Physical Science International Journal

14(3): 1-10, 2017; Article no.PSIJ.32708
ISSN: 2348-0130

Corrosion Inhibition of Mild Steel and Aluminium in 1 M Hydrochloric Acid by Leaves Extracts of *Ficus sycomorus*

K. D. Ogwo[1,2*], J. C. Osuwa[2], I. E. Udoinyang[1] and L. A. Nnanna[2]

[1]*College of Basic and Applied Sciences, Rhema University, Aba Abia State, Nigeria.*
[2]*Department of Physics, Michael Okpara University, Umudike, Abia State, Nigeria.*

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/PSIJ/2017/32708
Editor(s):
(1) Daniel Beysens, OPUR International Organization for Dew Utilization, France.
(2) Christian Brosseau, Distinguished Professor, Department of Physics, Université de Bretagne Occidentale, France.
Reviewers:
(1) S. Srinivasa Rao, V. R. Siddhartha Engineering College (Autonomous), Andhra Pradesh, India.
(2) Ben Ugi, Cross River University of Technology, Calabar, Nigeria.
Complete Peer review History: http://www.sciencedomain.org/review-history/19149

Original Research Article

Received 10th March 2017
Accepted 7th April 2017
Published 20th May 2017

ABSTRACT

Inhibitory effects of *Ficus sycomorus* leaves extracts on the corrosion of mild steel and aluminium in 1 M hydrochloric acid (HCl) solution was studied at temperature of 30°C 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 5 g/L of *Ficus sycomorus* leaves extracts. The results obtained show that aluminium had correlation coefficients (R^2) of 0.999 and 0.876 for Langmuir and Temkin isotherms respectively while Mild steel had correlation coefficients of 0.989 and 0.751 for Langmuir and Temkin isotherms respectively. However, the inhibitor adsorption was found to fit Langmuir adsorption isotherm better than Temkin isotherm. The free energy of adsorption ($\Delta G°_{ads}$) has negative values and this indicates that the adsorption of *Ficus sycomorus* on the metal surface follows a spontaneous process.

**Corresponding author: E-mail: ogwodede@gmail.com, ifomag@yahoo.com;*

Keywords: Ficus sycomorus; inhibition efficiency; isotherms; 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 [1]. 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 [2]. 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 [3]. Organic compounds capable of serving as inhibitors must have active adsorption centers and should also possess hetero-atoms 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 [4,5,6].

In recent times, several scientific studies have been made on the corrosion inhibiting effect of some plant extracts which include; *Eichhornia crassipes* [7], *Citrullus lanatus* rind [8], *Juniprus* plant [9], *Azadirachta indica* [10], *Uncaria gambir* [11], *Ananas comosus* leaves [12], *Justicia gendarussa* [13], *Telfaria occidentalis* [14], and *Treculia africana* leaves [15]. 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.

The aim of this work is to study the inhibitory effect of *ficus sycomorus* (African Sycamore) leaves extracts on mild steel and aluminium in 1 M of HCL using weight loss method. *Ficus sycomorus* is a large, semi-deciduous spreading savannah tree, growing up to 21 m in height [16]. It is a common savannah tree that grows in high water table areas. It is 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: 0.080% C, 0.050% Si, 1.000% P, 0.020% Pb, 0.020% Cu and the remainder iron. The aluminium alloy (AA801) specimen contains: 0.796%-Si, 0.796%-Fe, 0.0227%-Cu, 0.075%-Mn, 0.013%-Mg, 0.003%-Zn, 0.015%-Ti, 0.002%-Cr, 0.002%-Ni, 0.007%-V, 0.007%-Pb, and 98.276%-Al. The mild steel and aluminium were pressed cut into 2 cm x 2 cm coupons. Mild steel had thickness of 1.1 mm while aluminium had thickness of 0.5 mm. The coupons were mechanically polished with emery paper of different grades, degreased in ethanol, air dried and stored in dry desiccators 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°C 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 - 0.5 g/l were weighed and dissolved in 1 M HCl.

