

Corrosion Inhibitory Properties of Vernonia Amygdalina Stem Extract in 0.1 M H₂SO₄ Solution

¹Olawale Olamide, ²Adediran Adeolu and ³Talabi Segun Isaac

¹Department of Chemical Engineering, College of Science and Engineering,

²Department of Mechanical Engineering, College of Science and Engineering, Landmark University, Omu-Aran, Kwara State, Nigeria

³Department of Materials and Metallurgical Engineering, University of Ilorin, Ilorin, Nigeria

Key words: Adsorption, inhibition, H₂SO₄, *Vernonia amygdalina*, carbon steel, corrosion

Abstract: The inhibition potential of Vernonia Amygdalina Stem Extract (VASE) on the corrosion of mild Carbon Steel (CS) immersed in 0.1M H₂SO₄ solution containing varied concentration of the inhibitor was reported. Corrosion rate measurements, inhibition efficiency, FT-IR spectroscopy and Scanning Electron Microscopic analysis (SEM) were used to assess the inhibitory properties of the extract. The highest inhibition efficiency of 97% was attained when 0.8 g L⁻¹ of VASE was added to the acidic medium. The inhibitive ability of the extract was adjudged to be due to the presence of alkanoids, saponins, tannins, flavonoids and phytate as indicated by the functional groups detected with FTIR analysis. The surface morphology of the corroded samples as revealed by SEM showed the formation of protective oxide layer. Furthermore, the adsorption process between the inhibitor molecules and metal surface obeyed Langmuir isotherm model and indicate a physisorption mechanism. Consequently, the extract is recommended as a safe, cheap and efficient corrosion inhibitor for mild carbon steel in acidic environment.

Corresponding Author:

Olawale Olamide

Department of Chemical Engineering, College of Science and Engineering, Landmark University, Omu-Aran, Kwara State, Nigeria

Page No.: 3089-3094

Volume: 15, Issue 16, 2020

ISSN: 1816-949x

Journal of Engineering and Applied Sciences

Copy Right: Medwell Publications

INTRODUCTION

In manufacturing, metallurgical, chemical and petrochemical industries, inhibitors have proven to be proficient and economical in mitigating corrosion^[1,2]. This has led to prolonged material's shelf life, reduction in maintenance and parts replacement. Inorganic and organic compounds with high inhibition efficiency have been deployed to protect against corrosion. However, the high cost associated with synthetic inhibitors is a major challenge. Besides, the toxic nature of these substances

poses challenges to health and the environment^[3, 4]. Recently, increased awareness has led to the establishment of regulations and legislations to protect the environment against the use of such materials. Therefore, there is need to source for low cost alternative materials that can serve as effective inhibitors, which must be non-toxic and environmentally friendly^[5]. Plant based inhibitors have been explored as likely alternatives. The choice of plant is informed by several desirable characteristics such as processing route, biodegradability, availability and non-toxicity characteristics^[6]. Some of the

plants that have been reported to have inhibitory properties in acidic environment include, Aloe vera plant extract^[7]; *Psidium guajava*^[5]; Jatropha stem extract; *Moringa oleifera*; *Chromolaena odorata*^[8]; Bamboo leaf^[9]; Banana peels^[6]; Watermelon^[10]; *Vernonia amygdalina* extract^[4, 11-13]; *Sida acuta*^[14]; *Nauclea latifolia*^[15]. The phytochemical screening of these plants revealed the presence of substances such as oxalate, phytate, tannins, saponins, flavonoids, etc. These compounds are generally adjudged to be responsible for their inhibitive characteristics to metals corrosion^[16].

More specifically, Okafor *et al.*^[15] have shown that *Vernonia amygdalina* leaf extract exhibit infinitive effect for Al-alloy and mild steel using weight loss and gasometric measurement techniques. However, the present study focused on *Vernonia amygdalina* stem. The corrosion inhibition effect of VASE in 0.1 M H₂SO₄ as a corrosive medium was studied at 30°C.

MATERIALS AND METHODS

Mild steel sheet with the following elemental composition (Fe = 99.4%, C = 0.2%, P = 0.024%, Mn = 0.35%, Si = 0.003%) was used for this study. It was mechanically cut to coupons of dimension 5.0×4.0 cm and then polished using different grades of silicon carbide papers (400, 600, 800,1200 grits). The surface treatment was done using the method described by Olawale *et al.*^[4]. Prepared samples were stored in the desiccator while the experiments were carried out under non-stirred and aerated conditions.

