhibition efficiency of *Triumfetta rhomboidea* (TR) in 1M HCl solution was studied by weight loss measurement over temperature range from 303 – 323 K. It is observed from Table 1 that the inhibition efficiency decreases on increasing the temperature of the solution. Increase in the temperature of the solution increases the kinetic energy of the inhibitor and therefore decreases the interaction between the inhibitor and metal surface and thus decreases the inhibition efficiency. Decrease in inhibition efficiency with increase in temperature is suggestive of physical adsorption of TR onto the carbon steel surface [19].

The apparent activation energy E_a for the corrosion of carbon steel samples in 1 M HCl solutions in the absence and presence of TR were calculated from Arrhenius-type equation given as:

$$\mathrm{CR} = A \exp\left(\frac{-E_a}{RT}\right) \qquad (4)$$

Where R is the gas constant, A is the pre-exponential factor, T is absolute temperature. The values of E_a were determined by plotting ln (CR) against 1/T which gives a straight line with a slope permitting the determination of E_a as shown in Figure 2. The values of E_a are given in Table 2. The values of E_a for inhibited solution are higher than that for uninhibited solution. The higher value of E_a in presence of TR suggested that there is a reduction in corrosion rate which indicates that more energy barrier is required for the corrosion reaction to occur.

To calculate other activation thermodynamic parameters, an alternative form of Arrhenius equation which is the Eyring's transition state equation was used (equ. 5)

$$\mathrm{CR} = \left(\frac{\mathrm{RT}}{Nh}\right)\exp\left(\frac{\Delta S^*}{\mathrm{R}}\right)\exp\left(\frac{\Delta H^*}{\mathrm{RT}}\right) \qquad (5)$$

Where N is the Avogadro's number, h is the Planck's constant, ΔS* is the entropy of activation, and Δ H* is the enthalpy of activation. A plot of log (CR/T) vs 1/T gave a straight line as shown in Figure 3 with a slope of (-Δ H*/2.303R) and an intercept of [log(R/Nh) + (ΔS*/R)], from which the values of ΔH* and ΔS* were calculated and listed in Table 2. The positive values of ΔH* for corrosion of carbon steel in 1 M HCl in the presence of TR reflect a strong adsorption of the inhibitor on the surface of the metal and it also shows the endothermic nature of metal corrosion process. The negative increment in ΔS* with increase in the concentration of the inhibitor reveals that decrease in randomness takes place on going from reactant to the activated complex [20]. This reflects the formation of an ordered stable film of inhibitor on carbon steel surface.