2.3 Weight Loss Studies

Pre-weighed metal coupons were placed in 100 ml of 1 M HCl solution (blank) and in 100 ml of

1 M HCl solution containing various concentrations of *Ficus sycomorus* extract ranging from 0.1 to 0.5 g/l 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, air dried, and re-weighed. The weight loss was taken as the difference in weight of the specimen before and after immersion which was determined by weighing with the aid of a digital measuring balance. From the weight loss values, corrosion rates (C.R) of metals, surface coverage (θ) and inhibition efficiencies $I\%$ of inhibitors were computed using the Eqs. 1 –3.

Corrosion rate (C.R) can be measured in terms of mils per year penetration (mpy) or milli-meter per year (mm/yr) 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.

The inhibition efficiency (I%) was evaluated using the equation;

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

where; ρ_1 is the corrosion rate in the presence of inhibitor and ρ_0 is the corrosion rate in the absence of inhibitor.

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

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

3. RESULTS AND DISCUSSION

3.1 Energy Dispersive Spectroscopy (EDS)

Energy Dispersive spectroscopy (EDS) system consist of x-ray detector which is used to analyze x-ray of different elements into an energy spectrum, a pulse processor and a software analyzer to collect and analyze the energy spectra [17,18,19]. The x-ray detector detects and converts x-rays into electrical pulses, the pulse processor measures the pulses to determine the energy characteristics of each x-ray, and the analyzer displays and interpretes the x-ray data. Analyzed EDS result shows the plot of x-ray counts against energy in kilo electron volt (keV).

The EDS analysis of *Ficus sycomorus* leaves was performed with JSM-6010LA analytical scanning electron microscope (SEM) instrument (JOEL Technologies, USA) which has an EDS system integrated into it. The EDS was performed to ascertain the compound composition of *Ficus sycomorus* leaves and the EDS result is shown in Fig. 1.

A close examination of Fig. 1 confirms the presence of the hetero-atoms of oxygen, sulphur and phosphate which authenticates the leave extract to be a good and efficient inhibitor.

A brief summary of the EDS result is shown in Table 1. Oxygen has atomic and mass percentage of 33.84% and 39.63% respectively, sulphur has atomic and mass percentage of 0.06 % and 0.14% respectively, while phosphate has atomic and mass percentage of 0.05 and 0.12% respectively.

Table 1. EDS of *Ficus sycomorus* leaf showing mass and atomic % content

Element	Mass %	Atomic %
C	57.00	64.83
O	39.63	33.84
Na	0.09	0.05
mg	0.12	0.07
Al	0.04	0.02
Si	0.74	0.36
P	0.12	0.05
S	0.14	0.06
Cl	0.00	0.00
K	0.13	0.04
Ca	1.83	0.62
Fe	0.16	0.04
Hg	0.00	0.00
Total	100.00	100.00

3.2 Weight Loss Measurements

Weight loss measurements were taken to evaluate the effectiveness of *Ficus sycomorus* leaves extracts 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° is shown Figs. 2 and 3.

A close inspection of Figs. 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 Figs. 4 and 5. An inspection of the plots (Figs. 4 and 5) show that the leaves extracts of *Ficus sycomorus* inhibited the corrosion of mild steel and aluminium in 1 M of HCL.