Extract preparation: About 4 kg of fresh stems (*Vernonia amygdalina*) was sun dried for 28 days to completely remove the moisture content. The stems were then grounded into powder and sieved (75 μm). The 20 g of the powdered material was soaked in 700 mL ethanol solution and kept inside a desiccator to prevent evaporation for a period of 24 h and filtered. Finally, the filtrate was heated at 80°C for 25 min inside a rotary evaporator to remove the ethanol. FT-IR (Shimadzu, model IR AFFINITY, IS FTIR) was used to determine the functional groups responsible for the inhibition.

Corrosion rate and inhibition efficiency measurement: For the corrosion experiment, the mild steel coupons were totally immersed in 250 mL capacity beakers containing 100 mL of 1M H₂SO₄ solution. The initial weight of the mild steel coupons was taken before they were immersed in the acid solution with and without the added inhibitor. To achieve total coverage, the coupons were suspended in the beaker with the aid of rod and hook. The experiments were conducted with 0.2-0.8 g L⁻¹ inhibitor concentration addition to the corrosion medium at ambient temperature

during a total period of 360 h (15 days). The weight of the specimens after immersion was taken at every 72 h (3 days) using electronic weighing balance (HX 302T with 0.01 g accuracy). The experiment was carried out in duplicate to ensure reproducibility. The Corrosion Rate (CR) and Inhibition Efficiency (I.E) were calculated using Eq. 1 and 2:

$$CR = \frac{\Delta W}{AT} = \frac{W_1 - W_2}{AT} \quad (1)$$

$$I.E(\%) = \left(\frac{CR_1 - CR_2}{CR_1} \right) \times 100\% \quad (2)$$

Where:

- W₁ = The mild steel weight before immersion
- W₂ = The mild steel weight after immersion
- A = The surface area of the coupon (cm²)
- T = The period of immersion (h)
- IE (%) = Inhibition Efficiency
- CR₁ = Corrosion rate of mild steel coupons in the absence of inhibitors
- CR₂ = The corrosion rate of mild steel coupons in the presence of concentration of inhibitors

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy analysis: The corrosion inhibition property of plant/root extract has been observed to be connected to the presence of complex organic species such as tannins, alkaloids, bases, carbohydrates, amino acids and proteins as well as hydrolysis products. These organic compounds contain polar functions with N, S and O atoms as well as conjugated double bonds or aromatic rings in their molecular structures which are the major adsorption centers^[17]. Figure 1 shows the representative FTIR spectra of the extract. The spectra showed the presence of O-H, C = O, C-O, N-H and C = C functional groups related to alkaloids, flavonoids, tannins, etc. which are known to have inhibitory properties. This observation agrees with the report on phytochemical analysis of *Vernonia amygdalina* stem extracts carried out by other researchers^[18-20]. Furthermore, the corrosion product analysis (Fig. 2) shows the presence of similar functional group and confirmed that the inhibition process occurs by adsorption process.

Corrosion rate measurements: A representative variation in the corrosion rate obtained by weight loss method at different concentrations of VASE against exposure time was presented in Fig. 1. The corrosion rate of mild carbon steel in the absence of VASE increased throughout the exposure time.

