

Palm Olein as an Eco-Friendly Corrosion Inhibitor for Aluminium in Corrosive Solution

J. Jai and W. S. Wan-Ali

Faculty of Chemical Engineering, Universiti Teknologi MARA, 60340450 Shah Alam, Selangor, Malaysia,

junejai@salam.uitm.edu.my

Abstract

The use of natural products as corrosion inhibitors has been extensively studied. Palm olein, which contains carbonyl groups and double bonds, is one of the promising materials as corrosion inhibitor. This paper will focus on the behaviour of palm olein as corrosion inhibitor for aluminium in 1 M HCl solution at different temperatures and concentration of inhibitors using weight loss measurement test. Results had shown that the corrosion rate decreases with the increase in concentration of the inhibitor and increases with the increase in temperature. The palm olein inhibitor adsorbed on the aluminium surface through physical adsorption.

Keywords: Aluminium alloy, weight loss test, corrosion inhibitor, HCl solution, palm olein.

Introduction

Aluminium (Al) has an amazing economic and industrial importance due to its low cost, lightweight, high thermal and electrical conductivity. The most important feature of Al is its corrosion resistance due to the formation of a protective film on its surface upon its exposure to atmosphere or aqueous solutions [1]. When Al is exposed in high concentrations of acids or bases or in neutral solution containing pitting agents such as chloride ions, these solutions dissolve the passive film. The dissolution leads to the formation of pitting corrosion. The inhibition of aluminum corrosion was extensively studied using organic and inorganic compounds [2]. Organic compounds are found to be effective corrosion inhibitors due to the adsorption of molecules and ions on the metal surface. The presence of large molecules with functional groups containing of heteroatoms (such as oxygen, nitrogen, sulphur, phosphorus), triple bonds or aromatic rings in the inhibitor's chemical structure enhance the adsorption process [3].

Considerable efforts are made to find suitable compounds to be used as corrosion inhibitors in various corrosive media. Many works were conducted to examine extracts from natural substances [2,5,6]. The extracts contain mixtures of compounds having oxygen, sulphur and nitrogen elements, which help in the corrosion inhibition process. These compounds naturally are antioxidants, cheap and environmentally safe. Their use as corrosion inhibitor has been preferred, both for economic and environmental goals [4].

El-Etre [5] reported the use of vanillin as a good corrosion inhibitor for Al in HCl solution. Vanillin is an aromatic aldehyde containing carbonyl, methoxy and hydroxyl groups arranged around the aromatic ring. The adsorption of vanillin on Al surface would take place through all these functional groups. Subsequently, *opuntia ficus mill* (family of cactaceae) extract was also found to be a good corrosion inhibitor for Al [2]. The *opuntia* extract contains mainly polysaccharide which is a mixture of mucilage and pectin. It also contains at least seven non-volatile acids including malic and citric acids. The adsorptions of these compounds on the electrode surface forms a barrier for mass and charge transfers. This situation leads to a protection of the metal surface from the attack of the aggressive anions. The degree of protection increases with increasing of the surface fraction occupied by the adsorbed molecules. As the extract concentration is increased, the number of the adsorbed molecules on the surface increases.

Recently, Yaakob [6] reported the promising use of palm olein from crude palm oil (CPO) as corrosion protector for mild steel in acidic solution. The CPO contains equal amounts of saturated and unsaturated fatty acids which are palm stearin and palm olein, respectively. The unsaturated fatty acid portion consists of oleic and linoleic acids. Both acids contain carbonyl groups and double bonds [7]. Consequently, El-Etre [3] stated that the large molecular structure, double bonds, reactive centres or groups are among the features that give the compound the ability to cover a large area of a metal surface. Hence, palm olein has a promising characteristic as a corrosion inhibitor. However, almost no work has been reported on the used of palm olein as corrosion inhibitor for Al. Therefore, this work will focus on the adsorption isotherm and kinetics of the palm olein as corrosion inhibitor for Al exposed in 1 M HCl solution.

