Original Article

Study of corrosion inhibition of Aluminum in nitric acid solution using Anisaldehyde (4-methoxy benzaldehyde) as inhibitor

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ABSTRACT

The inhibitive action of Anisaldehyde (4–methoxy benzaldehyde) on corrosion of Aluminum in nitric acid solution was studied through weight loss method. Fourier Transform Infrared Spectroscopic Analysis (FTIR) was used to characterize the inhibitor and the corrosion product. The effect of different inhibitor concentrations was studied at 308, 313 and 318 K. The present study showed that the percentage of inhibition efficiency (% I.E.) is enhanced with increase of inhibitor concentration and decrease with rising in temperature. Maximum I.E. of Anisaldehyde was found 86.32 % at 308 K and 0.1M inhibitor concentration in 1.4M HNO_3 solution. The inhibitive action of the inhibitor is discussed in view of adsorption of Anisaldehyde molecule on the metal surface. It was found that the adsorption of the inhibitor on the metal surface follows Langmuir adsorption isotherm. Activation parameters governing the adsorption process were evaluated and discussed in detail.

1. Introduction

Corrosion is the damage to metal as a result of reaction with its environment; damage is specified on purpose to exclude processes, like anodizing of Aluminum, chemical milling and bluing of steel, which modify the metal intentionally. Rusting is a type of corrosion but it is the corrosion of ferrous metals (irons and steels) only, producing that familiar brownish-red corrosion product called rust [1]. Corrosion is a natural process for metals that causes them to react with their environment to become more stable compounds [2]. Aluminum is among the most commonly used metal in the world. Its lightness coupled with its strength, conductivity, barrier properties and its excellent corrosion resistance has all been its most important advantages and the main reasons for the continual growth in the usage of Aluminum [3]. Impure Aluminum has very good corrosion resistance in most environments. This is normally because Aluminum forms a thin, but effective oxide layer that prevents further oxidation. However, the oxide layer dissolve at a pH less than 4 or greater than 9,

thus leading to the rapid corro-sion of Aluminum [4]. Mineral acids and strong alkaline solutions are thus very corrosive for Alumi-num. Acidic solutions are used for pickling, chemical and electrochemical etching of Aluminum [5]. Therefore, prevention of Aluminum corrosion in acidic media has great importance. One of the most common methods to prevent metals against acid corrosion is the use of organic compounds containing functional groups, heteroatoms such as (P, S, N and O), and pi electrons in their structure, as corrosion inhibitors [6]. Corrosion inhibitor is a chemical added to the corrosive environment in small quantity, so that they can adsorb on the metal surface to block the active sites on the surface, thus reduce the corro-sion rate. Certain inhibitors interfere with the anode reaction, some with the cathode reaction, and some with both [7]. They are normally used to prevent general corrosion but majority are not effective in preventing localized attack, like pitting corrosion, crevice, or stress cracking corrosion. Inhibitors usually interact with the metal surface in some way to form a protective film of adsorbed inhibitor [8,9]. These inhibitors are commonly used in acids solution, although a few functions in neutral or alka-line solutions. Several organic compounds have been evaluated as corrosion inhibitors for Aluminum in acidic media, so, this work aims to study the inhibiting effect of Anisaldehyde for the corrosion of Aluminum in 1.4M HNO^3 by using weight loss method. However, the inhibitor and the corrosion product were characterized by FTIR analysis.

2. Materials and Methods

2.1. Specimen Preparation

Pure Aluminium metal (purity 99.5 %) obtained from Metal Focus Fabrication Technology Incubation Centre Kano State, Nigeria, was used for the study. Each sheet was about 0.1 cm thickness and was mechanically press cut into 2 cm x 3 cm coupons. These coupons were with different grade emery pa-per. They were also degreased in absolute ethanol, rinsed in acetone, air-dried at room temperature and stored in a desiccator devoid of

moisture before use in corrosion studies.

2.2. Preparation of Solutions

Nitric acid with percentage purity (68%) and density (1.51 g/L) was used as corrosive solution. The stock solution was used to prepare 1.4 M concentration by diluting analytical grade of HNO_3 using double distilled water. Anisaldehyde (4–methoxy benzaldehyde) with percentage purity (98%) and density ($1.11 g/cm^3$), thus, concentrations of the inhibitor used for the study were 0.02, 0.04, 0.06, 0.08 and 0.1M. Each of these concentrations was diluted in the prepared desired concentrations of acids for use as test solutions in weight loss.