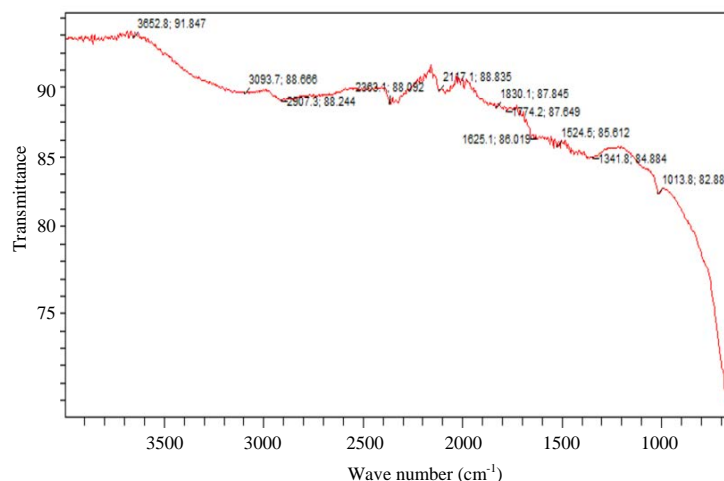


Fig. 1: FT-IR spectra of coupon without inhibition

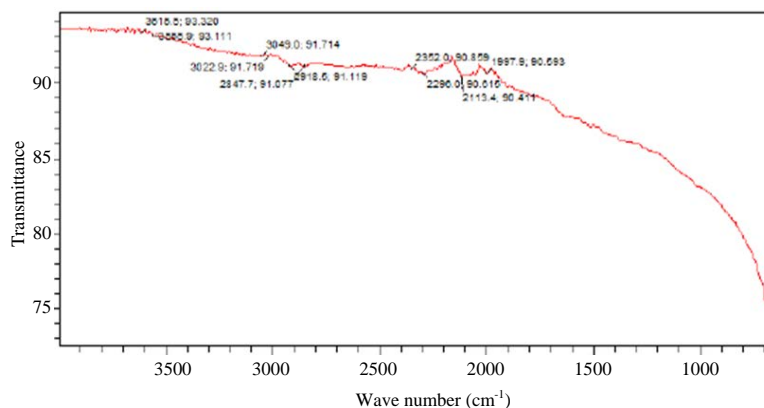


Fig. 2: FT-IR spectra of corrosion product in the presence of acidic medium

However, the samples corrosion rate was observed to decrease with increased concentration of VASE in the corrosive medium. The results indicated that the extract inhibits mild steel corrosion and its concentration determines corrosion rate as shown in Fig. 3. More importantly, the samples in the medium containing either 0.6 or 0.8 g L⁻¹ VASE show significant improvement to corrosion resistance. This trend suggests that the extract adsorption to the mild steel surface is taking place leading to increase in the thickness of oxide layer. However, the loss rates per inhibitor concentration increased gradually with exposure time after 144 h. Furthermore, the results implied that up to 0.8 g L⁻¹ VASE can be used without experiencing the protective oxide film failure.

The inhibitive efficiency of the extract was presented in Fig. 3. It is evident that I.E. increased with the inhibitor concentration throughout the considered exposure time (Fig. 3a). This may likely be due to protective oxide growth which led to a better surface coverage. The

adsorbed film prevents a direct attack by the aggressive environment and protects the metal from rapid loss. Moreover, the effect of VASE was more pronounced with the addition of 0.6 g L⁻¹ to the corrosion medium (Fig. 3b). Moreover, the curves pattern in Fig. 3b indicated the extract inhibitive ability decreased slightly with increased exposure time. This may be attributed to the formation of discontinuous protective oxide layer as a result of the transition of metal/ solution interface. Nevertheless, some stability was observed in the corrosion medium containing 0.8 g L⁻¹ VASE. Similar trend has been reported by other authors^[21-24].

Adsorption isotherms and thermodynamics characterization: Adsorption isotherms are very useful model in understanding the interactions between inhibitor molecules and substrate surfaces. In this study, the adsorption model that best fit the θ values was found to obey Langmuir adsorption isotherm^[25]. The surface coverage (θ) for the different concentration of VASE (C)

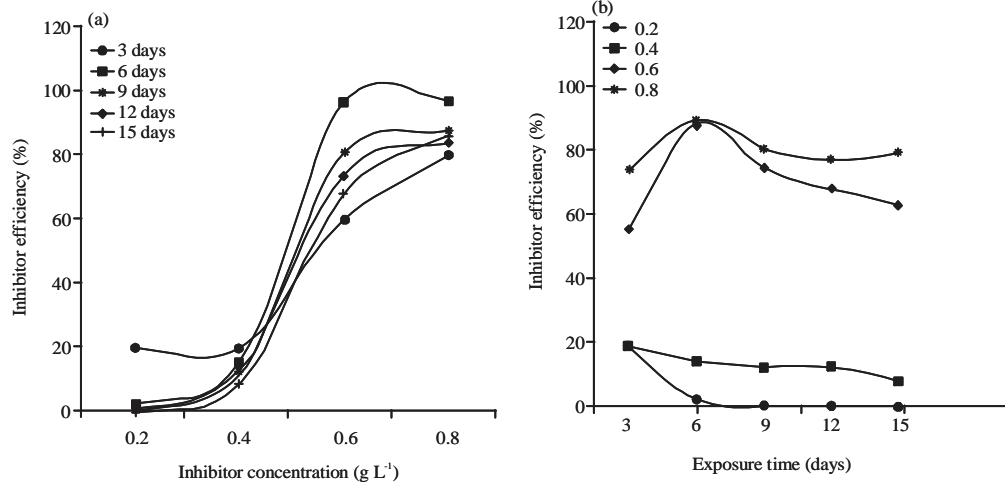


Fig. 3(a, b): Inhibition efficiency of VASE against mild steel corrosion in 0.1 M H₂SO₄ (a) Against inhibitor concentration and (b) Against exposure time