Materials and Experimental Procedure

The material studied was an Al alloy (Al 6061) sheet. A stock solution of the tested material was prepared by blending the palm olein (PO) and poly(oxyethylene)x-sorbitane-monolaurate (T20) with the weight ratio of PO to T20 as 5:1. The PO was obtained from crude palm oil supplied by Jugra Palm Oil, Banting, Selangor, Malaysia and the main composition is oleic acid. T20 was used as emulsifier to enhance the solubility of the palm olein in aqueous solution.

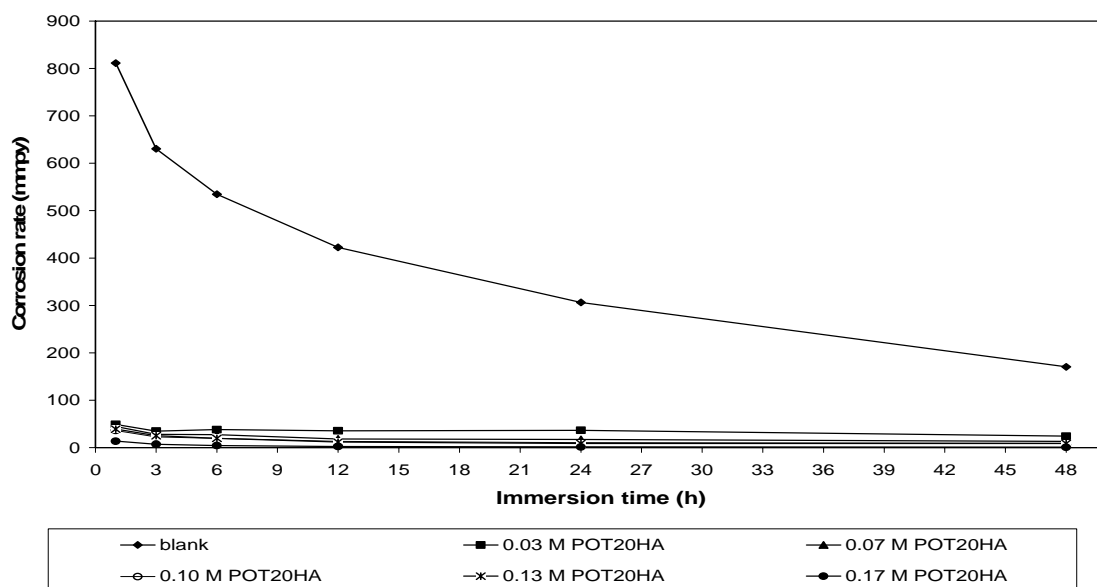
The inhibitor was prepared by blending 25 vol% stock solution (POT20), 0.5 vol% hexane and the balance distilled water at pH 7, 50°C for 1 hour. The blended solution was then allowed to settle down in a separating funnel for 1 day before the bottom layer (labeled as POT20H) was collected. Diethyl triamine (DETA) was added to the POT20H with the volume ratio of POT20H to DETA as 50:2 before stirring for 30 min at room temperature and labeled as POT20HA. In preparing the desired concentration of corrosive media, a specific volume of POT20HA was added directly to the corrosive solution which was 1 M HCl solution.

For the weight loss test, the Al 6061 sheet was cut into pieces of dimensions 2 cm x 3 cm x 0.03 cm. The sample plate was hand-polished with 180 followed by 600 grade sand paper and rinsed with distilled water. The dimensions and weight of the plate were accurately measured. Before conducting the corrosion test the Al plate was degreased by acetone, rinsed with distilled water and finally air dried. The plate was suspended with the aid of nylon thread and glass rod in a 300 ml beaker with 250 ml corrosive solution at the required temperature and stirring speed at 125 rpm. To prevent the solution from evaporation and contamination, the corrosion cell was covered with a parafilm. The sample was retrieved at 1, 3, 6, 12, 24 and 48 hours. The collected sample was cleaned according to the ASTM G31-72 as described in the ASTM Standards [8] whereby, the sample was rinsed with distilled water, dipped in concentrated HNO₃ acid, scrubbed with bristle brush under running water, rinsed in distilled water and finally air dried before reweighed. The corrosion tests were performed at different temperatures of 299, 323 and 343 K with different concentrations of POT20HA of 0, 0.03, 0.07, 0.10, 0.13 and 0.17 M in 1 M HCl solutions.

