

PERFORMANCE OF KETONAZ AS A CORROSION INHIBITOR FOR ALUMINIUM IN 18% HYDROCHLORIC ACID SOLUTION

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Abstract

Safe and cheap inhibitors can replace expensive and harmful inhibitors such as chromates and dichromate, etc. This study investigates the corrosion inhibition of aluminium in aggressive media (18% Hydrochloric acid solution) by using ketonaz (used widely in medicine to treat dandruff and fungi) as an inhibitor. To get an insight into ketonaz functionality, three values of concentrations, viz. 2, 4 and 6g/l respectively of solution were used at 300°C for a period of immersion up to 50 minutes using weight loss and electrochemical method; current-time technique. The addition of ketonaz was done by two ways; the first is the addition of 6g/l of ketonaz after an elapsed of about 300 seconds of immersion of aluminium in the solution which gave a moderate inhibition efficiency of ≈50% after elapsed of about 900 seconds suggesting a dissolution-precipitation mechanism of inhibition. This period represents an unsafe factor due to pronounced losses of weight and reduction in dimensions of pieces. In the second way, the same quantity of ketonaz was added initially before immersion the aluminium in the solution. A very good inhibition was obtained by the second way especially at the early stages of the immersion process suggesting adsorption of ketonaz on the surface of aluminium.

Keywords: 18% Hydrochloric acid, Adsorption, Aluminium, Corrosion, Ketonaz, Weight loss.

1. Introduction

Aluminium and its alloys gained very wide importance in engineering applications due to low cost, lightweight, high thermal and electrical conductivity as well as its durability against corrosion. Approximately all the utilities of aluminium and its alloys must pass through preparation processes. Acid solutions are widely used in industry, the most important fields of applications being acid pickling, industrial acid cleaning, acid descaling, and oil well acidizing [1]. Since aluminium is amphoteric in nature, care must be taken due to severe reaction of aluminium with these media. Such reactions could dissolve the metal violently through preparation processes and this could affect the engineering design of the metal as well as the cost embodied by the losses of metal and of chemicals used therein and the related environmental problems. The most expected strategy to deal with the above problem is to use inhibitors and to control the time of exposure.

Inhibitors represent a wide field in corrosion science ranged from mineral or inorganic to organic in the aqueous phase and in vapor phase. The use of organic inhibitors is well established [2-5]. Most of the effective and efficient inhibitors were those who have π bonds and contained hetero-atoms such as oxygen, nitrogen sulphur and phosphorous which allowed adsorption on the metal surface. The action through adsorption is to block the active site by displacing water molecules and forming a compact layer that decreases corrosion. Actually, some of these could be so dangerous materials on human beings and on the environment as a whole. In last year's tremendous searches took the line to find friendly materials that have no such risks, and a replacement for inorganic corrosion inhibitors, surface treatment using green corrosion inhibitors has become a rewarding alternative [3]. Sometimes these are called green inhibitors (natural materials). One of the famous categories of inhibitors for aluminium is the chromium compounds family-like chromates, dichromates and so on, because of their risks imposed on human health [2] many new types were elected and can be found elsewhere [2-10].

Drug inhibitors are inorganic green inhibitors that occupy a wide field of research work as can be shown in Fig. 1. They are considered as the most alternative corrosion inhibitor for aluminium in acidic media as they are biological origin, exhibit a high inhibition performance at relatively low concentration and also are biodegradable in nature [3, 11]. Ketoconazole [12, 13] or ketonaz is available in the medicine industry as an antidandruff and antifungal, it is a heterocyclic compound containing N, O an aromatic ring containing several π bonds as in Fig. 2. and its source for this paper was from ketonaz shampoo. In recent study conducted by Obot and Obi-Egbedi [12] ketoconazole was used as a corrosion inhibitor thereby protecting steel against corrosion in sulphuric acid and the efficiencies of protection were about 40% and 20% at 30°C and 50°C respectively through physisorption. To the best of our knowledge ketonaz has not been used in any further study, thus, a trial was made to check the performance of ketoconazole as an inhibitor of aluminium in HCl solution for a specified time interval. The reason behind using HCl solution in this study was due to that it is efficient in the cleaning of almost all metals, available and safer in using and handling than sulphuric or nitric acids.

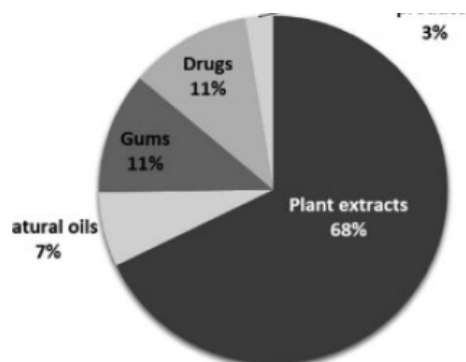


Fig. 1. Natural inhibitors distribution in research work [3].

