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Inhibition of mild steel corrosion using *Jatropha Curcas* leaf extract

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Abstract

Jatropha Curcas leaf was investigated as a green inhibitor on the degradation of mild steel in 4 M HCl and 4 M H_2SO_4 aqueous solutions using gasometric technique. Mild steel coupons of dimension 2 × 1.5 cm were immersed in test solutions of uninhibited acid and also those with extract concentrations of 4 ml, 6 ml, 8 ml and 10 ml at 30 ^{o}C, for up to 30 minutes. The results showed that as the concentration of the extract increases, there was reduction in the corrosion rate. As the extract concentration increased from 4 ml to 10 ml at 30 minutes exposure, the volume of hydrogen gas evolved decreased from 19.1 cm^3 to 11.2 cm^3 in H_2SO_4 medium, while it reduced to 5 cm^3 from 9 cm^3 in HCl medium. Also, the metal surface-phytoconstituent interaction mechanism showed that 6 minutes is the best exposure time for the adsorption of the extract in both acidic media. The Jatropha Curcas leaf extract was adsorbed on the mild steel surface to inhibit corrosion, while the experimental data obtained at 30 minutes exposure in both acidic media were well fitted with the Langmuir adsorption isotherm. Hence, Jatropha Curcas leaf extract is a good and safe inhibitor in both acidic solutions.

Keywords

Gasometric, Inhibitor, adsorption, mild steel, Langmuir isotherm

Introduction

Mild steel is a material commonly used in industries due to its low cost, availability and excellent mechanical properties [1]. However, the major drawback to its application is corrosion attack, which usually leads to structures degradation, equipment shutdown, loss of machines efficiency, and loss of valuable products, to mention but few [2]. The average corrosion cost has been reported to be about 3.5-4.5 % of the Gross National Product of most industrialized nations [3].

Corrosion can be prevented in several ways but the use of inhibitors is one of the most acceptable practices. The use of synthetic inhibitors has been seriously discouraged due to its high cost, non-biodegradability and harmfulness. Hence, naturally occurring compounds from plants origin have been a subject of interest for researchers because of their abundant availability, cost effectiveness and environmentally friendly [4]. Several studies have been carried out on the use of these naturally occurring compounds as corrosion inhibitors for metals in different media [5-19].

Jatropha Curcas (JC) is a perennial, multi-purpose and drought resistant plant that belongs to the family of *Euphorbiaceous* JC is also a tropical plant that can be grown in low to high rainfall regions [20], on both fertile and even in less fertile soil. *Jatropha* oil, obtained by crushing the seeds is used as biodiesel fuel. The plant is planted by farmers all over the world, because it is not browsed by animals. Non-toxic variety of *Jatropha* could be a potential source of oil for human consumption and the seed cake can be a protein source for humans as well as for livestock [21]. Another potential application of the leaves as corrosion inhibitor for mild steel in acidic media is established in this study.

Experimental Procedure

The chemical composition of the mild steel specimen used for this experiment in wt % is 0.17 % C, 0.21 % Si, 0.55 % Mn, 0.02 % P, 0.02 % S, 0.18 % Cu, 0.01 % Ni, 0.02 % Sn and 98.81 % Fe. Specimens were press cut into pieces with dimension of 1.5 × 2 cm coupons. The specimens were polished using LINN MAJOR STRUER-ITALY (Model No. 224732) with emery papers 140/0304 − 140/0308 grades. Subsequently, they were degreased in ethanol, dried in acetone and stored in desiccators. The solutions of HCl and H_2SO_4 were prepared by using double distilled water. The fresh leaf of *Jatropha Curcas* (JC) plant was taken, washed under running water, cut into pieces, air dried and then grounded well and sieves into powdery form. Then, 10 g each of the powdery leaf was put into flat bottom flask containing 200 cm^3 of 4 M HCl and H_2SO_4 aqueous solutions. This concentration was used in order to fasten the rate of reaction between the metal surface and the acidic extract of the inhibitor within the period of the experiment. The resulting solutions were refluxed for 2 hours and left overnight before it was carefully filtered. The stock solution was prepared from the filtrate and into the desired concentrations. In this study, extract amount of 4-10 ml correspond to 0.2 g dm^{-3}, 0.3 g dm^{-3}, 0.4 g dm^{-3} and 0.5 g dm^{-3}, respectively.