2.3. Weight loss measurement

For weight loss experiment, the prepared Aluminium coupons were each suspended completely in 1.4 M HNO_3 solutions without and with different concentrations of Anisaldehyde with the help of glass hooks at 308 K for 3h. The volume of solution kept 100 cm^3, the coupons are retrieved after 3h, washed by distilled water, dried well and reweighed. From the weight loss data, corrosion rate in mg/cm^2 was calculated.

2.4. Temperature effect

To study the effect of temperature on corrosion rate, the prepared Aluminium coupons were complete-ly immersed in 100 cm3 of 1.4 M HNO_3 solution without and with different concentrations of Anisal-dehyde at 308, 313 and 318 K for 3h.

2.5. Fourier Transform Infrared Spectroscopic Analysis

FTIR analysis of the fresh inhibitor and that of the corrosion product obtained from the reaction of Aluminum immersed in 1.4 M HNO_3 for 3h immersion time in the presence of 0.1 M inhibitor at 308 K were carried out using Agilent Technology, FTIR (Cary 630) Fourier Transform Infrared Spectro-photometer. 650 – 4000 cm^{-1} wave number was used to scan the sample during the analysis.

3. Results and discussion

3.1. Weight loss experiments

The weight loss and corrosion rate of Aluminum in 1.4 M of HNO_3 solution without and with 0.02, 0.04, 0.06, 0.08 and 0.10M concentration of Anisaldehyde for an exposure period of 3h was calculated from the weight loss data using following equation:

$$\Delta W = W1 - W2 \qquad (1)$$

Where W1 and W2 are the weight of coupons before and after immersion

$$C_R \ (mg/cm^2 h^{-1}) =$$

$$\frac{\text{Weight loss (g)}}{\text{Metal surface area (cm}^2) \times \text{Time (hrs)}} \qquad (2)$$

The degree of surface coverage (Θ) and inhibition efficiency (I.E.) for different concentrations of the inhibitor in acidic media have been evaluated from weight loss experiments using the equations below:

$$\Theta = \frac{W_0 - W}{W_0} \qquad (3)$$

$$I.E \ (\%) = \frac{W_0 - W}{W_0} \times 100 \qquad (4)$$

Where WO and W are the weight of the coupon in the absence and presence of inhibitor.

3.2. Effect of inhibitor on corrosion rate and inhibition efficiency

Results from this study as presented in Figure 1 for the plot of corrosion rate against inhibitor concentration for Aluminum corrosion in 1.4M HNO_3 at different temperatures reveals that the corrosion rate of the metal decreases with increase in inhibitor concentrations at all studied temperature. Inspection of the result further indicates that the protection ability of the inhibitor

was concentration dependent. The corrosion rates in the presence of inhibitors were reduced indicating the inhibiting action of the compounds as inhibitors. This suggests that as the concentration of inhibitors increases, there was an increase in surface coverage of the adsorbed molecules on the Aluminum surface which provided a barrier (film) and reduced further corrosion as reported by Olasehinde et al. [10].
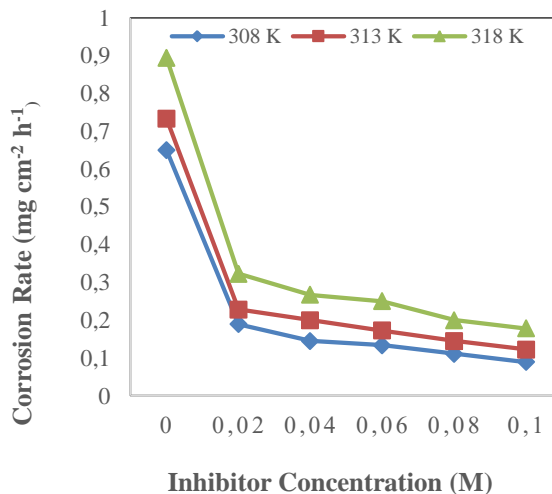

Fig 1. Variation of Corrosion Rate with Inhibitor Concentration for Al Corrosion in 1.4 M HNO_3