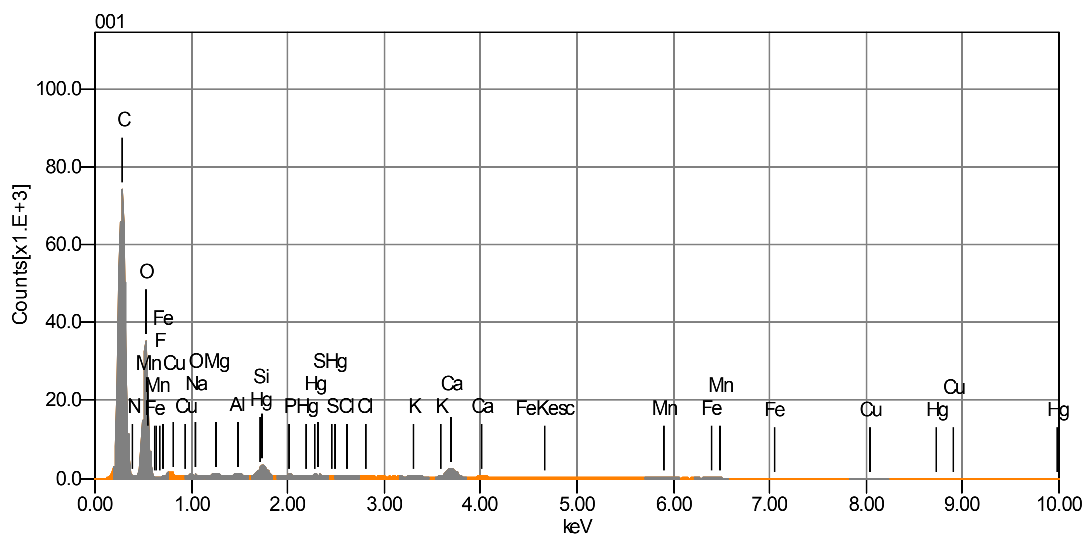

Fig. 1. EDS Micrograph of ground *Ficus Sycomorus* leaves

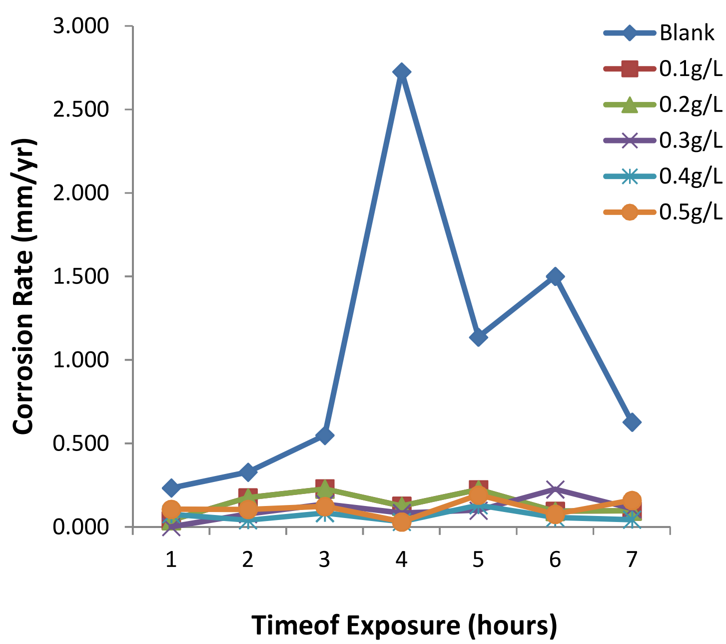

Fig. 2. Variation with time of the corrosion rate of Aluminium in 1 M of HCl for various concentrations of *Ficus sycomorus* at 30°C temperature

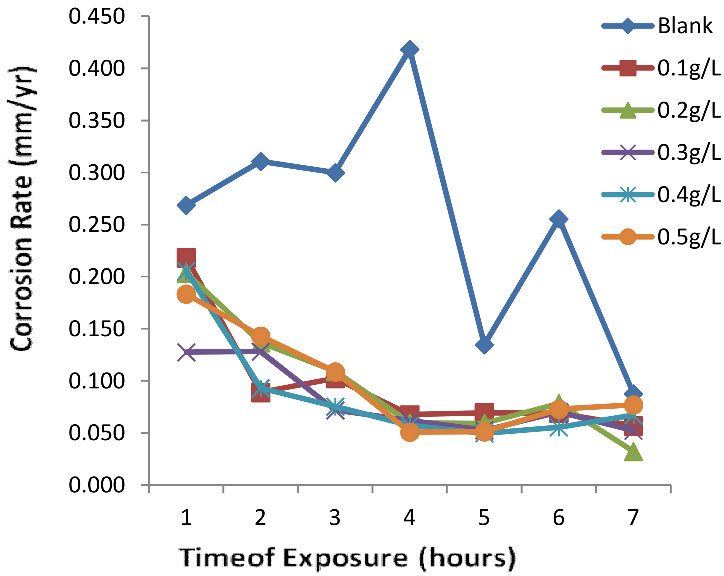

Fig. 3. Variation with time of the corrosion rate of mild Steel in 1 M of HCl for various concentrations of *Ficus sycomorus* at 30°C temperature