The gasometric assembly used for the measurement of hydrogen evolution was as reported by Aisha *et al.* [22]. A reaction vessel was connected to a burette through a delivery tube. The 4 M HCl solution was introduced into the mylius cell, and the initial volume of air in the burette was recorded. Then, mild steel coupon was dropped into the HCl solution, and the mylius cell was quickly closed. The volume of hydrogen gas evolved from the corrosion reaction was monitored by the volume change in the level of water in the burette. The change in volume was recorded every 120 seconds for up to 30 minutes. Similar procedure was repeated with the inhibitor. The same experimental procedure was followed for 4 M H_2SO_4 solution.

The inhibition efficiency and the degree of surface coverage were determined using Equations 1 and 2 [21]:

$$\text{Inhibition efficiency (I.E.), \%} = \frac{V_{H0} - V_{H1}}{V_{H0}} \times 100 \tag{1}$$

$$\text{Surface coverage - } \theta = \frac{V_{H0} - V_{H1}}{V_{H0}} \tag{2}$$

where V_{H0} is the volume of H$_2$ gas evolved without inhibitor and V_{H1} is the volume of H$_2$ gas evolved with inhibitor.

Results and discussion

Figure 1 shows the variation of volume of hydrogen gas evolved with time for the corrosion of mild steel in various concentrations of the inhibitor in HCl aqueous solution. As shown in the figure, the hydrogen gas was not evolved in the first 8 minutes due to slow rate of corrosion reaction at the initial stage resulting from the inability of the acidic extract to quickly penetrate the metal surface. Above this exposure time, the volume of hydrogen gas evolved increased with increasing period of exposure, but decreases with increasing concentration of acidic extract of *Jatropha Curcas* leaf. The volume of hydrogen gas evolved at 30 minutes was 21.8 cm^3 for the blank solution, while that of 4 ml, 6 ml, 8 ml and 10 ml concentrations of *Jatropha Curcas* leaf extract are 9.0, 8.0, 6.8 and 5.0 cm^3, respectively. This shows that oxide film developed faster on the surface of mild steel coupon with higher inhibitor concentration, and thus reduces the corrosion rate. The blank system having no inhibitor gave the highest hydrogen gas evolution and is far apart when compared to when varying concentration of the extract of *Jatropha Curcas* leaf was added. This may be due to the absence of inhibitor that will prevent acidic solution from reaching the metal surface [22]. Presence of oxide film causes the rate of hydrogen gas evolution to decrease (*i.e.* decrease in the rate of corrosion) [22]. Aisha *et al.* [21] also opined that increase in hydrogen evolution gas in the blank system may be due to direct reaction between the acid and the metal, since there is no adsorption layer to inhibit the reaction. Hence, the rate of hydrogen gas evolution, that is, the corrosion rate will be faster in the blank solution as compared with the inhibited. Ulaeto *et al.* [11] found that the leaf and root extracts of *Eichornia Crassipe* effectively inhibited the corrosion of mild steel in 5 M HCl, and that the extracts performed better at higher concentration.
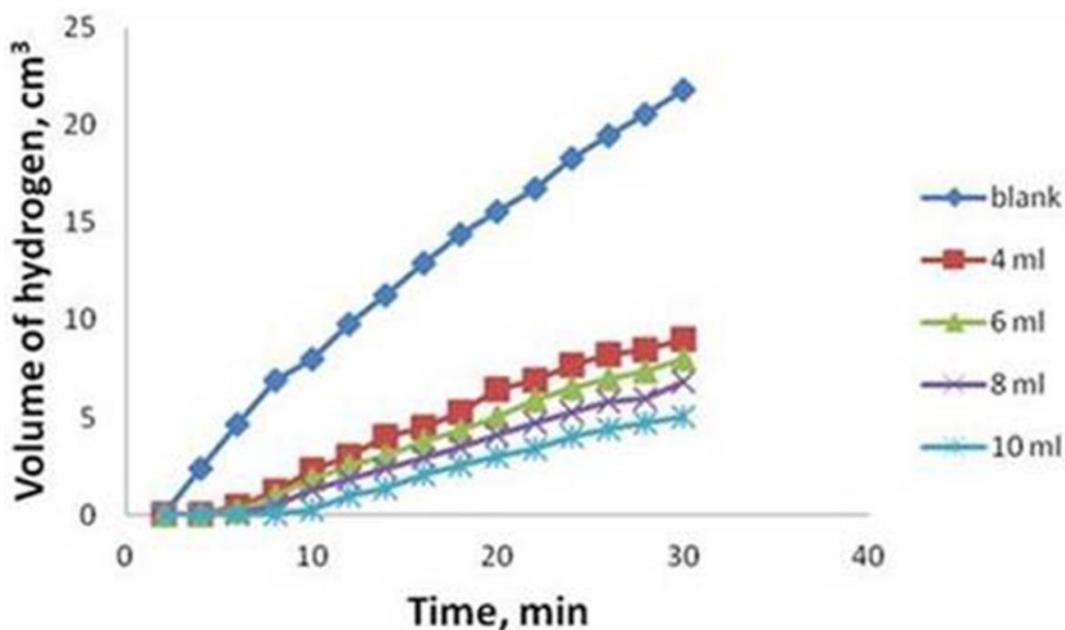