The surface coverage (Θ) and inhibition efficiency (% I E) were found to increase with increasing inhibitor concentration. The variation of inhibition efficiency against inhibitor concentration is shown in Figures 2. The highest inhibition efficiency was observed at the highest inhibitor concentration (0.1 M) at 308 K.
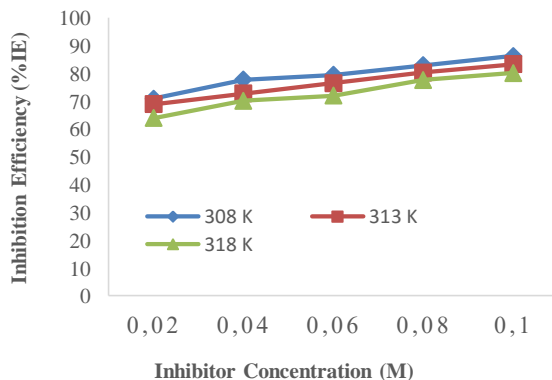

Fig 2. Variation of Inhibition Efficiency with Inhibitor Concentration for Al Corrosion in 1.4M HNO_3.

This trend was observed due to increase in surface coverage (Θ) of adsorbed specie on surface of the metal as a result of increase in inhibitor concentration. This shows that more inhibitor molecule is adsorbed on the metal surface, thus lead to increase in inhibition efficiency. A similar result was reported by Nnanna et al. [11].

3.3. Effect of Temperature on Corrosion Rate and Inhibition Efficiency

The result of the effect of temperature on the corrosion rate of Aluminum for inhibited and uninhibited solution is presented on Figure 3 at 308, 313 and 318K. From the result, it can be seen that the rate of inhibited and uninhibited solution increases with increase in temperature. It can be observed from the results that the highest corrosion rate of Aluminum was observed at the highest temperature (318 K). This observation is due to the fact that chemical reaction rates generally increase with rising temperature. Increase in temperature leads to increase in the kinetic energy possessed by the reacting molecules thereby making the molecules to overcome the energy barrier faster [12,13]. Similar work was reported by Fouda et al [14].
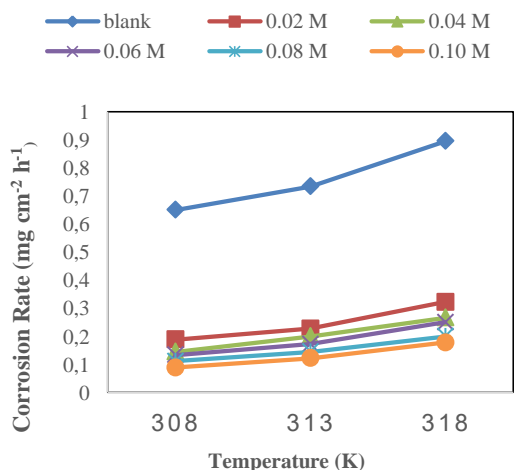

Fig 3. Variation of Corrosion Rate with Temperature for Al Corrosion in 1.4M HNO$_3$

The result of the effect of temperature on the inhibition efficiency of Aluminium at 308, 313 and 318 K is presented in Figure 4. It can be seen that from the result inhibition efficiency decreases with increase in temperature. Increase in temperature cause the desorption and destabilization of the inhibitor molecule absorbed on the metal surface and thus results in decrease of inhibition efficiency. Such behaviour suggests that investigated inhibitor was physically adsorbed on the Aluminum surface. Similar result was reported by Mohamed et al [15].
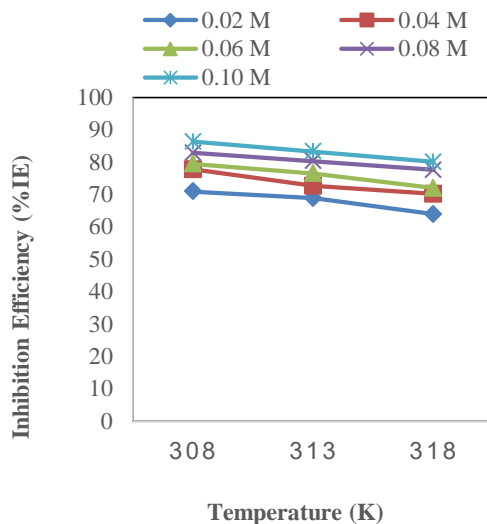