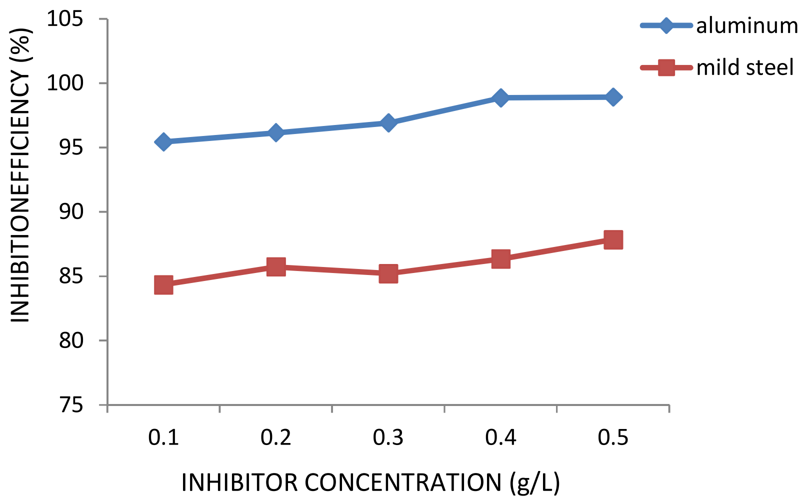

Fig. 4. Inhibition efficiency of *Ficus sycomorus* extracts in 1 M HCl on aluminum and mild steel against concentration of inhibitor at 30°C

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 [20]. The inhibition efficiency of the leaf extract of *Ficus sycomorus* in 1 M HCl was investigated at various concentrations. Fig. 4 shows the plot of inhibition efficiency against concentration of inhibitor at 30°C.

Inspection of the plots (Figs. 4 and 5) revealed that the corrosion rates of aluminium and mild steel in 1 M of HCl solution were reduced upon the introduction of *Ficus sycomorus* leaves extracts 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°C, inhibition efficiency of

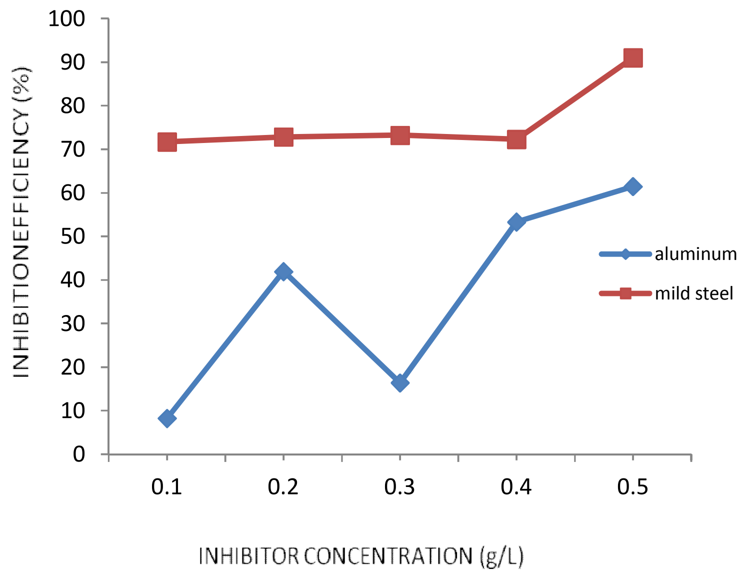

Fig. 5. Inhibition efficiency of *Ficus sycomorus* extracts in 1 M HCl on aluminium and mild steel against concentration at 60°C

98.92% was obtained for aluminum at 0.5 g/L concentration after 4 hours of exposure in 1 M HCl as shown in Fig. 4. For mild steel, inhibition efficiency of 87.84% was obtained at 0.5 g/L concentration as shown in Fig. 8. However, at higher temperature of 60°C, 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 [6].

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 [21]. 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 [15].

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

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

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

Figs. 6 and 7 show the Langmuir plot of $\frac{C}{\theta}$ against C for aluminium and mild steel at 30°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 2, 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.

