CORROSION INHIBITION OF MILD STEEL AND ALUMINIUM IN 1M HYDROCHLORIC ACID BY LEAVES EXTRACTS OF *FICUS SYCOMORUS*

ABSTRACT

Inhibitory effect of *Ficus Sycomorus* leaves extracts on the corrosion of mild steel and aluminium in 1M hydrochloric acid (HCl) solution was studied at temperature of 30℃ using gravimetric technique. Corrosion rates of mild steel and aluminium in the aggressive medium were found to increase as temperature increased, but decreased upon the addition of leaves extract of *ficus sycomorus* compared to the blank. At 30°C, the inhibition efficiency increased with increase in inhibitor concentration reaching 87.84% for mild steel and 98.92% for Aluminium in the presence of 5g/L of *Ficus Sycomorus* leaves extracts. The Electron Dispersive Spectroscopy (EDS) of *Ficus Sycomorus* leaves shows the presence of heteroatoms of oxygen, sulphur and phosphate which authenticates the leaf as a good inhibitor. The results obtained show that aluminium had correlation coefficients (R^2) of 0.999 and 0.876 for Langmuir and Temkin isotherms respectively. Mild steel had correlation coefficients of 0.989 and 0.751 for Langmuir and Temkin isotherms respectively. The correlation coefficients being close to unity imply some degree of agreement to the adsorption isotherms. However, the inhibitor adsorption was found to fit Langmuir adsorption isotherm better than Temkin isotherm. The free energy of adsorption (ΔG^0_{ads}) has negative values and this indicates that the adsorption of *ficus sycomorus* on the metal surface follows a spontaneous process

Keywords: ***Ficus Sycomorus*, inhibition efficiency, Adsorption isotherms, heteroatoms, correlation coefficient.**

1. INTRODUCTION

Corrosion is a major concern in industries where aggressive solutions are used for processes such as ore production, oil well acidizing, chemical cleaning and acid pickling of steel. However, corrosion processes can be inhibited by employing organic or inorganic inhibitors. Inorganic substances suitable as metal corrosion inhibitor must easily oxidize the metal to form an impervious layer which prevents direct ions-metal interaction and hence retard the rate of metal dissolution in the medium (Nnanna et al., 2014). Over the years, the high toxicity of inorganic inhibitors such as chromate, phosphate and arsenic compounds, gave rise to environmental and health related issues. As a result, strict international laws were imposed (Dariva C. G. et al., 2013). The ban on some inorganic compounds as inhibitors led to search for environmentally benign alternatives such as green (organic) inhibitors. These green inhibitors are plant extracts which have the qualities of being biodegradable, eco-friendly, low toxicity, cost effective and readily available (Sethuraman and Raja, 2008). Organic compounds capable of serving as inhibitors must have active adsorption centers and should also possess heteroatoms such as oxygen, sulphur, phosphorous, chlorine, bromine, iodine and nitrogen. Organic inhibitors can be adsorbed on the metal surface either through physical adsorption which is due to electrostatic attraction between the inhibitor and the metal surface or chemical adsorption, a process that involves charge sharing or transfer between the inhibitor molecules and the metal surface (Sastri, 1998; Fragoza-Mar et al., 2012; Nnanna et al., 2015).

In recent times, several scientific studies have been made on the corrosion inhibiting effect of some plant extracts which include; Eichhornia Crassipes (Ulaeto et al., 2012), Water Melon Rind (Odewumi et al., 2014), Juniprus Plant (Al-Mhyawi, 2014), Azadirachta Indica (Okafor et al., 2010), Uncaria Gambir (Mohammed et al., 2010), Pineapple Leaves (Ekanem et al., 2010), Justicia Gendarussa (Satapathy et al., 2009), and African breadfruit leaves (Ejikeme et al., 2015). These plant extracts were confirmed to inhibit the corrosion of aluminum and mild steel in acidic solutions. The inhibition effect of these plants extracts can be attributed to the presence of organic species such Carbohydrates, tannins, alkaloids and nitrogen bases, amino acids and proteins.