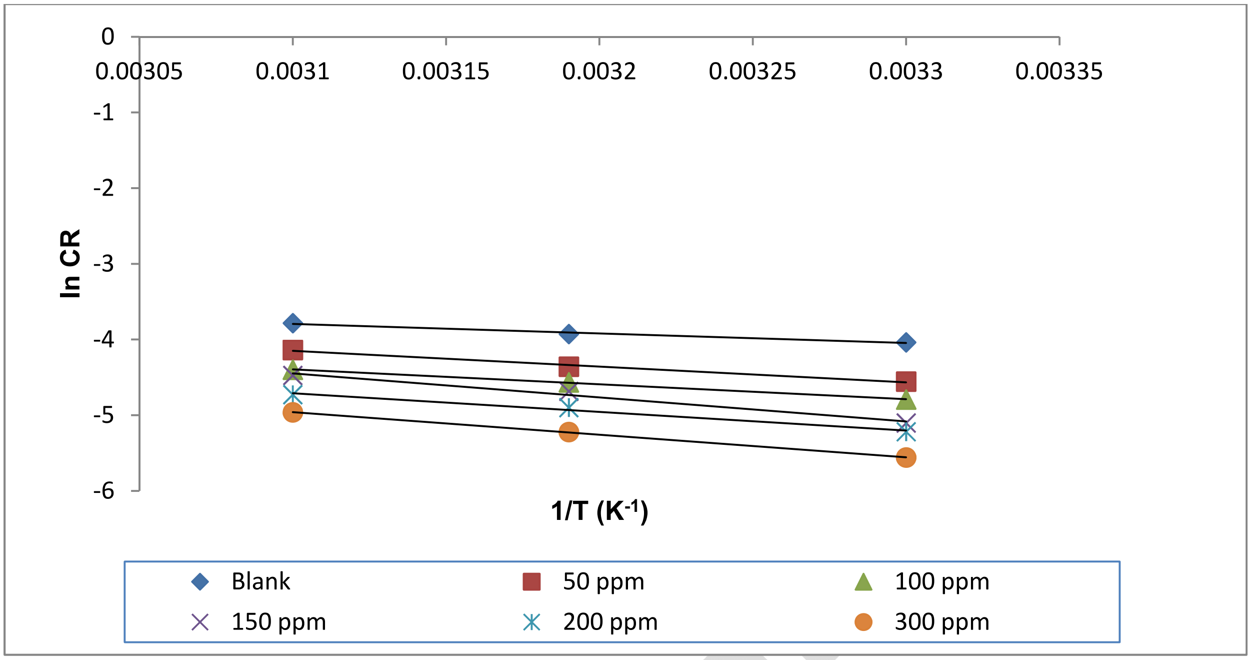

Fig. 2: Arrhenius plots for carbon steel corrosion in 1 M HCl without and with different concentrations of *Triumfetta rhomboidea*

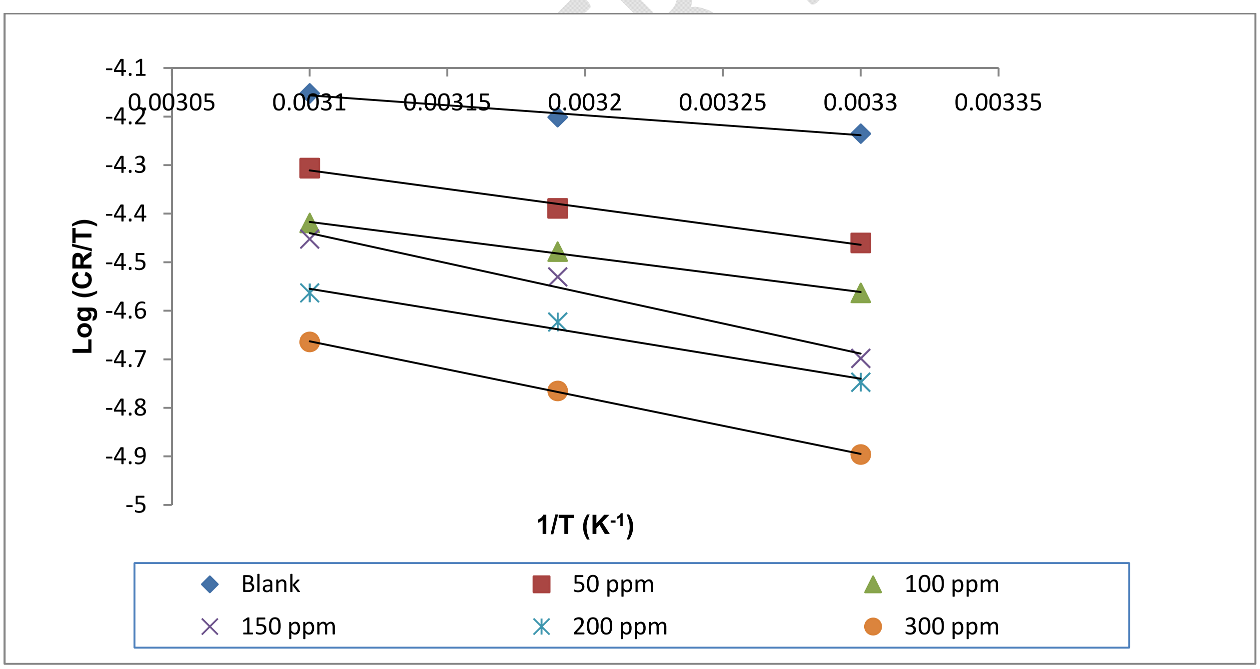

Fig. 3: Eyring's plot of log CR/T against 1/T for the corrosion of carbon steel in 1 M HCl in the absence and presence of *Triumfetta rhomboidea*