Figure 1. *Variation of volume of H$_2$ evolved with time of mild steel coupons for different volumes of JC extract in 4 M HCl solution*

The variation of inhibition efficiency against time of immersion with varying concentration of the inhibitor in 4 M HCl aqueous solution is shown in Figure 2. The results show that from 0 to

4 minutes, the inhibition efficiency was 0 %, corresponding to the latency period [23]. The corrosion rate was faster at the initial stage above 4 minutes, resulting in higher inhibition efficiency. However, at 6 minutes there was a re-ordering of the inhibition efficiencies from highest to the least value in descending order of the inhibitor concentration *i.e.* (10 ml < 8 ml < 6 ml < 4 ml) at all the exposure times. This revealed that there is an adsorption of the constituents of the *Jatropha Curcas* leaves extract on the surface of mild steel with 10 ml concentration of the inhibitor having the highest inhibition efficiency. The adsorption of the constituents resulted in the steady rate of corrosion (Fig. 2) due to the formation of oxide film separating the metal surface from the corrosive medium. Aisha *et al.* [21] investigated the use of *Plectranthus Tenuifloros* (Sahara) plant as safe and green inhibitor of mild steel corrosion in acidic solutions and observed that as the concentration of the extract increases, the inhibition efficiency increases. This was reported to be due to the adsorption layer formed on the surface of mild steel which inhibits the rate of corrosion. It was reported by Kuznetsov [23] that the longer the latency period, the higher the inhibition efficiency.
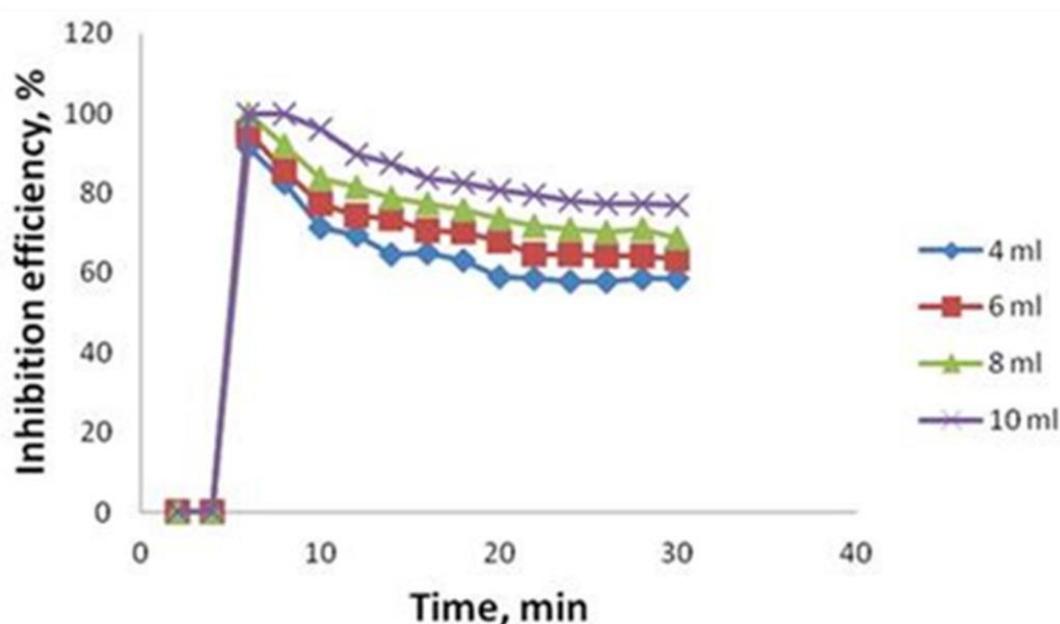

Figure 2. *Variation of inhibition efficiency with the time of immersion in 4 M HCl.*