African Sycamore *(Ficus sycomorus)* is a large, semi-deciduous spreading savannah tree, growing up to 21 (max. 46)m in height (Orwa et al., 2009) It is a common savannah tree that grows in high water table areas. Often found along watercourses such as streams and rivers, swamps and waterholes. The sycamore tree is sensitive to frost but can withstand cold. It is found in afro-montane rain forests, undifferentiated afro-montane forests, riverine forests, and riparian woodland. Sycamore leaves are broadly ovate or elliptic in shape. Sycamore trees are readily available and the Sycamore leaves used for this experiment were collected at a location in Aba South, Abia State, Nigeria.

2. MATERIALS AND METHODS

2.1. Materials

The composition of the mild steel is as follows: 0.08% C, 0.05% Si, 1.00% P, 0.02% Pb, 0.02% Cu and the remainder iron. The aluminium alloy (AA801) specimen contains: 0.79600%-Si, 0.79624%-Fe, 0.02217%-Cu, 0.07513%-Mn, 0.01268%-Mg, 0.00281%-Zn, 0.01528%-Ti, 0.00156%-Cr, 0.00226%-Ni, 0.00717%-V, 0.00670%-Pb, and 98.2755%-Al. The mild steel and aluminium were pressed cut into 2cm x 2cm coupons. Mild steel had thickness of 1.1mm while Aluminium had thickness of 0.5mm. The coupons were mechanically polished with emery paper of different grades, degreased in ethanol, dried in acetone and stored in dry dessicators prior to use for corrosion studies.

2.2. Preparation of *Ficus sycomorus* Leaves Extract

The *Ficus sycomorus* Leaves were obtained from Aba, Abia State, Nigeria. The leaves were air-dried and crushed to powder using a manual grinding machine. The leaves were boiled at 60^0C in reflux apparatus for 2 hours, cooled and then filtered. The amount of ground leaves extracted into the solution was calculated by comparing the weight of dried residue with the initial weight of grounded leaves before extraction. Various concentrations of the inhibitor ranging from 0.1 - 0.5g/l were weighed and dissolved in 1M HCl.

2.3. Weight Loss Studies

Pre-weighed metal coupons were placed in 100 ml of 1M HCl solution (blank) and in 100 ml of 1M HCl solution containing various concentrations of *Ficus sycomorus* extract ranging from 0.1 to 0.5g in properly labeled transparent beakers. In each experiment, the clean metal coupons were suspended with the aid of wooden stick and hook. Immersed coupons were retrieved progressively at 1 hour intervals for 8h, washed, degreased in ethanol, dried in acetone and re-weighed. The weight loss was taken as the difference in weight of the specimen before and after immersion determined by weighing with the digital measuring balance. From the weight loss values, corrosion rates were computed using the expression:

2.4. Corrosion Studies

Assessment of corrosion rate, inhibition efficiency and surface coverage for aluminium and mild steel with different inhibitor concentrations was carried out using Eqns. 1 to 3, respectively.

2.4.1. Corrosion Rate

Corrosion rate (C.R) can be measured in terms of mils per year penetration (mpy) using the equation;

$$C.R = \frac{K\Delta W}{\rho A t} \qquad (1)$$

Where; K = constant for unit conversion with value of 87.6, ΔW = weight loss of the coupon in g, ρ= density of coupon in g/cm^3, A = Area of coupon in cm^2
t = time of exposure in hours.

2.4.2. Inhibition Efficiency

The inhibition efficiency (I%) was evaluated using Equation;

$$I\% = (1 - \frac{\rho_1}{\rho_0}) \times 100 \qquad (2)$$

2.4.3. Surface Coverage

The surface coverage (θ) was calculated by dividing the Inhibition Efficiency by 100.

$$\Theta = I\% \div 100 \qquad (3)$$

3.0 RESULTS AND DISCUSSION

3.1. Electron Dispersive Spectroscopy (EDS)

The EDS of the leaf extract of *Ficus sycomorus* was performed to ascertain the compound composition. The result of the EDS micrograph of ground *Ficus sycomorus* is shown in fig.1