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

$$\theta = \frac{1}{f}\ln(K_{ads}C) \quad (5)$$

where θ is the surface coverage, *f* determines the adsorbent-adsorbate interaction and K_{ads} is the equilibrium constant employed in calculating the Gibb's free energy of adsorption ($\Delta G°_{ads}$).

$$\Delta G^0_{ads} = -RT\ln(55.5K_{ads}) \quad (6)$$

where R is the gas constant with value of 8.314 kJ/mol and T is the temperature in Kelvin. 55.5 is the concentration of water in solution in mol/l [1].

Figs. 8 and 9 show the plot of θ against *In C* for aluminium and mild steel at 30°C. The graphs show that at 30°C, 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 ($\Delta G°_{ads}$) as shown in Tables 2 and 3, have negative values. This indicates that the adsorption of *Ficus sycomorus* on the metal surface follows a spontaneous process [22]. Tables 2 and 3 show positive values for the adsorbent-adsorbate interaction term (*f*), this implies that there exist lateral forces of attraction between the inhibitor's extract molecule and the adsorption layer.

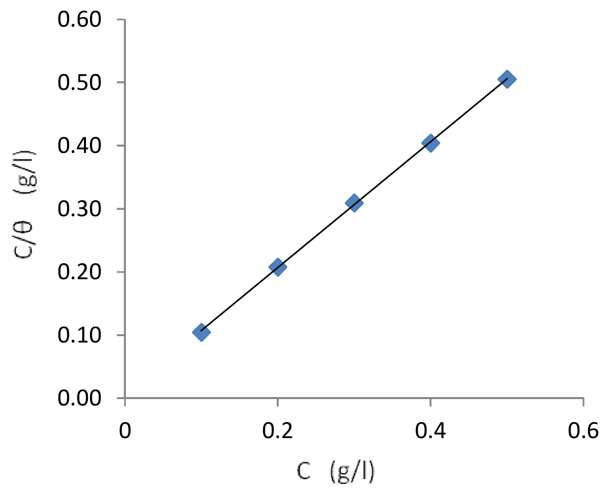

Fig. 6. Langmuir isotherm for *Ficus sycomorus* adsorption on aluminum in 1 M HCl at 30°C

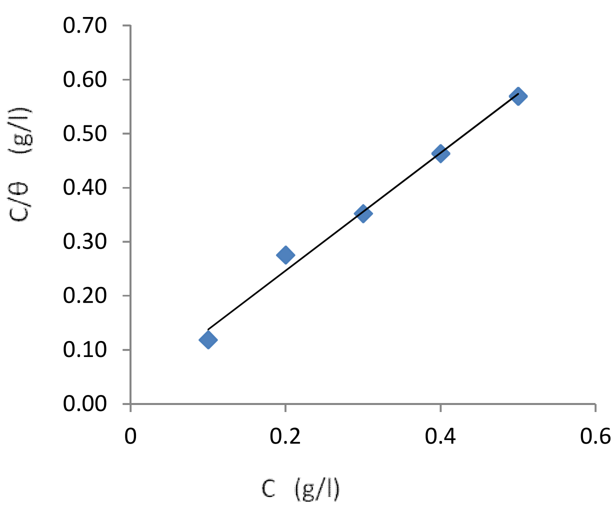

Fig. 7. Langmuir isotherm for *Ficus sycomorus* adsorption on mild steel in 1 M HCl at 30°C

A large value of K_{ads} is associated with a high value of inhibition efficiency [8]. From Tables 2 and 3, we can observe that the value of K_{ads} for aluminium is greater than that of mild steel. This indicates a stronger adsorption of the inhibitor extracts on aluminium's surface than that of mild steel.