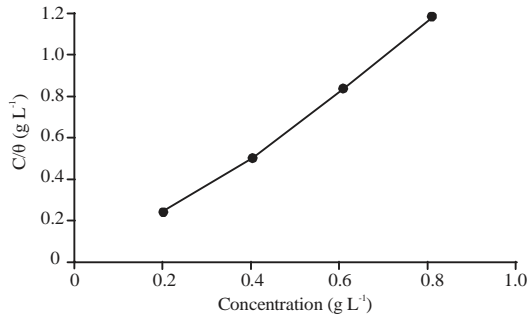


Fig. 4: Langmuir adsorption plot for mild steel in 0.1 M H₂SO₄ containing VASE at 30°C

was determined from Eq. 3. The value of C/θ was plotted against C as shown in Fig 4. Thereafter, the adsorptive equilibrium constant (K_{ads}) was determined from the inverse of the curve's intercept according to Eq. 3:

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

where, K_{ads} is the equilibrium constant of the inhibitor process. To establish the type of adsorption mechanism involved, K_{ads} value was related to the adsorption free energy (ΔG_{ads}) using Eq. 4 as reported by Khamis^[26]:

$$K_{ads} = 1/55.5 \exp(-\Delta G_{ads}/RT) \quad (4)$$

where, 55.5 is water concentration as reported by Olawale *et al.*^[4], R the universal gas constant and T is the temperature.

Firstly, a correlation coefficient >0.99 shows that the adsorption process suitably fit Langmuir isotherm. The

free energy, ΔG° is usually associated with adsorption mechanism. For >-40 kJ. mol⁻¹, a chemisorption mechanism being an electron transfer from inhibitor molecules to the substrate prevails while ΔG° was <-20 kJ mol⁻¹ indicate physical adsorption mechanism^[27]. The Langmuir adsorption parameters obtained at 30°C are presented in Table 1. The free energy adsorption value (-15.78 kJ mol⁻¹) suggests a spontaneous adsorption process. Hence, the extract adsorption process is consistent with physisorption mechanism. The adsorption is due to the electrostatic interactions between the charged inhibitor molecules and the metal involved.

SEM analysis: To further corroborate the earlier mentioned observations, surface morphology of the corroded samples with and without VASE was observed through a scanning electron microscope. The differences in the surface micrograph can be used to indicate the corrosion mechanism.

A representative SEM images showing the substrate exposed to 0.1 M H₂SO₄ without and with the addition of 0.8 g L⁻¹ VASE are shown in Fig. 5. The image in Fig. 6a shows corrosion products which uniformly covers the metal surface. This indicated that uniform corrosion occurs in the absence of the inhibitor. The effect of VASE, acting as protective layer can be seen on the specimen surface. It is clear that the oxide layer uniformly cover the metal surface protecting it against rapid corrosion compared to the inhibitor-free solution. A similar trend was observed by Debi *et al.*^[13]. However, after 360 h, the adherence/efficiency of the oxide layer appears to reduce as seen by the swell-like portion of the SEM image in Fig. 5b.

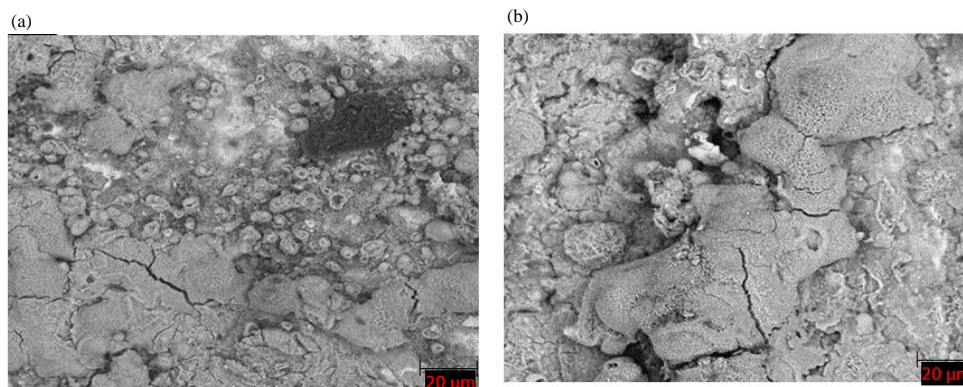


Fig. 5(a, b): SEM images of mild steel coupon in 0.1M H₂SO₄ solution in and absence of inhibitors after 360 h (a) Without inhibitor and (b) With inhibitor