Fig 4. Variation of Inhibition Efficiency with Temperature for Al Corrosion in 1.4 M HNO$_3$

3.4. Thermodynamic Study

3.4.1. Determination of Activation Energy (Ea)

In order to elucidate the inhibitive properties of the inhibitor and the dependence of the temperature on the corrosion rates, the activation energy (Ea) for the corrosion process in the absence and presence of the studied inhibitor was calculated from Arrhenius-type plot according to the equation given below:

$$\ln(C_R) = B - \frac{E_a}{RT} \qquad (5)$$

Where Ea is the apparent activation corrosion energy, R is the universal gas constant, T is the absolute temperature and B is a constant. Values of apparent activation energy for the corrosion of Aluminum in 1.4M HNO$_3$ without and with various

concentrations of inhibitor are shown in Table 1. These values were determined from the slope of in CR versus 1/T plots presented in Figure 5. The results of activation energy from Table 1 showed that the value of Ea for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of Aluminum is slow in the presence of the inhibitors. It is known from Arrhenius equation that the higher Ea values lead to the lower corrosion rate, this is due to the formation of a film on the
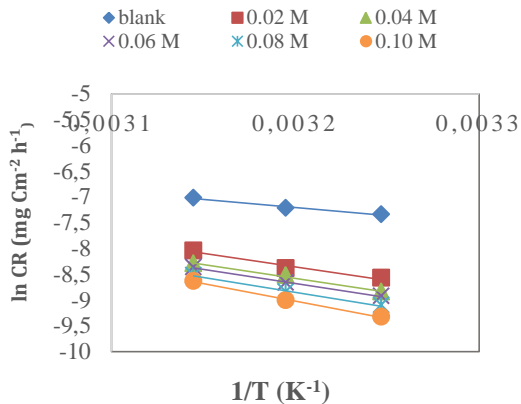
Aluminum surface serving as an energy barrier for Aluminum corrosion. Similar work was reported by Vashi and Prajapati [16] in their study for corrosion inhibition of Aluminum in hydrochloric acid using Bacopa monnieri leaves extract as green inhibitor. And the result of activation energy in uninhibited solution was 18.21 kJ/mol which increased to 58.26 kJ/mol in the presence of 0.6 g/L inhibitor concentration.
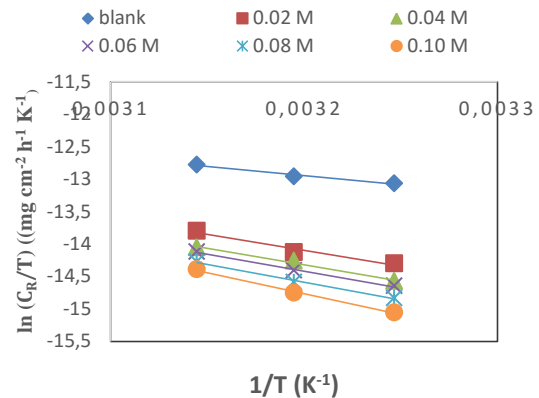

Fig 5. Arrhenius plot for Aluminium in 1.4 M HNO$_3$ in the blank and presence of the inhibitor

Fig 6. Transition State plot Aluminium in 1.4 M HNO$_3$ in the blank and presence of the inhibitor

Table 1: Activation Parameters for the Corrosion of Aluminum in 1.4 M HNO$_3$.

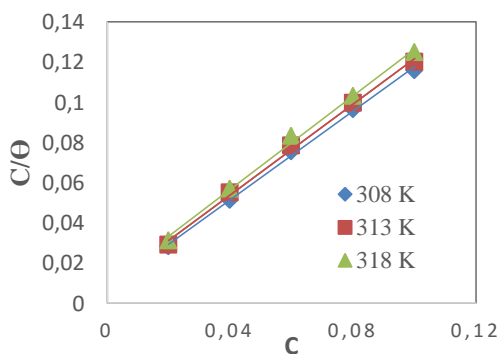| Inhibitor Conc. (M)	Ea (kJ mol^{-1})	ΔH (kJmol^{-1})	-ΔS (JK^{-1}mol^{-1})
Blank	25.95	23.35	230.48
0.02	43.45	40.84	184.07
0.04	44.73	42.12	181.77
0.06	45.55	42.95	197.98
0.08	47.84	45.23	174.09
0.10	56.46	53.85	147.96

Fig 7. Langmuir adsorption isotherm plot for Aluminum Corrosion in 1.4M HNO$_3$ with different inhibitor concentration at different temperatures.