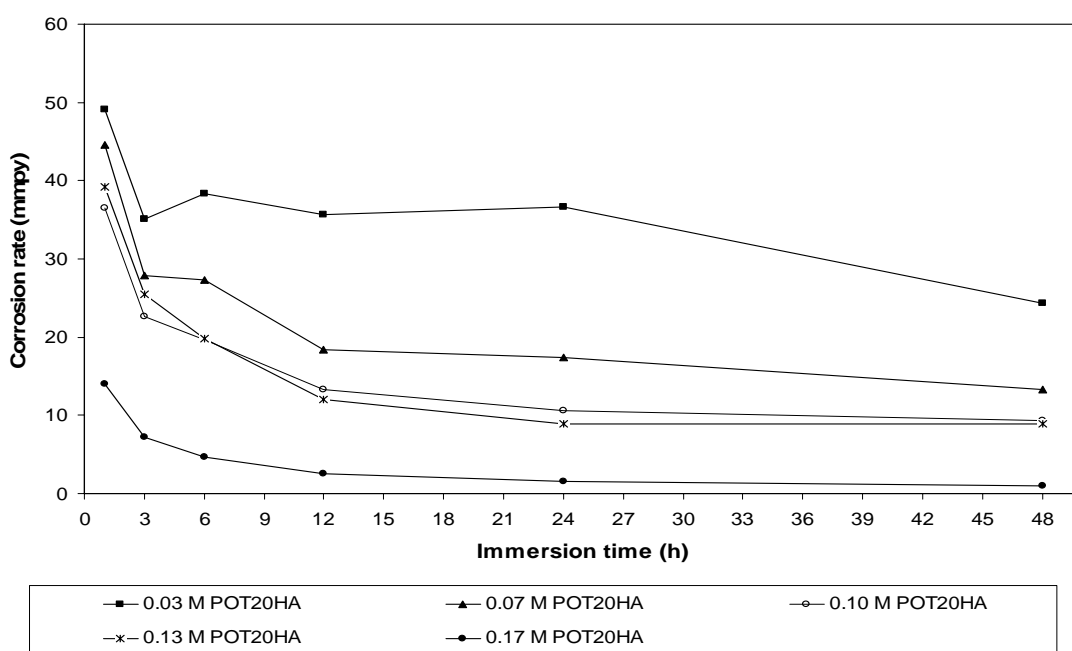
Results and Discussions

Fig. 1(a) shows the corrosion rate of Al 6061 in 1 M HCl solution with and without the presence of inhibitor POT20H at 299 K. The corrosion rate of Al 6061 in the absence of POT20H was very much higher as compared to the rates in other solutions in the presence of inhibitor. The corrosion was due to the presence of water, air, Cl^- and H^+ which accelerate the corrosion process of the Al. An increase of immersion time from 1 to 48 hours had reduced the corrosion rate. The reduction was due to the presence of the aluminium hydroxide layer that covered the Al 6061 surface [9]. Fig. 1(b) shows that an addition and increase in concentration of POT20HA had markedly reduced the corrosion rate of Al 6061 which indicated the positive effect of the inhibitor. The test solutions contain 0.03 and 0.07 M POT20HA had shown similar corrosion behaviour whereby, for the first three hours of immersion test, there was a reduction in the corrosion rate. This shows the ability of the POT20HA in forming the protective layer that covered the Al 6061 surface. However, an increase in immersion time from 3 to 6 and 12 hours had shown slight increase and reduction in the corrosion rate, respectively. Subsequently, after 24 hours there was a minor decrease in the corrosion rate of the 0.07 M POT20HA but a slight increase in the 0.03 M solution. The increase and reduction of the corrosion rate in the 0.03 and 0.07 M POT20HA solutions showed that there was insufficient surface coverage by the POT20HA on the Al 6061 surface. The aggressive ions in the corrosive solution act on the corrosive solution penetrate the uncovered surface, which leads to the dissolution of Al.