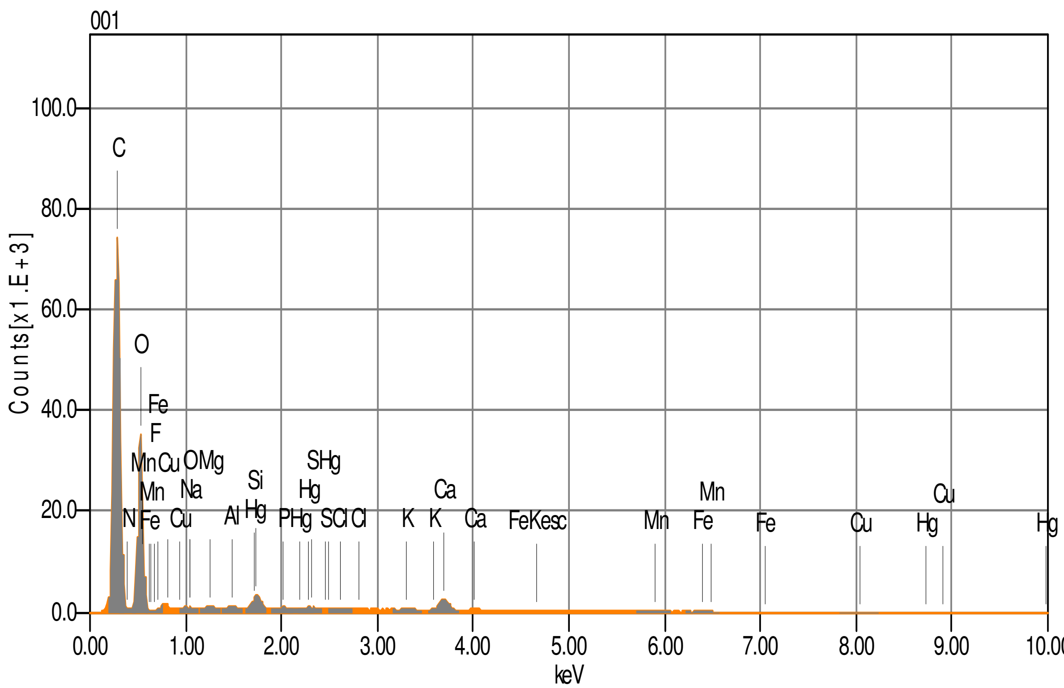

Figure 1: EDS Micrograph of ground Ficus Sycomorus leaves

A close examination of the figure above confirms the presence of the heteroatoms of oxygen, sulphur and phosphate which authenticates the leave extract to be a good and efficient inhibitor.

3.2. Weight Loss Measurements

Weight loss measurements were taken to evaluate the effectiveness of *Ficus Sycomorus* leaves extract as corrosion inhibitor of mild steel and aluminium. The plot of corrosion rate against exposure time for aluminium and mild steel in 1 M HCl without and with different concentrations of *Ficus sycomorus* leaves extracts at 30 ^{0}.

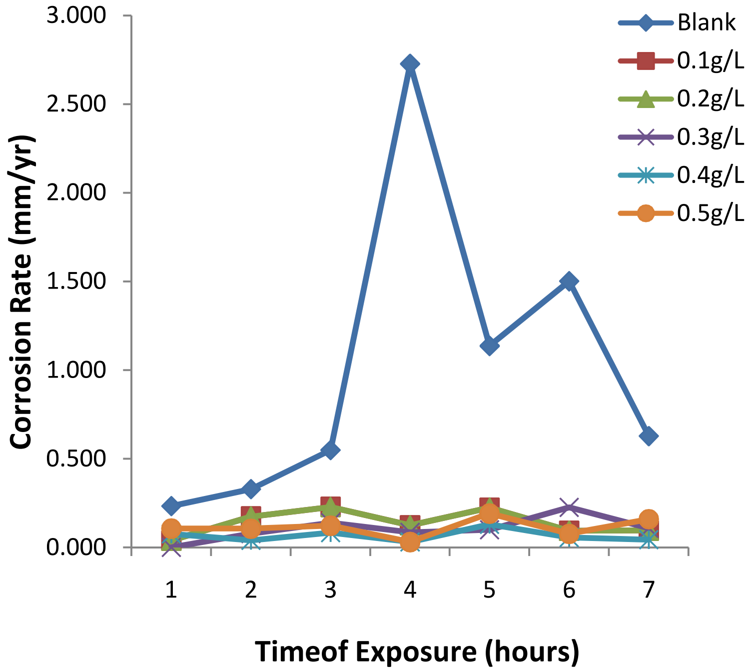

Figure 2: Variation with time of the corrosion rate of Aluminium in 1M of HCl for various concentrations of Ficus sycomorus at 30^0C temperature