Table 2. Activation parameters of the corrosion reaction of carbon steel in 1 M HCl in the absence and presence of *Triumfetta rhomboidea* extract

TR conc. (ppm)	E_a (kJ/mol)	ΔH^*(kJ/mol)	ΔS^* (J/mol/K)
Blank	16.29	23.47	-173.22
50	21.38	24.28	-181.84
100	23.90	26.14	-189.84
150	26.89	28.22	-193.22
200	28.02	29.28	-205.66
300	29.84	30.88	-216.04

3.2. Scanning Electron Microscopy (SEM) Analysis

The surface morphologies of the carbon steel specimens before immersion and after 24 h of immersion in 1 M HCl blank solutions were studied by SEM examination followed by SEM study after 24 h immersion in 1 M HCl solution containing 300 ppm *Triumfetta rhomboidea* extract. The SEM image of the carbon steel specimen before corrosion in the acidic solution is depicted in Figure 4 while the corresponding images after 24 h immersion in 1 M HCl without and with *Triumfetta rhomboidea* extract are depicted in Figure 5. Comparing the SEM images in absence and presence of *Triumfetta rhomboidea* extract, there was a smoother surface image of the carbon steel in the solution with the inhibitor as compared to without inhibitor. The result clearly shows that the introduction of *Triumfetta rhomboidea* reduced the corrosion of carbon steel by formation of a protective layer on its surface.