Consequently, the aluminium hydroxide from the Al reaction would lead to the formation of passive film which repassivated the Al surface, hence, reducing the corrosion rate. The corrosion behaviours in the solutions containing 0.10, 0.13 and 0.17 M POT20HA were slightly different than in those containing 0.03 and 0.07 M POT20HA. The concentrations of 0.10, 0.13 and 0.17 M POT20HA have caused continuous gradual decrease in corrosion rate from initial to 24 hours of immersion time. Consequently, after 24 hours, the corrosion rate has reached its equilibrium state. These concentrations had produced excellent surface coverage which was not easily attacked by the aggressive anions.



(a)



(b)

Figure 1: Corrosion rate of Al 6061 in 1 M HCl solution (a) without and with, and (b) with the presence of POT20HA at 299 K.

The corrosion rate of the Al 6061 which was immersed in different concentrations of POT20HA at 323 and 343 K are shown in Figs. 2 and 3, respectively. Corrosion behaviour of the Al 6061 was almost similar at both temperatures. For every concentration at both temperatures, an increase of immersion time from initial to 24 hours had shown continuous decrease in the corrosion rate. Furthermore, after 24 hours, the corrosion rate had reached its steady state. In general, the inhibition efficiency increased as the concentration of POT20HA solution was increased, at all tested temperature. As observed, the corrosion rate at 299 K was markedly low as compared to those obtained at 323 and 343 K.

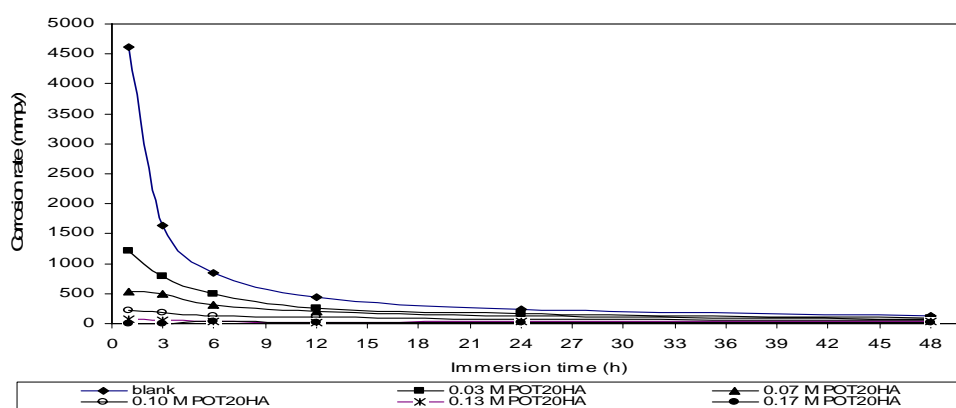


Figure 2: Corrosion rate of the Al 6061 in 1 M HCl solution with different concentrations of POT20HA at 323 K