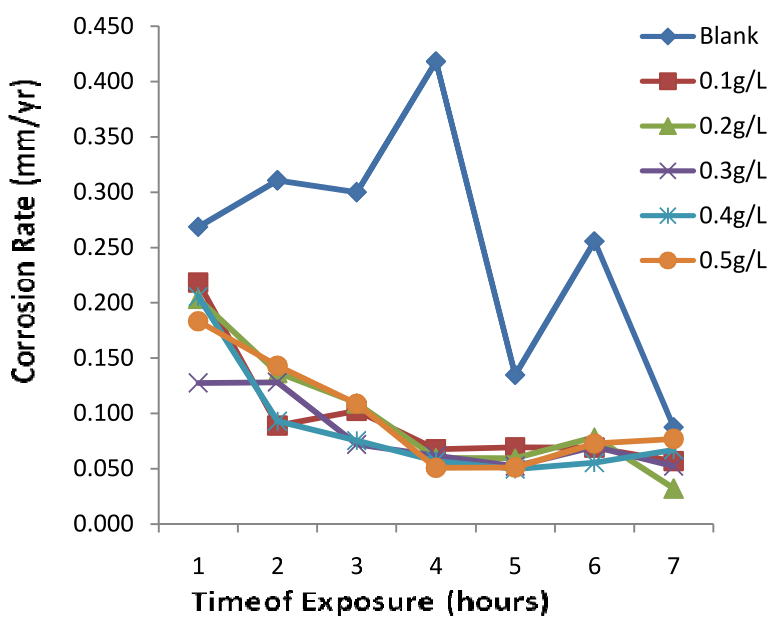

Figure 3: Variation with time of the corrosion rate of mild Steel in 1M of HCl for various concentrations of Ficus sycomorus at 30^0C temperature

A close inspection of figure 2 and 3 show that the corrosion rates of aluminium and mild steel in 1M HCL were significantly reduced upon the introduction of ficus sycomorus leaves extract. An optimum value of 0.0301 mm/yr was obtained for aluminum at 0.5 g/l concentration after 4 hours of exposure. However, for mild steel, an optimum value of 0.0508 mm/yr was obtained at 0.5 g/l concentration after 4 hours of exposure. Data derived from the weight loss experiment was also used to plot the graph of inhibition efficiency against the inhibitor's extract concentration as shown in figure 4 and 5. An inspection of the plots (fig 4 and fig 5) show that the leaf extracts of ficus sycomorus inhibited the corrosion of mild steel and aluminium in 1M of HCL.

The efficiency of an inhibitor is meant to increase with an increase in concentration of the inhibitor extract in an aggressive medium. Corroborative results were reported by (Chidiebere et al., 2012; Ebenso et al., 2005). The inhibition efficiency of the leaf extract of *Ficus sycomorus* in 1M HCl was investigated at various concentrations. Figures 4 and 5 show the plot of inhibition efficiency against concentration of inhibitor at 30^0C and 60^0C respectively.

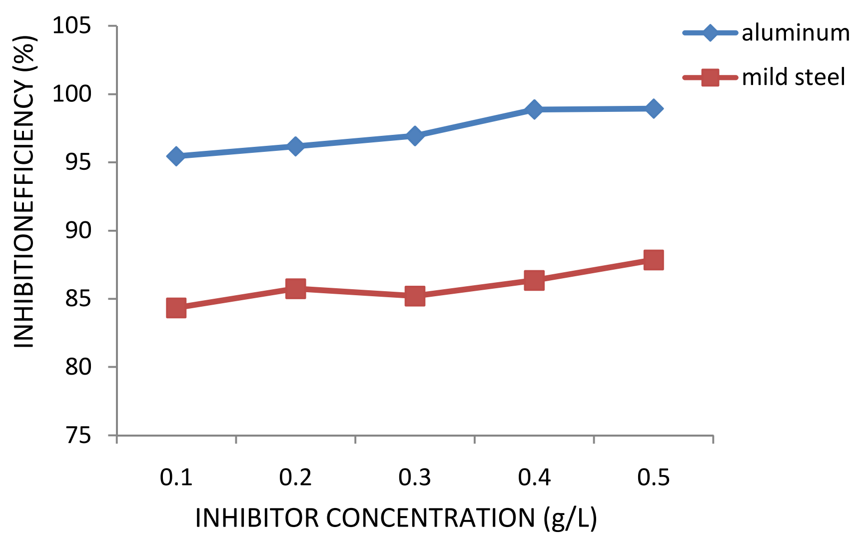

Figure 4. inhibition efficiency of Ficus sycomorus extracts in 1M HCl on aluminum and mild steel against concentration of inhibitor at 30^0C