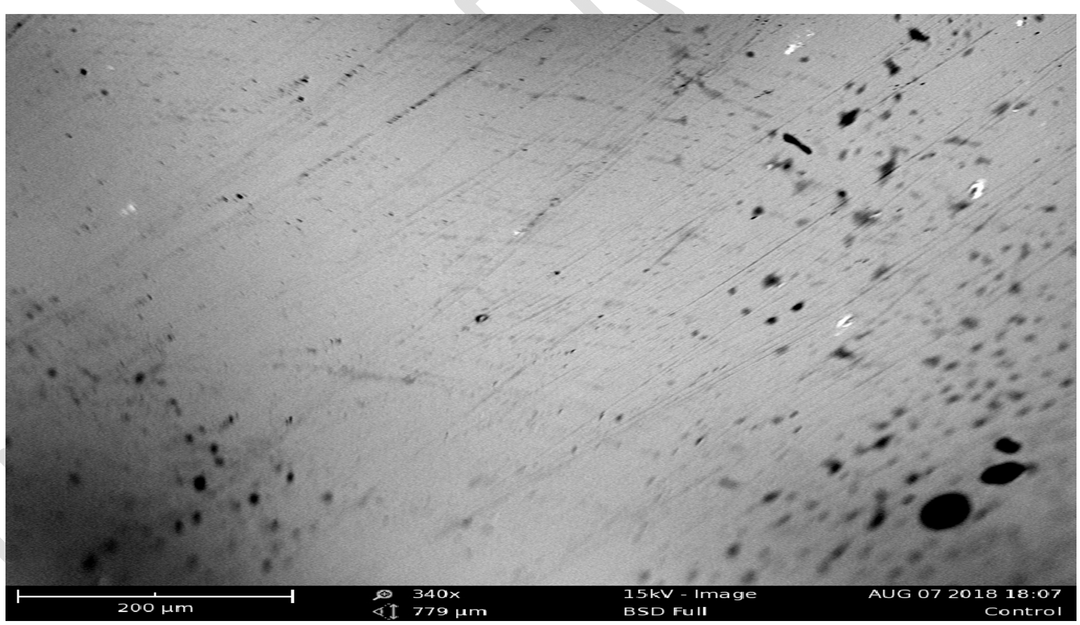

Fig. 4: SEM image of carbon steel surface before corrosion in 1 M HCl

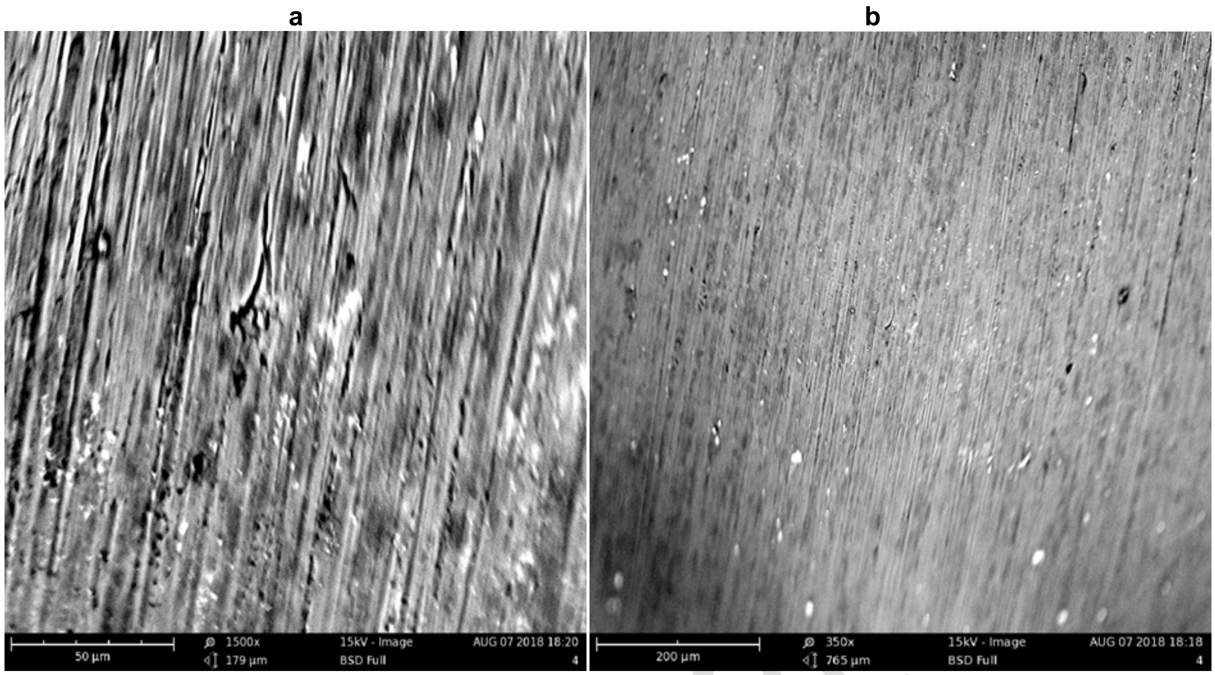

Fig. 5. SEM images from Carbon steel in 1 M HCl at 303 K for 6 h; (a) without MAL and (b) with 300 ppm *Triumfetta rhomboidea*

3.3. Adsorption Considerations

The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface. Adsorption isotherm values are important to explain the mechanism of corrosion inhibition of organo-electrochemical reactions. The frequently used adsorption isotherm include: Langmuir, Frumkin, Hill de Boer, Parsons, Temkin, Flory-Huggins, among others. Langmuir isotherm was tested for its suitability to the experimental data. Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \qquad (6)$$

Where θ is the degree of surface coverage, C is the inhibitor concentration, K_{ads} is the equilibrium constant of adsorption process. The plots of *C/*θ against C are shown in Fig. 6. Linear plots were obtained with good correlation coefficient (R^2) which suggests that adsorption of the inhibitor follow Langmuir adsorption isotherm. Since it obeys Langmuir adsorption isotherm, it implies monolayer adsorption of inhibitor. The adsorption of the inhibitor on the metal surface leads to high degree of surface coverage and hence shows better inhibitive property [21].The equilibrium constant of adsorption K_{ads} decreases with increase in temperature (Table 3), indicating that the interactions between the adsorbed molecules and the metal surface are weakened and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature [22].

The equilibrium constant of adsorption of *Triumfetta rhomboidea* (TR) extract on the surface of carbon steel is related to the free energy of adsorption ΔG_{ads} by Equation 7.

$$\Delta G_{ads} = -2.303\ RT \log (55.5K_{ads}) \qquad (7)$$

Where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution. The result is presented in Table 3. The negative values of ΔG_{ads} suggest that the adsorption of TR extract onto mild steel surface is spontaneous. The values of ΔG_{ads} obtained indicate that adsorption of TR extract occurs via physical adsorption mechanism. Generally, values of ΔG_{ads} less negative or equal to -20 $kJmol^{-1}$(as obtained in this study) are consistent with electrostatic interaction between the charged metals and charged molecules which signifies physical adsorption while values more negative than -40 $kJmol^{-1}$signify chemical adsorption [23-27].