3.4.2. Enthalpy change (ΔH) and Entropy change (ΔS)

An alternative formulation of Arrhenius equation is the transition state equation. Enthalpy change (ΔH) and entropy change (ΔS) of activation process were evaluated from the transition state equation.

$$\ln\left(\frac{C_R}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right) - \left(\frac{\Delta H_a}{RT}\right) \quad (6)$$

Where h is the Planck's constant, N is Avogadro number, ΔS_a is the entropy change of activation and ΔH_a is the enthalpy change of activation. Figure 6 shows a plot of ln (CR/T) against (1/T), straight line

is obtained with a slope of (-ΔH/R) and intercept of (ln R/Nh + ΔS/R) from which the value of ΔHa & ΔSa are calculated and presented in Table 1. It can be seen from Table 1 all the values of enthalpies (ΔHa) are positive and the positive signs of the enthalpies (ΔHa) reflect the endothermic nature of Aluminum dissolution process. The entropy of activation in presence and absence of the inhibitor was large and negative. This implies that the activated complex in the rate determining step represents association rather than dissociation, indicating that a decrease in disorder takes place, going from reactant to the activated complex. Similar work was reported by Udom et al. [17] during the study of the effect of Acanthus montanus leaves extract on corrosion of Aluminum in hydrochloric acid medium and the result of enthalpy was positive ranging from 17.41 to 24.42 kJmol-1 in $1×10-6$ to $5×10-2$M inhibitor concentration while that of entropy was large and negative.

3.5.   Adsorption Isotherm

Deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system is one of the most convenient ways of expressing adsorption quantitatively. Adsorption isotherm provide the basic information on the interaction between the inhibitor and the metal surface. The values of the degree of surface coverage (θ) were evaluated at different concentrations of the inhibitors in 1.4 M HNO_3 solution. Various adsorption isotherms were applied to fit θ values, but the best fit was found to obey Langmuir adsorption isotherm which are represented in Figure 7 at 308, 313 and 318K. Langmuir adsorption isotherm may be expressed by equation 7 [18].

$$\frac{c}{\theta} = \frac{1}{K} + C \qquad (7)$$

Where C is the concentration of the inhibitor in the bulk electrolyte, Ө is the degree of surface coverage, and Kads is the adsorption equilibrium constant. A plot of C/Ө gave a straight line with slope equals to

Kads. The correlation coefficient (R2) values obtained are presented in Table 2.

3.6.   Free Energy of Adsorption (ΔGads,)

Figure 7 shows relationship between C/Ө and C where K (equilibrium constant) is obtained from the intercept of the straight line and it is known that free energy adsorption (ΔGads) is related to equilibrium constant by the equation given below

$$\Delta G_{ads} = -RT \ln (55.5 \times K_{ads}) \qquad (8)$$

The values of free energy of adsorption calculated by using Equa.7 are all negative as presented in Table 2. The negative values of ΔGads indicate the spontaneous adsorption of the inhibitor molecules on the Aluminum surface. Generally, values of ΔGads around -20 kJ mol^{-1} or lower are consistent with physical adsorption, while those around -40 kJ mol^{-1} or higher involves chemical adsorption as reported by Toliwal et al. [19]. In the present study, the values of free energy obtained are all around -20 kJ mol^{-1} which is consistent with physical adsorption mechanism. Similar work was reported by Babatunde et al. [20].

Table 2: Adsorption parameters deduced from Langmuir adsorption isotherm for corrosion of Aluminum.