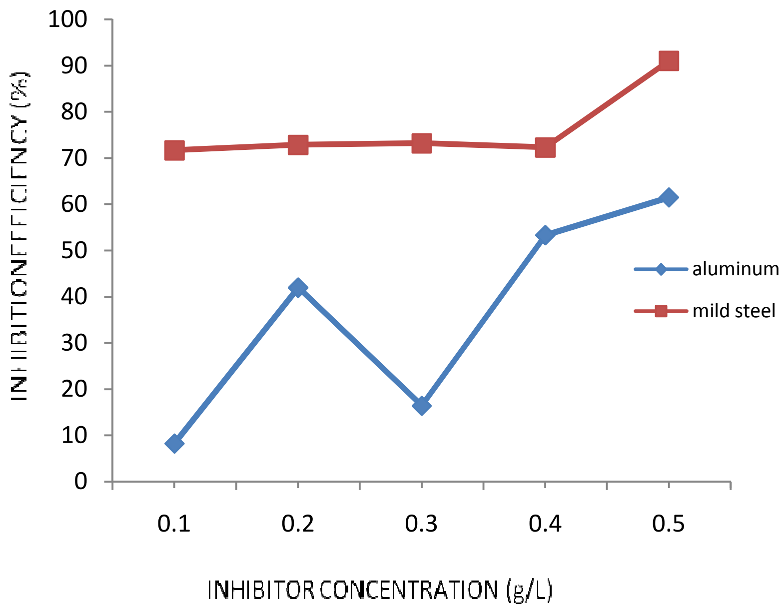

Figure 5: Inhibition efficiency of Ficus sycomorus extracts in 1M HCl on aluminium and mild steel against concentration at 60^0C

Inspection of the plots (fig. 4 and 5) revealed that the corrosion rates of aluminium and mild steel in 1M of HCl solution were reduced upon the introduction of *Ficus sycomorus* leaves extract into the corrosive environment. The corrosion rates of both aluminum and mild steel were also observed to reduce with increase in concentration of the inhibitor leaves extract. At room temperature of 30^0C, inhibition efficiency of 98.92% was obtained for aluminum at 0.5g/L concentration after 4 hours of exposure in 1M HCl as shown in fig 4. For mild steel, inhibition efficiency of 87.84% was obtained at 0.5g/L concentration as shown in fig 8. However, at higher temperature of 60^0C, the inhibition efficiency of *Ficus sycomorus* decreased slightly for mild steel but decreased significantly for aluminum. The decrease in the inhibition efficiency of the inhibitor as the temperature increases may be attributed to the desorption of the adsorbed molecular species of the extracts on the aluminium and mild steel surface (Nnanna et al., 2014).

3.3 Adsorption Isotherm

Inhibitory property of organic compounds can be seen in their ability to form protective film by adsorbing onto a metal surface. Isotherm studies provide information on the mechanism of adsorption. Adsorption of the inhibitor extracts on the metal surface can either be through chemisorption which involves charge sharing or transfer from the organic molecules to the metal surface or through physisorption which involves electrostatic interaction between the organic molecules and charged metal surface (Popova et al., 2003). Data obtained from weight loss measurements were employed to determine the fit to some adsorption isotherms which include; Langmuir and Temkin isotherms. However, the value of the correlation coefficient and linearity of the plot suggest which of the isotherms that adsorption of the inhibitor fits most (Ejikeme et al., 2015).