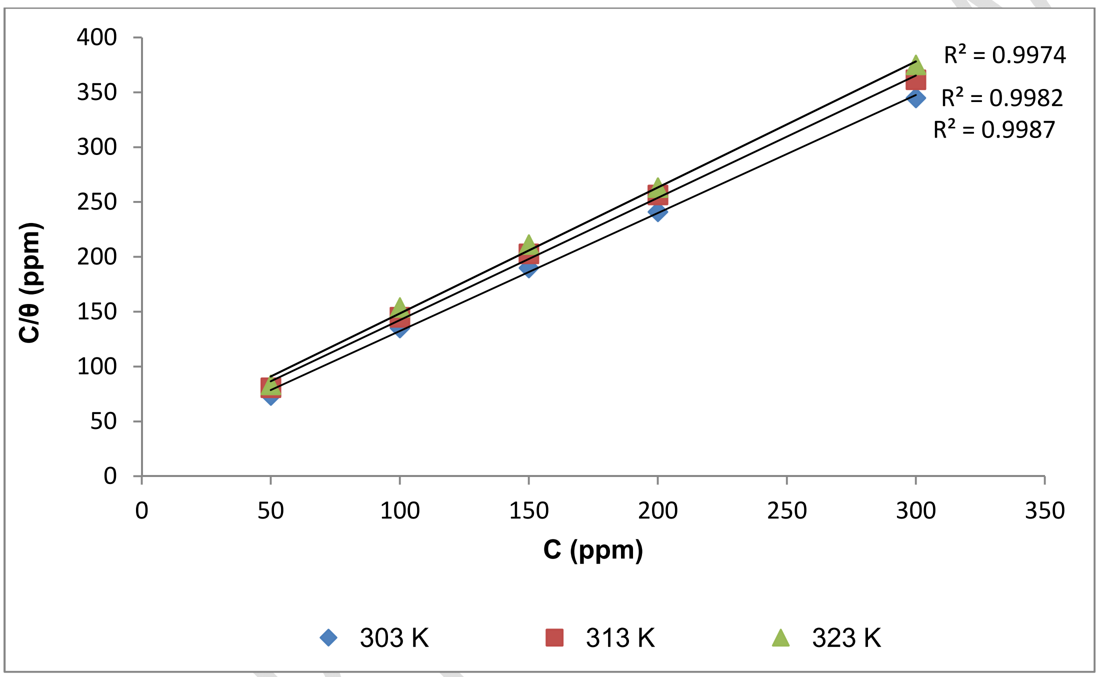

Fig. 6. Langmuir Isotherm for the adsorption of *Triumfetta rhomboidea* leaves extract on carbon steel in 1M HCl at different temperatures

Table 3. Calculated thermodynamic parameters from Langmuir adsorption isotherm

Temperature (K)	**K_{ads}**	**ΔG_{ads}(kJ/mol)**	**R^2**
303	1.18	-10.65	0.9974
313	0.99	-10.21	0.9982
323	0.83	-10.07	0.9987

4. CONCLUSION

Triumfetta rhomboidea extract was found to be an efficient inhibitor for carbon steel in 1M HCl solution. The rate of corrosion of the carbon steel in 1M HCl is a function of the concentration of the inhibitor. This rate decreased as the concentration of the inhibitor is increased. The percentage inhibition efficiency of this inhibitor decreased as the temperature increases which indicate that physical adsorption was the predominant inhibition mechanism. Adsorption of *Triumfetta rhomboidea* obeys the Langmuir adsorption isotherm. The value of ΔG^{o}_{ads} corroborates firm and spontaneous correlation between *Triumfetta rhomboidea* and the mild steel surface.The surface morphological investigation revealed the existence of a protective layer adsorbed on a mild steel surface.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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