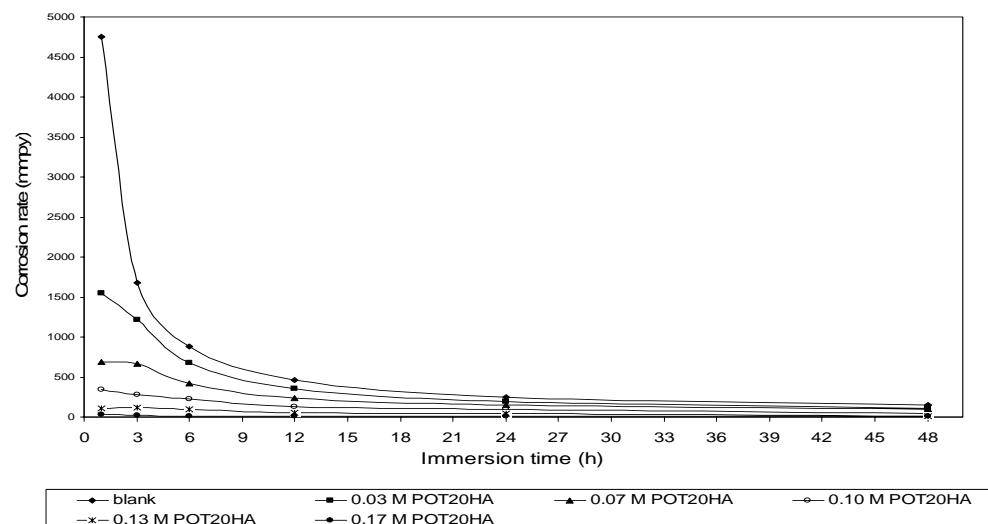


Figure 3: Corrosion rate of the Al 6061 in 1 M HCl solution with different concentrations of POT20HA at 343 K

Adsorption isotherm

From the weight loss measurement data, analysis on the adsorption isotherm relationship according to Frumkin, Temkin and Langmuir was performed. The following expressions show the adsorption isotherms relationships of Frumkin, Temkin and Langmuir [1, 10–17].

$$\text{Frumkin relationship:} \quad \ln \frac{\theta}{C(1-\theta)} = \ln K + 2a\theta \quad (1)$$

$$\text{Temkin relationship:} \quad \theta = \left(\frac{1}{f}\right) \ln(KC) \quad (2)$$

$$\text{Langmuir relationship:} \quad \frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

where C (M) is the concentration of POT20HA, K (M^{-1}) the equilibrium constant, a and f are constants for Frumkin and Temkin relationships, respectively. Table 1 shows the correlation coefficient (R^2) of the weight loss test after one hour of immersion time according to the respective adsorption isotherm relationship.

Table 1: The correlation coefficient (R^2) of the weight loss test after one hour of immersion time

Temperature (K)	R^2 (Frumkin)	R^2 (Temkin)	R^2 (Langmuir)
299	0.8917	0.6751	0.9988
323	0.7087	0.9837	0.9653

The R^2 values show that the Langmuir relationship fit the experimental data at all temperatures under study. Using the K value determined from the Langmuir isotherm relationship, the standard free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$ (kJ/mol) values at different temperatures can be determined according to the following equation;

$$\ln K = \ln \frac{1}{55.5} - \frac{\Delta G_{\text{ads}}^{\circ}}{RT} \quad (4)$$

where (1/55.5) is the standard molar of water in the solution. R is the gas constant 8.314 J/(mol.K) and T(K) is the temperature [18]. Table 2 shows the K and $\Delta G_{\text{ads}}^{\circ}$ values at different temperatures. The $\Delta G_{\text{ads}}^{\circ}$ values which were below 40 kJ/mol indicate physical adsorption on the transfer of unit mole of the inhibitor from solution onto the metal surface [18]. The negative sign of the free energy of adsorption indicates that the adsorption of the inhibitor at the metal surface is a spontaneous process [17].

Table 2: The K and $\Delta G_{\text{ads}}^{\circ}$ values at different temperatures

Temperature (K)	K (M ⁻¹)	$\Delta G_{\text{ads}}^{\circ}$ (kJ/mol)
299	267.1	-23.87
323	75	-22.38
343	56.32	-22.95

Kinetics

Activation energies (E_a) of the corrosion process were evaluated from the Arrhenius equation [19];

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (5)$$

where CR_1 and CR_2 are the corrosion rates at temperature T_1 and T_2 , respectively. Fig. 4 shows the E_a from weight loss test of Al 6061 in different concentrations of POT20HA solution at different temperatures after 6 hours of immersion time. An increase of temperature from 323 to 343 K had reduced the E_a value. On the other hand, an addition and increase in composition of POT20HA solution had increased the E_a value which indicated the increase in the resistance of Al 6061 towards corrosion. The increase in E_a indicated that physical adsorption of POT20HA occurred on the Al 6061 surface [20]. A

slight reduction and increase in the E_a has been observed with the increase in the concentration of 0.1 and 0.13 M, respectively, before a significant decrease of E_a at 0.17 M solution. The reduction was an indication of chemical adsorption [21]. Earlier, Oguzie [19] reported that the decrease in the E_a value at high concentration of inhibitor reveals the formation of a chemical adsorption of monolayer on the metal surface. This finding has shown that an increase in concentration of POT20HA solution has shifted the physical adsorption of the POT20HA towards chemical adsorption.