Langmuir isotherm plot shows the relationship between the ratios of inhibitor's concentration to surface coverage (C/θ) versus concentration (C) at a given temperature. It is expressed as

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

Where; K_{ads} is the equilibrium constant of the adsorption process, Θ is the surface coverage, C is the concentration of inhibitor in g/L

Figure 6 and 7 show the Langmuir plot of $\frac{C}{\theta}$ against C for aluminium and mild steel at 30^{0}C. The plots yield a linear graph with good correlation coefficient (R^2) of 0.999 and 0.989 for aluminium and mild steel respectively. Also, the slopes have values of 0.997 and 1.089 for aluminium and mild steel respectively. The high values of R^2 and slope of approximately unity as shown in table 1, indicate that the adsorption mechanism of *Ficus sycomorus* extracts on the metal surface obeys Langmuir isotherm. The slope being close to unity indicates an electrostatic interaction between the adsorbate (inhibitor molecule) and the adsorbent (metal surface) which corroborates to Langmuir isotherm prediction of physisorption.

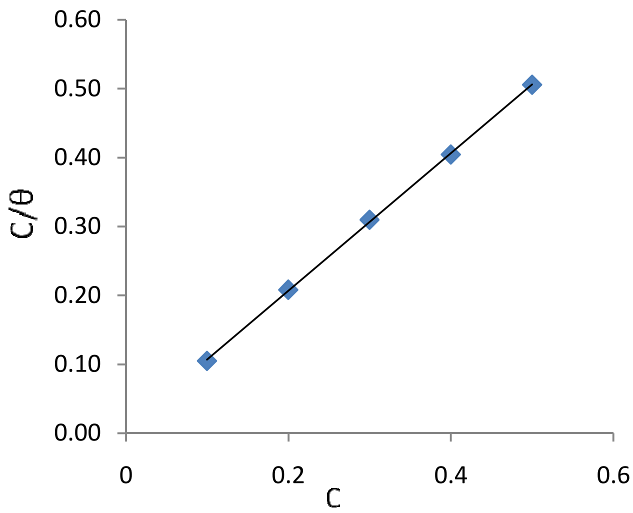

Figure 6: Langmuir isotherm for Ficus sycomorus adsorption On aluminum in 1M HCl at 30^0C.

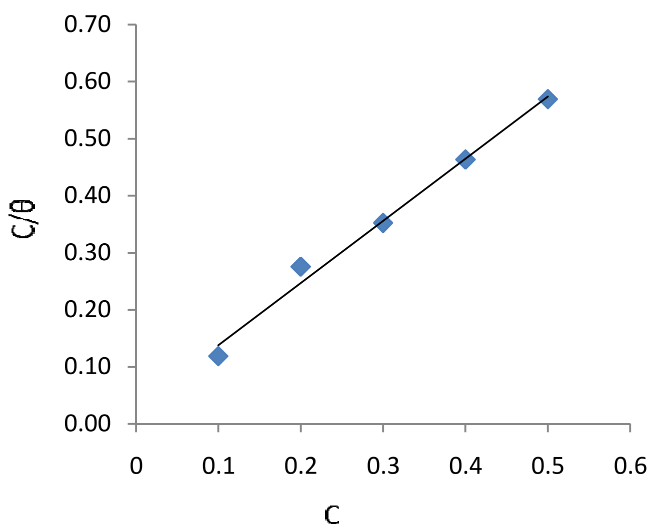

Figure 7: Langmuir isotherm for Ficus sycomorus adsorption on mild steel in 1M HCl at 30^0C

Temkin isotherm plot shows the relationship between surface coverage (θ) and log of concentration (In C)

$$\theta = \frac{1}{f}\ln(\mathrm{K_{ads}C}) \qquad (4.2)$$

where θ is the surface coverage and f determines the adsorbent-adsorbate interaction.

Figure 8 and 9 show the plot of θ against *In C* for aluminium and mild steel at 30^0C. The graphs show that at 30^0C, correlation coefficient of 0.876 and 0.751 were obtained for aluminium and mild steel respectively. Also, the slopes have values of 0.023 and 0.018 for aluminium and mild steel respectively. The free energy of adsorption (ΔG^0_{ads}) as shown in table 1, have negative values. This indicates that the adsorption of *ficus sycomorus* on the metal surface follows a spontaneous process (Ehteram and Aisha, 2008).