Figure 3 shows the variation of the volume of hydrogen gas evolved with time of exposure in sulphuric acid solution. The results revealed that the corrosion rate of mild steel as indicated by the amount of H_2 gas evolved decreased in the presence of *Jatropha Curcas* leaf extract when compared to the control. The volume of hydrogen gas for blank solution was the highest as compared to those with different concentrations of *Jatropha Curcas* leaf extract. This infers that the JC leaf extract in the solution had a retarding effect on the corrosion of mild steel in H_2SO_4. Thus, the degree of inhibition can be said to be governed by the amount of JC extract present. The 10 ml concentration of the inhibitor was able to reduce the rate of hydrogen gas evolution further due to the formation of more adsorption layer on the surface of mild steel sample. The trend agrees with the result of Eddy *et al.* [10] during the determination of the inhibition efficiency of ethanol extract of *Phyllanthus Amarus* on corrosion of mild steel in H_2SO_4 solution. They reported that the volume of hydrogen decreased as the concentrations of *Phyllanthus Amarus* increased and the highest concentration of 0.5 g/L gave the least value of hydrogen gas evolution.
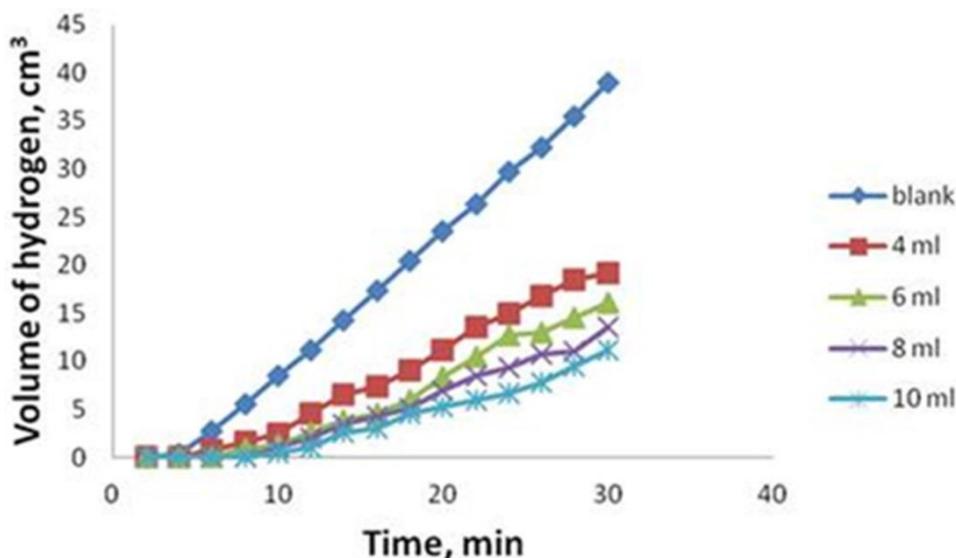
Figure 3. *Variation of volume of H₂ evolved with time of mild steel in coupons for different volumes of JC extract in 4 M H₂SO₄.*

Figure 4 shows the variation of percentage inhibition efficiency with time of immersion in sulphuric acid solution. The results obtained revealed that the inhibition efficiency increases as the concentration of *Jatropha Curcas* leaf extract increases, which follow similar trends with results in HCl medium. Similar observations were made when gravimetric method was used [24]. Also, from 6 minutes there was a re-ordering of the inhibition efficiencies from the highest to the least value in descending order of the inhibitor (10 ml < 8 ml < 6 ml < 4 ml) for the time of immersion. The corrosion inhibition of the plant extract on the surface of mild steel may be due to presence of the phytochemical constituents such as 1.610 mg/L alkaloid, 0.672 mg/L flavonoid, 0.412 mg/L saponins, 0.124 mg/L tannins and 0.465 mg/L phenol in the extract [24]. From the plot, it can be seen that the inhibition efficiencies of varying concentrations begin to reduce after reaching the maximum at the initial or transient stage up to 6 minutes. This stage was preceded by the latency period [23]. This reduction may be due to the faster rate of corrosion resulting from breakaway of the oxide film formed from extract inhibitor adsorption into the metal surface. However, above 20 minutes exposure at all the inhibitor concentrations, the efficiencies become relatively steady due to the protective nature of the barrier film separating the metal surface from the acidic medium.
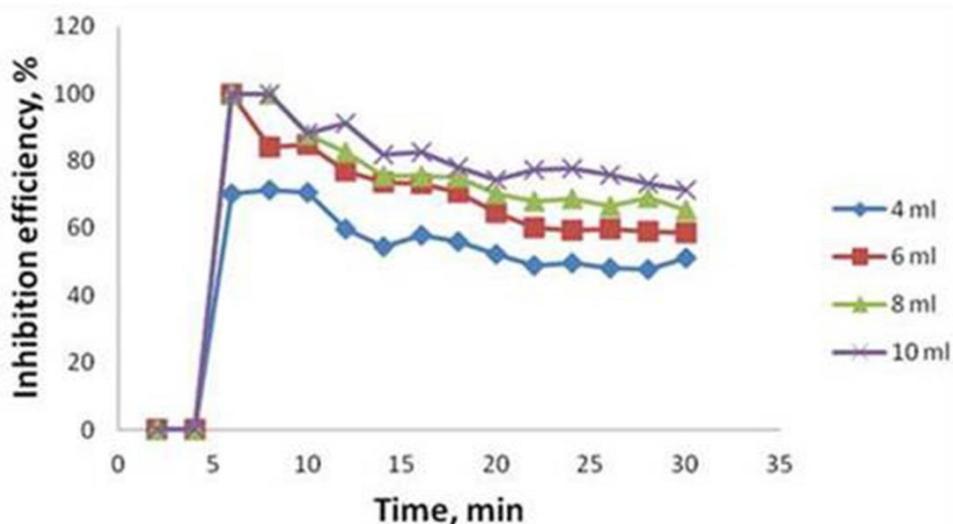