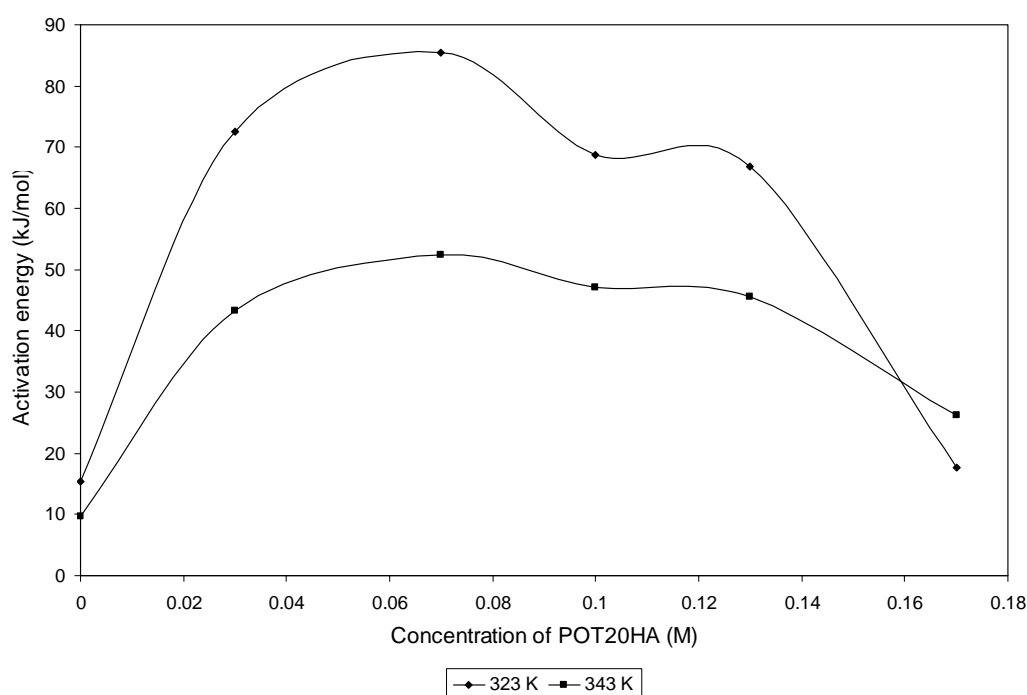


Figure 4: The E_a from weight loss test of Al 6061 in different concentrations of POT20HA solution at different temperatures after 6 hours of immersion time.

Conclusions

- Corrosion rate at 299 K was lowest as compared to those at 323 and 343 K where the corrosion rate and the behaviour of 323 and 343 K were almost similar.
- The Langmuir adsorption isotherm relationship is suitable for the experimental data at all temperatures under study.
- E_a increases together with increasing concentration from 0 to 0.07 M. However, a further increase in the concentration of POT20HA solution from 0.07 to 0.10 M and 0.17 M had shown reduction in the activation energies. The increase in E_a indicates

that physical adsorption of POT20HA occurred on the Al 6061 surface. An increase of concentration of POT20HA solution shifted the physical adsorption behaviour of the POT20HA more towards chemical adsorption.

Acknowledgement

The authors express their grateful acknowledgement for the technical support from the Research Management Institute (RMI), Universiti Teknologi MARA and the financial support from the Fundamental Research Grant Scheme (FRGS) from the Ministry of Higher Education, Malaysia.