Temp. (K)	R^2	K_{ads}	ΔG (kJ mol^{-1})
308	0.9981	135.13	22.84
313	0.9974	119.04	22.88
318	0.9966	101.01	22.82

3.7. Infrared Spectroscopy Analysis Results

The result presented in Figures 8 and 9 shows the FTIR analysis of the inhibitor (Anisaldehyde) and the corrosion product of Aluminium in 1.4 M HNO_3 with 0.1 M inhibitor concentration. The analysis of the inhibitor in figure 8 shows C-H aromatic stretching frequency, C-H aldehyde stretching frequency, C=O carbonyl stretching frequency and OCH_3 bending frequency. The analysis of the

corrosion prod-uct presented in Figure 9 shows the appearance of C-H aromatic stretching frequency, C-H aldehyde stretching frequency, C=O carbonyl stretching frequency and OCH_3 bending frequency and this con-firmed that the adsorption of the inhibitor on the metal surface took place.
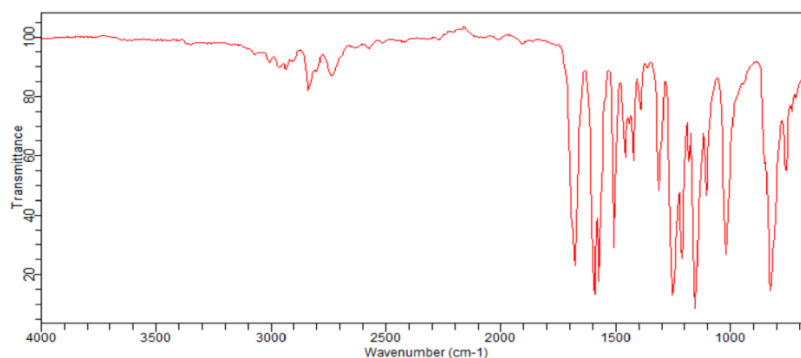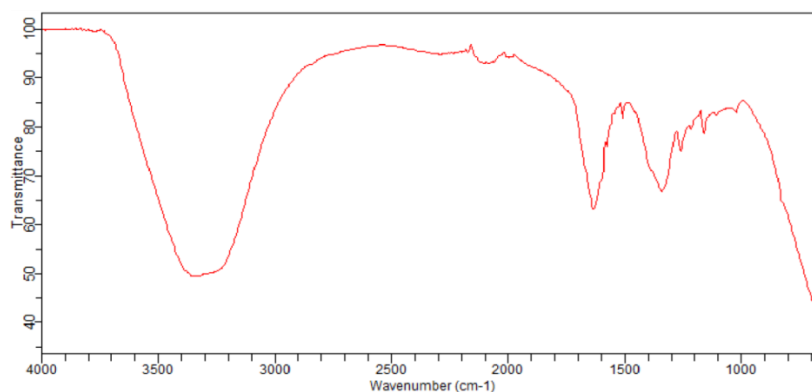

Fig 8. FT-IR Spectra of Anisaldehyde

Fig 9. FT-IR Spectra of Aluminum in 1.4M HNO_3 with 0.1M Anisaldehyde.

4. Conclusion

The present study shows that Anisaldehyde (4-methoxy benzaldehyde) was found to be a good inhibitor for the corrosion protection of Aluminum in nitric acid solution. Corrosion rate decreases with increasing inhibitor concentration and increases with rising temperature. The inhibition efficiency was increased with increase in concentration of the inhibitor and decreases with rises temperature. The maximum I.E., was found 86.32 % at 308K and 0.1M inhibitor concentration in 1.4 M HNO_3 solution. The adsorption of the inhibitor on the surface of Aluminum follows Langmuir adsorption isotherm and undergoes physical adsorption mechanism.

References

1. Rabab, M. N. (2017). Novel Green Soybean Oil Derivatives as Corrosion Inhibitors for Mild Steel at 0.5 N HCl. *Pelagia Research Library*. 8(2):282-290.
2. Bradford, S. A. (1993). Corrosion control, Van Nostrand Reinhold, New York, pp.1-238.

3. Ashassi, H. Shabani, B. Aligholipour, B. Seifzadeh, D. (2006). The effect of some Schiff bases on the corrosion of aluminiumin hydrochloric acid solution. *Appl.Surf.Sci.*, 252, 4039.4047.

4. Abdallah, M. (2004). Antibacterial drugs as corrosion inhibitors for corrosion of aluminiumin hydrochloric solution. Corros.Sci., 46: 1981 - 1996.

5. Aljourani, J., Raeissi, .K. and Golozar, M.A. (2009). Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1 M HCl solution. *Corros.Sci.*, 51: 1836 – 1843.