Figure 4. *Variation of inhibition efficiency with the time of immersion in 4 M H₂SO₄.*

Adsorption Isotherm

Adsorption isotherms are very important in knowing the mechanism of inhibition of corrosion reaction of metals. The most frequently used adsorption isotherms are Frumkin, Temkin, Freund-lich, Flory Huggins and Langmuir Isotherms. However, only Langmuir Isotherms is reported in the present study, while other adsorption methods were evaluated and reported elsewhere [26,27]. Langmuir gives an expression for the concentration to the degree of surface coverage (θ) according to Equation 3 [28]:

$$C/\theta = 1/K_{ads} + C \qquad\qquad (3)$$

Figures 5 and 6 represent the Langmuir isotherm plots of *Jatropha Curcas* leaves extract in both HCl and and H_2SO_4 aqueous solutions, respectively, showing the variation of C/θ against C at 30 minutes exposure. The plots showed that Langmuir adsorption isotherm model is appropriate for the determination of the adsorption mechanism of the extract of *Jatropha Curcas* leaves in both acidic media, since the points were well fitted linearly (as indicated by the values of coefficient of correlation, R^2, as given in Table 1) at a fixed slope of 1 according to Equation 3. The equilibrium constant of adsorption isotherm, K_{ads}, of the *Jatropha Curcas* leaf extract in both HCl and H_2SO_4 media were obtained from the intercept and the results are presented in Table 1. However, due to the complexity of the compounds in the extracts of leaves of *J. curcas* [29], it is not possible to determine the exact molecular weight of the inhibitor and hence the concentration in mol dm^{-3}. As a result, values of the standard free energy of adsorption (ΔG_{ads}) in both media could not be calculated [30].

Table 1. *Calculated values of Langmuir adsorption isotherm parameters of* Jatropha Curcas *extract in HCl and H_2SO_4 aqueous solution at 30 minutes*

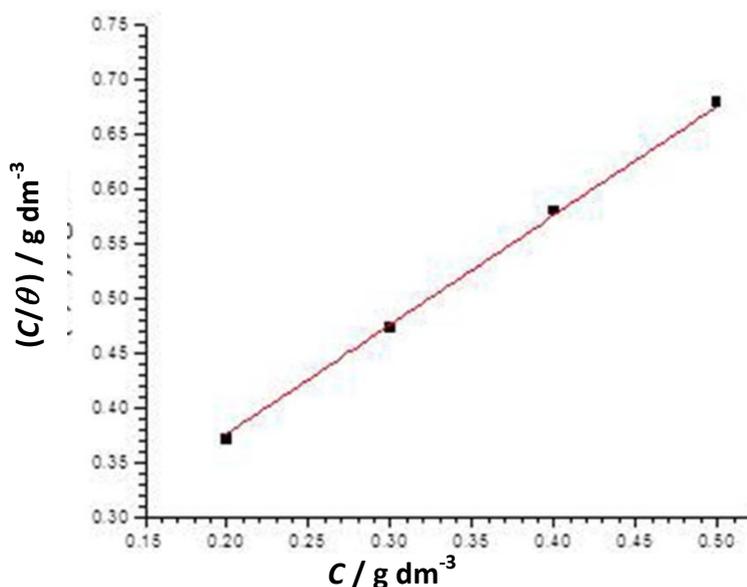| Plant Extract	Concentration on intercept point, g dm^{-3}	Slope	K_{ads} / g dm^{-3}	R^2
JC in 4M HCl	0.177	1.000	5.65	0.999
JC in 4M H_2SO_4	0.206	1.000	4.85	0.995