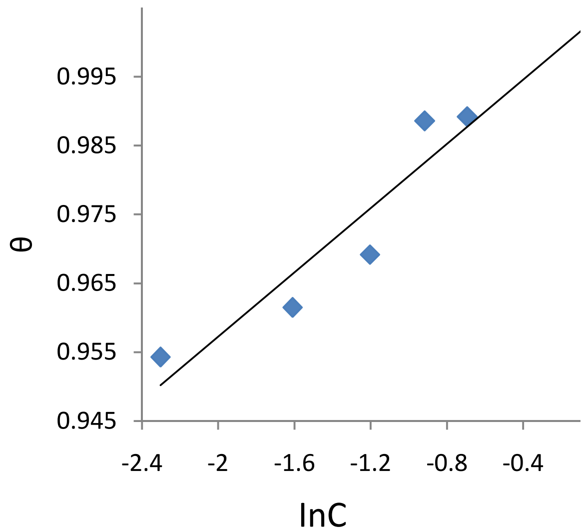

Figure 8: Temkin isotherm for Ficus sycomorus adsorption aluminum in 1M HCl at 30^0C

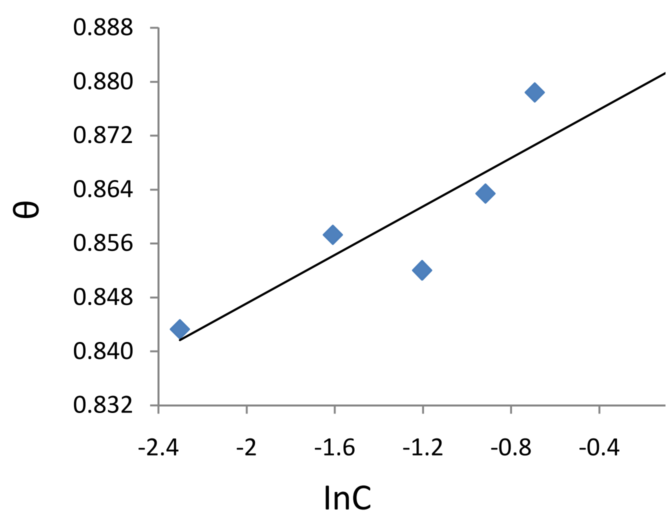

Figure 9: *Temkin isotherm for Ficus sycomorus adsorption on mild steel in 1M HCl at 30^0C*

Table 1. Adsorption isotherms parameters obtained from the corrosion data for aluminium and mild steel in 1M HCl containing *ficus sycomorus* leaf extract at 30 ^{0}C.

Isotherm	Aluminum					Mild Steel				
	Intercept	Slope	K_{ads}	R^2	$\Delta G^0{}_{ads}$ (kJ/Mol)	Intercept	Slope	K_{ads}	R^2	$\Delta G^0{}_{ads}$ (kJ/Mol)
Langmuir	0.007	0.997	142.86	0.999	-22.606	0.029	1.089	34.48	0.989	-19.027
Temkin	1.003	0.023	1.023	0.876	-10.170	0.883	0.018	1.016	0.751	-10.153

4.0 CONCLUSIONS

1. The EDS of *Ficus Sycomorus* leaves shows the presence of heteroatoms of oxygen, sulphur and phosphate which authenticates the leaf as a good inhibitor.

2. The leaves extract of *Ficus sycomorus* inhibited the corrosion of mild steel and aluminium in 1M HCL solution. The inhibition efficiencies were found to increase with increase in concentration of inhibitor with a maximum value of 98.92% and 87.84% obtained at 0.5g/l for mild steel and aluminium respectively.

3. The free energy of adsorption ($\Delta G^0{}_{ads}$) has negative values. This indicate that the adsorption of *ficus sycomorus* on the metal surface follows a spontaneous process.