6. Obot, I.B. Obi-Egbedi, N.O. and Umoren, S.A. (2009). The synergistic inhibitive effect and some quantum chemical parameters of 2,3-diaminonaphtalene and iodide ions on the hydrochloric acid corrosion of Aluminium, *Corros.Sci.*, 51: 276 - 282.

7. Abdel, M. S. Morad, M. S. (2001). Inhibiting effects of some quinolines and organic phosphonium compounds on corrosion of mild steel in 3 M HCl solution and their adsorption characteristics. *Br Corros J*. 36: 253-260.

8. Mouayed, Y. K., Abdulsada, A. M. and Alshawi, J. M. S. (2014). Synthesis, identification and the study of some new azo dyes as corrosion inhibitors for copper in (1 M) HCl. *Journal of Basrah Researches (Sciences)*. 108-127.

9. Afolabi, A. S, Muhirwa AC, Abdulkareem AS, Muzenda, E. (2014). Weight loss and Microstructural Studies of Stressed Mild Steel in Apple Juice. *Int J Electrochem Sci*., 9: 5895-5906.

10. Olasehinde, E.F., Ogunjobi, J. K., Akinlosotu, O. M. and Omogbehin, S. A. (2015). Investigation of the Inhibitive Properties of Alchornea laxiflora leaves on the Corrosion of Mild Steel in HCl: Thermodynamics and Kinetic Study. *Journal of American Science*. 11(1): 32-39.

11. Nnanna, L. A., Anozie, I. U., Avoaja, A. G. I., Akoma, C. S. and Eti E. P. (2011). Comparative Study of Corrosion Inhibition of Aluminium Alloy of Type AA3003 in Acidic and Alkaline Media by Euphorbia hirta extract. *African Journal of Pure and Applied Chemistry*. 5(8): 265-271.

12. Ekpe, U.J., Okafor, P.C. and Ebenso, E.E. (2004). Inhibition of the Acid Corrosion of Aluminium by some derivatives of Thiosemicarbazon. *Bulletin of Chemical Society of Ethiopia*. 18(2): 181-192.

13. Musa, H., Bishir, U. and Muhammad. B. I. (2018). Evaluation of corrosion behaviour of aluminium in different environment. *Bayero Journal of Pure and Applied Sciences*. 11(1): 88-92.

14. Fouda, A. S., Ibrahim, A. A. and El-behairy, W. T. (2014). Thiophene derivatives as corrosion inhibitors for carbon steel in hydrochloric acid solutions. *Scholars Research Library*. 6(5):144-157

15. Mohamed, M.I., Abdel Hameed, R.S. Abd-Alhakeem, H. A. Sawsan, E. M. (2014). Schiff.s bases and their metal complexes as corrosion inhibitors for Aluminum alloys in corrosive media. *OCAIJ* 10 (7): 271-281.

16. Vashi, R. T. and Prajapati, N. I. (2017). Corrosion Inhibition of Aluminium in Hydrochloric Acid Using Bacopa monnieri Leaves Extract as Green Inhibitor. *International Journal of ChemTech Research*. 10(15): 221-231.

17. Udom, G. I., Cookey, G. A. and Abia, A. A. (2017). The Effect of Acanthus montanus Leaves Extract on Corrosion of Aluminium in Hydrochloric Acid Medium. *Journal of Applied Science and Technology*. (25) 1-11.

18. Al-Sabagh, A. M., Kandile, N. G., Nasser, N. M., Mishrif, M. R. and El-Tabey, A. E. (2013). Novel surfactants incorporated with1,3,5-triethanolhexahydro-1,3,5-triazine moiety as corrosion inhibitors for carbon steel in hydrochloric acid: Electrochemical and quantum chemical investigations. *Egypt J Pet* 22: 351-365.

19. Toliwal, S. D. Kalpesh, J. and Pavagahh, I. (2010). Inhibition of corrosion of mild steel INHCL solutions by Schiff base derived from nontraditional oils. *Journal of Applied chemical Research*. 12: 24 -36.

20. Babatunde, A. I., Gundele, O. O., Oyelola, O. T. and Abiola, O. K. (2012). The inhibitive effect of Irvingia gabonensis extract on the corrosion of aluminium in 1M HCl solution. *Advances in Applied Science Research*. 3 (6): 3944-3949

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