Figure 5. *Langmuir isotherm for the adsorption of the extract of* Jatropha leaves *on the surface of mild steel in 4 M HCl at 30 minutes exposure.*
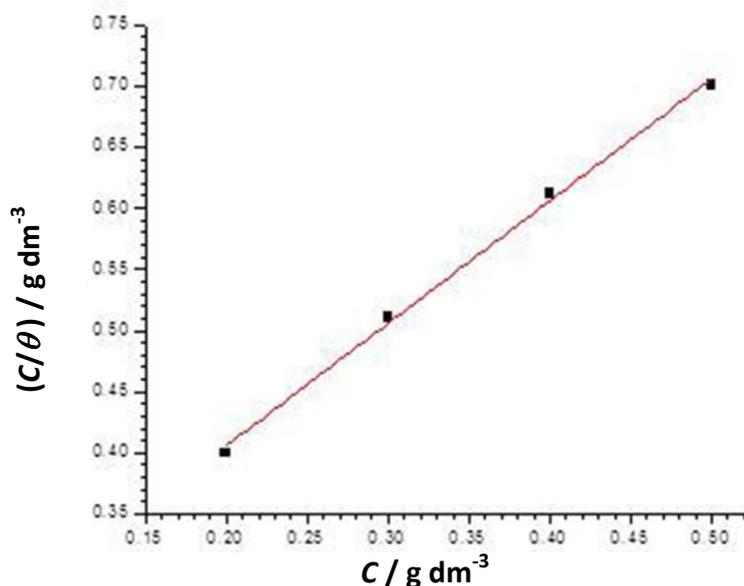
Figure 6. *Langmuir isotherm for the adsorption of the extract of* Jatropha leaves *on the surface of mild steel in 4 M H₂SO₄ at 30 minutes exposure.*

Plant extract contains organic compounds having polar atoms or groups which are adsorbed on the metal surface. Obot and Obi-Egbedi [13] reported that compounds interact by mutual repulsion or attraction when *Ipomoea Involcrata* plant extract was used as an inhibitor. This may be advocated as the reason for the slight departure of the slope values from unity as explained by Obot and Obi-Egbedi [13]. Although, in this study, the slope is fixed at 1 prior to linear fitting but few points were still slightly deviated from the straight line, which may be due to mutual repulsion or attraction of the polar atoms or groups as observed by Obot and Obi-Egbedi [13].

In addition, the adsorption of the *Jatropha Curcas* leaves extract on the mild steel surface may not involve the interaction of the adsorbate molecules with one another. According to Nnanna *et al.* [7], it was assumed that there was no interaction between the adsorbate molecules in the derivation of Langmuir isotherm. The adsorption was also assumed to be monolayer because the sites on the metal surface were taken to be energetically identical and uniformly distributed [8]. However, the adsorption process may be assumed to be due to an electrostatic interaction between the polar atoms/ions on the metal surface and the adsorbate molecules [7,29].

Conclusions

- The leaf extract of *Jatropha Curcas* acts as a good and efficient inhibitor for corrosion of mild steel in HCl and H₂SO₄ solutions.
- Inhibition efficiencies of the *Jatropha Curcas* leaf extract in HCl medium were higher than those in H₂SO₄ environment. After 30 minutes exposure with extract concentration of 10 ml, the efficiency is 77.1 % in HCl medium while 71.3 % was obtained in H₂SO₄ medium.
- The inhibition of the corrosion of mild steel by acid extract of JC is due to the phytochemical constituents in the plant extract.
- The experimental data obtained at 30 minutes exposure in both HCl and H₂SO₄ solutions with *Jatropha Curcas* leaf extract were well fitted with the Langmuir adsorption isotherm indicating that the Langmuir adsorption model is applicable in the corrosion inhibition mechanism.
- Further work will be carried out using other techniques with micrographs from SEM to show the effect of temperature and/or pH on the corrosion efficiency of *Jatropha Curcas* leaf extract on mild steel and other materials.

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