Table 1: Some parameters from Langmuir isotherm

Method	Temperature	ΔG_{ads} (kJ mol ⁻¹)	Slope	K_{ads} (g L ⁻¹)	R ²
Weight loss	30°C	-15.78	1.603	9.470	0.994

R² = Correlation coefficient

CONCLUSION

From the experimental results, the following can be drawn: Vernonia Amygdalina Stem Extract (VASE) was found to inhibit the corrosion of mild carbon steel in 0.1 M H₂SO₄ solution. Inhibitor efficiency increased with the concentration of VASE up to 0.6 g L⁻¹. The inhibition efficiency increases with increase in extract concentration and the effect become pronounced with the addition of 0.6 g L⁻¹ VASE. The highest inhibition efficiency of 97% was obtained with the addition of 0.8 g L⁻¹ VASE after 6 days. The adsorption model described with Langmuir adsorption isotherms indicate physisorption mechanism. All the techniques employed are in good agreement showing that VASE is an efficient inhibitor to control mild steel corrosion in 0.1 M H₂SO₄ within the concentration range investigated in this study.

REFERENCES

- Ahamad, I. and M.A. Quraishi, 2009. Bis (benzimidazol-2-yl) disulphide: An efficient water soluble inhibitor for corrosion of mild steel in acid media. *Corros. Sci.*, 51: 2006-2013.
- Avdeev, Y.G., Y.I. Kuznetsov and A.K. Buryak, 2013. Inhibition of steel corrosion by unsaturated aldehydes in solutions of mineral acids. *Corrosion Sci.*, 69: 50-60.
- Abiola, O.K., M.O. John, P.O. Asekunowo, P.C. Okafor and O.O. James, 2011. 3-[(4-amino-2-methyl-5-pyrimidinyl) methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride as green corrosion inhibitor of copper in HNO₃ solution and its adsorption characteristics. *Green Chem. Lett. Rev.*, 4: 273-279.
- Olawale, O., A.A. Adediran, S.I. Talabi, G.C. Nwokocha and A.O. Ameh, 2017. Inhibitory action of Vernonia Amygdalina Extract (VAE) on the corrosion of carbon steel in acidic medium. *J. Electrochem. Sci. Eng.*, 7: 145-152.
- Victoria, S.N., R. Prasad and R. Manivannan, 2015. *Psidium guajava* leaf extract as green corrosion inhibitor for mild steel in phosphoric acid. *Int. J. Electrochem. Sci.*, 10: 2220-2238.
- Ji, G., S. Anjum, S. Sundaram and R. Prakash, 2015. Musa paradisica peel extract as green corrosion inhibitor for mild steel in HCl solution. *Corros. Sci.*, 90: 107-117.
- Mehdipour, M., B. Ramezanzadeh and S.Y. Arman, 2015. Electrochemical noise investigation of Aloe plant extract as green inhibitor on the corrosion of stainless steel in 1 M H₂SO₄. *J. Ind. Eng. Chem.*, 21: 318-327.
- Obot, I.B., E.E. Ebenso and Z.M. Gasem, 2012. Eco-friendly corrosion inhibitors: Adsorption and inhibitive action of ethanol extracts of *Chlomolaena odorata* L. for the corrosion of mild steel in H₂SO₄ solutions. *Intl. J. Electrochem. Sci.*, 7: 1997-2008.
- Li, X., S. Deng, H. Fu and X. Xie, 2014. Synergistic inhibition effects of bamboo leaf extract/major components and iodide ion on the corrosion of steel in H₃PO₄ solution.
- Odewunmi, N.A., S.A. Umoren and Z.M. Gasem, 2015. Watermelon waste products as green corrosion inhibitors for mild steel in HCl solution. *J. Environ. Chem. Eng.*, 3: 286-296.
- Corros. Sci.*, 78: 29-42. Loto, C.A., 2003. The effect of bitter leaf extract on the inhibition of mild steel in HCl and H₂SO₄. *Corros. Prev. Control*, 50: 43-49.
- Avwiri, G.O. and F.O. Igho, 2003. Inhibitive action of *Vernonia amygdalina* on the corrosion of aluminum alloys in acidic media. *Mater. Lett.*, 57: 3705-3711.