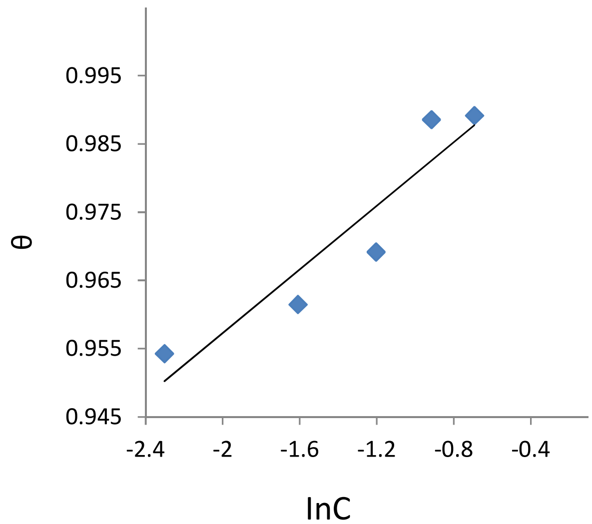

Fig. 8. Temkin isotherm for *Ficus sycomorus* adsorption aluminum in 1 M HCl at 30°C

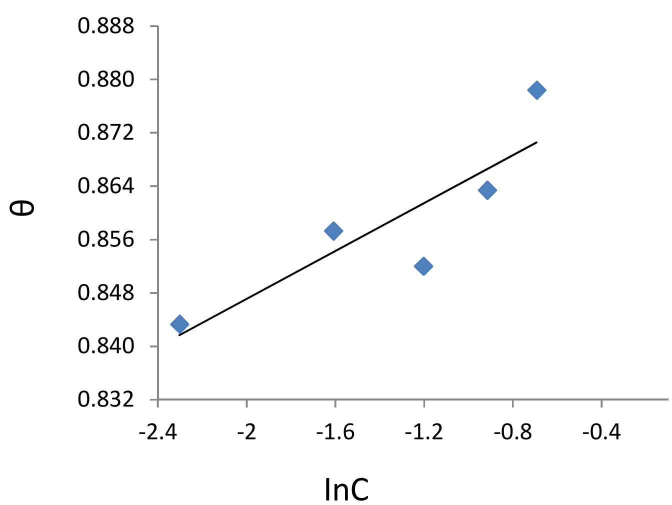

Fig. 9. Temkin isotherm for *Ficus sycomorus* adsorption on mild steel in 1 M HCl at 30°C

Table 2. Adsorption isotherms parameters obtained from the corrosion data for mild steel in 1 M HCl containing *Ficus sycomorus* leaf extract at 30°C

Isotherm	Mild steel					
	Intercept	Slope	*f*	K_{ads}	R^2	$\Delta G°_{ads}$ (kJ/Mol)
Langmuir	0.029	1.089	_	34.48	0.989	-19.027
Temkin	0.883	0.018	55.56	1.016	0.751	-10.153

Table 3. Adsorption isotherms parameters obtained from the corrosion data for aluminium in 1 M HCl containing *Ficus sycomorus* leaf extract at 30°C

Isotherm	Aluminum					
	Intercept	Slope	*f*	K_{ads}	R^2	$\Delta G°_{ads}$ (kJ/Mol)
Langmuir	0.007	0.997	_	142.86	0.999	-22.606
Temkin	1.003	0.023	43.48	1.023	0.876	-10.170