References

- [1] 'The inhibition effect of some amino acids towards the corrosion of aluminium in 1 M HCl + 1 M H₂SO₄ solution', H. Ashassi-Sorkhabi, Z. Ghasemi, D. Seifzadeh, *Applied Surface Science*, 249, pp408–418, 2005.
- [2] 'Inhibition of aluminium corrosion using opuntia extract', A.Y. El-Etre, *Corrosion Science*, 45, pp2485–2495, 2003.
- [3] 'Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves', A.Y. El-Etre, *Journal of Colloid and Interface Science*, 314, pp578–583, 2007.
- [4] 'Inhibition of steel corrosion in 2 M H₃PO₄ by artemisia oil', M. Benabdelah, M. Benkaddour, B. Hammouti, *Applied Surface Science*, 252, pp6212–6217, (2006).
- [5] 'Inhibition of acid corrosion of aluminium using vanillin', A.Y. El-Etre, *Corrosion Science*, 43, pp1031–1039, 2001.
- [6] 'Development of palm oil based anti-corrosion material for underwater protection', N. Yaakob, *Master dissertation, Universiti Teknologi MARA*, pp56, 2007.
- [7] J. McMurry, *Organic Chemistry*, sixth ed., United State of America, 2004.
- [8] ASTM International, United State of America, *Annual Book of ASTM Standard Section 3: Metal test methods and analytical procedures. Volume 03.02: Wear and erosion; metal corrosion*. 2003.
- [9] 'A study on stress corrosion behaviour of Al6061/albite composite in higher temperature acidic medium using autoclave', S.C. Sharma, *Corrosion Science*, 43, pp1877–1889, 2001.

- [10] 'Corrosion inhibition of aluminium by 1,1(lauryl amido)propyl ammonium chloride in HCl solution', S. Abd El Rehim, H.H. Hassan, M.A. Amin, *Materials Chemistry and Physics*, 70, pp64–72, 2001.
- [11] 'Inhibition of acid corrosion of pure aluminium by some organic compounds', A.K. Maayata, A.A.F. Al-Rawashdeh, *Corrosion Science*, 46, pp1129–1140, 2004.
- [12], 'Inhibition of iron corrosion in acid solutions by Cefatrexyl: behaviour near and at the corrosion potential', M.S. Morad, *Corrosion Science*, 50, pp436–448, 2008.
- [13] 'Corrosion inhibition of some metals using lawsonia extract', A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, *Corrosion Science*, 47, pp385–395, 2005.
- [14] 'Temperature effects on the corrosion inhibition of mild steel in acidic solutions by aqueous extract of Fenugreek leaves', E.A. Noor, *International Journal of Electrochemical Science*, 2, pp996–1017, 2007.
- [15] 'Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of leaves of *Nypa fruticans* Wurmb', K.O. Orubite, N.C. Oforka, *Material Letters*, 58, pp1768–1772, 2004.
- [16] 'Adsorption and inhibitive properties of ethanol extracts of *Musa sapientum* peels as a green corrosion inhibitor for mild steel in H₂SO₄', N.O. Eddy, E.E. Ebenso, *African Journal of Pure and Applied Chemistry*, 2, 6, pp046–054, 2008.
- [17] 'Khillah extract as inhibitor for acid corrosion of SX 316 steel', A.Y. El-Etre, *Applied Surface Science*, 252, 24, pp8521–8525, 2006.
- [18] 'Carboxymethylchitosan as an ecofriendly inhibitor for mild steel in 1 M HCl', S. Cheng, S. Chen, T. Liu, X. Chang, Y. Yin, *Materials Letters*, 61, 14–15, pp3276–3280, 2007.
- [19] 'Studied on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel', E.E. Oguzie, *Material Chemistry and Physics*, 99, pp441–446, 2006.
- [20] 'Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media', R.Solmaz, et al., *Electrochimica Acta*, 53, 20, pp 5941–5952, 2008.

- [21] 'Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media', P.C. Okafor, et al., *Corrosion Science*, 50, 8, pp310–2317, 2008.