13. Debi, G.E., H. Esah, I. Mohammad, S.A. Asipita, M. Neelam and M. Aminu, 2013. Effect of *Vernonia amygdalina* extract on corrosion inhibition of mild steel in simulated seawater. Aust. J. Basic Applied Sci., 7: 257-263.
14. Umoren, S.A., U.M. Eduok, M.M. Solomon and A.P. Udoh, 2016. Corrosion inhibition by leaves and stem extracts of *Sida acuta* for mild steel in 1 M H₂SO₄ solutions investigated by chemical and spectroscopic techniques. Arabian J. Chem., 9: S209-S224.
15. Okafor, P.C., M.E. Ikpi, U.I. Ekanem and E.E. Ebenso, 2013. Effects of extracts from *Nauclea latifolia* on the dissolution of carbon steel in H₂SO₄ solutions. Int. J. Electrochem. Sci., 8: 12278-12286.
16. Helen, L.Y.S., A.A. Rahim, B. Saad, M.I. Saleh and P.B. Raja, 2014. *Aquilaria crassna* leaves extracts-a green corrosion inhibitor for mild steel in 1 M HCl medium. Int. J. Electrochem. Sci., 9: 830-846.
17. Deng, S. and X. Li, 2012. Inhibition by Ginkgo leaves extract of the corrosion of steel in HCl and H₂SO₄ solutions. Corros. Sci., 55: 407-415.
18. Dongmo, F., E. Oben, N. Momo and E. Mandob, 2007. Phytochemical constituents and antioxidant potential of some Cameroonian medicinal plants. Pharmacologyonline, 2: 436-452.
19. Oyeleke, G.O., J.O. Odedeji, A.D. Ishola and O. Afolabi, 2014. Phytochemical screening and nutritional evaluation of African oil bean (*Pentaclethra macrophylla*) seeds. IOSR. J. Environ. Sci. Toxicol. Food Technol., 8: 14-17.
20. Nnanna, L., G. Nnanna, J. Nnakaife and P. Eti, 2016. Aqueous extracts of *Pentaclethra macrophylla* bentham roots as eco-friendly corrosion inhibition for mild steel in 0.5 M KOH medium. Int. J. Mater. Chem., 6: 12-18.
21. Abiola, O.K., 2007. Organic Corrosion Inhibitor for Steel and Aluminium in Acid Systems. Nova Science Publishers, Hauppauge, New York, USA.,.
22. Noor, E.A. and A.H. Al-Moubaraki, 2008. Corrosion behavior of mild steel in hydrochloric acid solutions. Int. J. Electrochem. Sci., 3: 806-818.
23. Ajanaku, K.O., C.O. Ajanaku, A.A. Akinsiku, A. Falomo, A. Edobor-Osoh and M.O. John, 2012. Eco-friendly Impact of *Vernonia amygdalina* as corrosion inhibitor on Aluminium in acidic media. Chem. J., 2: 153-157.
24. Ajanaku, K.O., O. Aladesuyi, C.O. Ajanaku, E.A. Adedapo, A.A. Akinsiku and F.E. Sodiya, 2015. Adsorption properties of *Azadirachta indica* extract on corrosion of Aluminium in 1.85M Hydrochloric acid. J. Int. Assoc. Adv. Technol. Sci., 16: 1-11.
25. Langmuir, I., 1917. The constitution and fundamental properties of solids and liquids. II. Liquids. J. Am. Chem. Soc., 39: 1848-1906.
26. Khamis, E., 1990. The effect of temperature on the acidic dissolution of steel in the presence of inhibitors. Corrosion, 46: 476-484.
27. Soltani, N., N. Tavakkoli, M.K. Kashani, A. Mosavizadeh, E.E. Oguzie and M.R. Jalali, 2014. *Silybum marianum* extract as a natural source inhibitor for 304 stainless steel corrosion in 1.0 M HCl. J. Ind. Eng. Chem., 20: 3217-3227.