4. 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 1 M 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 0.5 g/l for mild steel and aluminium respectively.
3. The free energy of adsorption ($\Delta G°_{ads}$) has negative values. This indicates that the adsorption of *Ficus sycomorus* on the metal surface follows a spontaneous process.
4. Results obtained show that *Ficus sycomorus* leaves extracts is a good and efficient inhibitor and can be employed in oil and gas industries for processes such as acid pickling of steel, oil well acidizing etc.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Nnanna LA, Owate IO, Oguzie EE. Inhibition of mild steel corrosion in HCL solution by *Petaclethra macrophylla* bentham extract. Int'l Journ. of Mat. Eng. 2014;4(5):171-179.
2. Dariva CG, Galio AF. Corrosion inhibitors principle, mechanisms and applications. Intech Publisher. 2014;365-380.
3. Sethuraman MG, Raja PB. Corrosion inhibition of mild steel by *Datura metel* in acidic medium. Pig. Resin Tech. 2008; 34(6):327-331.
4. Sastri VS. Corrosion inhibitors. Principles and Applications. 1st Ed. New York: J. Wiley; 1998.
5. Fragoza-Mar L, Olivares-Xometi O, Dominguez-Aguilar MA, Arellanes-Lozada P, Jimenez-Cruz F. Corrosion Inhibitor activity of 1,3-diketone malonates for mild steel in aqueous hydrochloric acid solution. Corrosion Science. 2012;61:171-84.
6. Nnanna LA, Owate IO. Electrochemical study of corrosion inhibition of mild steel in acidic solution using *Gnetum africana* leaves extract. British Journal of Applied Science and Technology. 2015;54:2231-0843.
7. Ulaeto SB, Ekpe UJ, Chidiebere MA, Oguzie EE. Corrosion inhibition of mild steel in hydrochloric acid by acid extract of *Eichhornia crassipes*. Int'l Journal of Materials and Chemistry. 2012;2(4):158-164.
8. Odewunmi NA, Umoren SA, Gasem ZM. Utilization of watermelon (*Citrullus lanatus)* rind extract as a green corrosion inhibitor for mild steel in acidic media Journal of Ind. and Eng. Chem. 2015;21:239-247.
9. Al-Mhyawi SR. Inhibition of mild steel corrosion using *Juniperus* plants as green inhibitor. Afri. Journ. of Pure and Applied Chemistry. 2014;8(1):9-22.
10. Okafor PC, Ebenso EE, Ekpe UJ. *Azadirachta Indica* extract as corrosion Inhibitor for mild steel in acidic medium. Int'l Journal of Electrochemical Science. 2010;5:114-122.
11. Mohamed H, Mohd. jain K. Electrochemical studies of mild steel corrosion inhibition in aqueous solution by *Uncaria Gambir* extract. Journal of Physical Science. 2010;21(1):1-13.
12. Ekanem UF, Umoren SA, Udousoro SA, Udoh AP. Inhibition of mild steel corrosion in hcl using pineapple (*Ananas comosus)* Leaves Extract. Journal of Material Science. 2010;45:5558-5566.
13. Satapathy AK, Gunasekaran G, Sahoo SC, Amit K, Rodrigues PV. Corrosion

inhibition by *Justicia gendarussa* plant extract in hydrochloric acid solution. Corrosion Science. 2009;51:2848-2856.
14. Oguzie EE. Inhibition of acid corrosion of mild steel by *Telfaria occidentalis* extract. Pigment Resin Tech. 2005;34(6):321-326.
15. Ejikeme PM, Umana SG, Menkiti MC, Onukwuli OD. Inhibition of mild steel and aluminium in 1M H_2SO_4 by leaves extract of African Breadfruit. Int'l Journ. of Mat. and Chem. 2015;5(1):14-23.
16. Orwa C, Mutua A, Kindt R, Jamnadass R, Anthony S. Agroforestree database: A tree reference and selection guide version; 2009. Available:http://www.worldagroforestry.org/sites/treedbs/treedatabases.asp (Retrieved on 30/11/2016)
17. Reimer L. Scanning electron microscopy: Physics of image formation and microanalysis. 2nd Ed. Springer; 1998.
18. Goldstein J. Scanning electron microscopy and x-ray microanalysis. Kluer Academic/ Plenium Publishers; 2003.
19. John G. Energy dispersive X-ray spectroscopy. University of Minnesota. Available:http://serc.carleton/geochemsheets/edu.html (Retrieved on 15/03/2017)
20. Chidiebere MA, Ogukwe KI, Oguzie CN, Eneh CN, Oguzie EE. Corrosion inhibition and adsorption behavior of *Punica granatum* extract on mild steel in acidic environments: Experimental and theoretical studies. Ind. and Eng. Chem. Res. 2012;51(2):668–677.
21. Popova A, Sokolova E, Raicheva S, Christov M. AC and DC study of temperature effect on mild steel corrosion in acidic media in the presence of benzimidazole derivatives. Corrosion Sci. 2003;45:33-58.
22. Ehteram AN, Aisha HA. Thermodynamic study of metal corrosion and inhibitor adsorption process in mild steel/1-methyl-4/hydrochloric acid systems. Materials Chemistry and Physics. 2008; 110:145-154.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/19149