REFERENCES

1. Chauhan L., Gunasekaran G. (2007). Corrosion inhibition of mild steel by plant extract in dilute HCl medium. *Corrosion Science*. 49(3), 1143-1161.
2. Chidiebere, M. A., Ogukwe, K. I., Oguzie, C. N., Eneh, C. N., Oguzie, E. E. (2012). Corrosion inhibition and adsorption behavior of *Punica granatum* extract on mild steel in acidic environments: Experimental and theoretical studies. *Ind. and Eng. Chem.*
3. Dariva C. G., Galio A. F. (2014). Corrosion inhibitors principle, Mechanisms and Applications. *Intech Publisher,* pp.365-380
4. Deng S., Li x. (2012).Inhibition by Ginkgo leaves extract of the corrosion of steel in HCl and H_2SO_4 solutions. *Corrosion science*. 55, 407-415
5. Ebenso, E. E., Oguzie,E. E., (2005). Corrosion inhibition of mild steel in acidic media by some organic dyes. *Materials letters. 59, 2163-5.*
6. Ebenso E. E, Umoren S. A. (2007). The synergy effect of polyacrylamide and iodide on the corrosion inhibition of mild steel in H_2SO_4. *Material Chem.and Phys*. 5, 106: 387
7. Ehteram A. N, Aisha H. A. (2008). Thermodynamicstudy ofmetalcorrosion and inhibitor adsorption process inmildsteel/1-methyl-4/hydrochloric acid systems. Materials Chemistry and Physics 110 (2008), 145-154
8. Ejikeme, P.M., Umana, S. G., Menkiti, M. C., Onukwuli, O. D. (2015). Inhibition of mild steel and aluminium in 1M H_2SO_4 by leaves extract of African Breadfruit. *Int'l Journ. of Mat. and Chem. 5(1), 14-23.*
9. El Bribri A., Tabyaoui M., Tabyaoui B., El Attari H., Bentiss F. (2013). The use of Euphorbia falcate extract as eco-friendly corrosion inhibitor of carbon steel in hydrochloric acid solution. *Materials Chem. and Phys*. 141(1), 240-247
10. Mejaha A., Ekeoma K., Alozie G. (2010). The inhibitive effect of Solanum melongena leaf extract on the corrosion of alumimiun in tetraoxosulphate (VI) acid. *African Journ. of Pure and applied Chem*. 4(8), 158-165.
11. M.N. Moussa, A.S. Foula, A.I. Taha, A. Elnenaa, Some thiosemicarbazide derivatives as corrosion inhibitors for aluminium in sodium hydrogen solution, Bulletin of the Korean Chemical Society 9 (1998) 192–5 .

12. Nnanna L. A., Owate I. O. (2015). Electrochemical study of Corrosion inhibition of mild steel in acidic solution using Gnetum Africana leaves extract. *British Journal of Applied Science and Technology*. 54, 2231-0843
13. Nnanna L. A., Owate I. O., Oguzie E.E. (2014). Inhibition of mild steel corrosion in HCL solution by Petaclethramacrophylla Bentham extract. *Int'l Journ. of Mat. Eng*. 4(5), 171-179
14. Obot I. B., Obi-Egbedi N. O., AUmoren S. (2009). Antifungal drugs as corrosion inhibitors for aluminiumin 0.1 M HCL. *Corrosion Sci.* 51, 1868-1875.
15. Oguzie, E. E. (2005). Inhibition of acid corrosion of mild steel by Telfaria occidentalis extract. *Pigment Resin Tech*. 34(6), 321-326.
16. Okafor P. C., Ebenso E. E., Ekpe U. J. (2010). Azadirachta Indica Extract as Corrosion Inhibitor for Mild Steel in Acidic Medium. *Int'l Journal of Electrochemical Science*. 5, 114-122.
17. Orwa C., Mutua A., Kindt R., Jamnadass R., Anthony S. (2009). Agroforestree Database: a tree reference and selection guide version 4.0. Retrieved from http://www.worldagroforestry.org/sites/treedbs/treedatabases.asp
18. Popova, A., Sokolova, E., Raicheva, S., Christov, M. (2003). AC and DC study of temperature effect on mild steel corrosion in acidic media in the presence of benzimidazole derivatives. *Corrosion Sci*. 45, 33-58.
19. Sanyal B. (1981). Organic compounds as corrosion inhibitors in different environments – A review. Progress in organic coatings. 14, 25-82
20. Sastri V. S. (1998). Corrosion Inhibitors. Principles and Applications. J. Wiley, New York, p. 39
21. Sethuraman M. G., Raja P. B. (2008). Corrosion inhibition of mild steel by Daturametel in acidic medium. *Pig. Resin Tech*, 34(6), 327-331.
22. Ulaeto S. B., Ekpe U. J., Chidiebere M. A., Oguzie E. E. (2012). Corrosion inhibition of mild steel in hydrochloric acid by acid extract of Eichhornia Crassipes. *Int'l Journal of Materials and Chemistry*. 2(4), 158-164