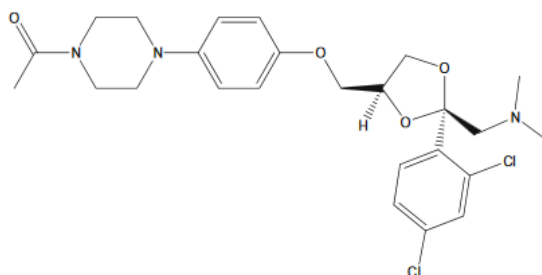


Fig. 2. The chemical structure of ketoconazole [10].

2. Experimental Work

Aluminium specimens of dimensions 1cm x 2cm with a thickness of 1mm having composition listed in Table 1 were grinded by abrasive papers ranged from 400 to finer 600 grade then the specimens were washed in acetone and kept after drying in desiccator till use. A beaker of 500ml was used as a container for 18% HCl solution, the HCl acid was from industrial type (32%), and it was used in such a case in order to match that used in the industry. After the above steps of preparations, the prepared specimen was taken and weighted by a 4 digits balance to get an initial weight of w_1 after that the specimen was put in 18% HCl solution for a time interval (10, 20, 30, 40 and 50 minutes) at 30°C then the specimen was taken from the beaker and washed with water while brushing with a soft brush to remove corrosion products, dried and reweighted to get the second weight w_2 . The procedure was repeated with and without ketoconazole which was sold from the pharmacy. The measurements were repeated twice to get reliable and trusted results. The Ketoconazole concentration values used were 0, 2, 4, and 6g/l in 18% HCl solution. It is important to mention that ketoconazole was added in two ways, the first is the addition of ketoconazole after 300 seconds of aluminium immersion in the solution while the second way is the addition of ketoconazole by the normal route, i.e. before immersion of aluminium in the solution. The first way is conducted for the case of inspection of the mode of ketoconazole inhibition and comparing it with that of the second way.

Electrochemical technique current-time measurements were also done at anodic, cathodic as well as corrosion potential to get some information about the

mode of action of ketonaz by using a normal corrosion cell with three electrodes assembly; aluminium as working electrode and platinum as a counter one while saturated calomel was used as a reference using a computerized wenking potentiostat. The inhibition efficiency, η was calculated according to Eq. (1) [6].

$$\eta_{\%} = (w_1 - w_2)/w_1 \tag{1}$$

Table 1. Aluminium specimen’s composition weight %

| Mg | Mn | Ti | Fe | Cu | Cr | Al |
|-----|------|------|------|------|------|---------|
| 1.5 | 0.18 | 0.02 | 0.26 | 1.45 | 0.00 | Balance |

3. Results and Discussion

All the data of the weight loss were collected in Table 2 below, where one can see that the way of variation of weight loss Δw against the time of exposure, knowing that 30°C was selected since it represents the safe mode in industrial handling with HCl solutions.

Table 2. Weight loss-efficiency versus time at different Ketonaz concentrations at 30°C

| Concentration of inhibitor, g/l | Δw and (efficiency %) at a time interval (in minutes) | | | | |
|---------------------------------|---|--------------|--------------|--------------|---------------|
| | 10 | 20 | 30 | 40 | 50 |
| 0 | 0.0007 | 0.0014 | 0.0018 | 0.0027 | 0.0041 |
| 2 | 0.0004(75.1) | 0.0004(71.4) | 0.0003(83.3) | 0.0000(100) | 0.000(95.1) |
| 4 | 0.0000(100) | 0.0003(78.5) | 0.0000(100) | 0.0001(76.3) | 0.0007(83.99) |
| 6 | 0.0000(100) | 0.0000(100) | 0.0000(100) | 0.0000(100) | 0.0004(90.2) |

From Fig. 3. below, it is shown that by increasing the time of exposure, weight loss Δw is increased accordingly because the corrosion process is a rate process, and it is affected by the time [14]. Also, Fig. 3. below shows the behaviour of aluminium with and without different concentrations of ketonaz. From this figure, it can be shown that ketonaz inhibited the corrosion process and this inhibition is proportional to the inhibitor quantity as well as that one can see the stability of the inhibition process at 6g/l during all over the whole period of exposure according to the progress of the inhibition efficiency with time as in Fig. 4. see also Table 2.

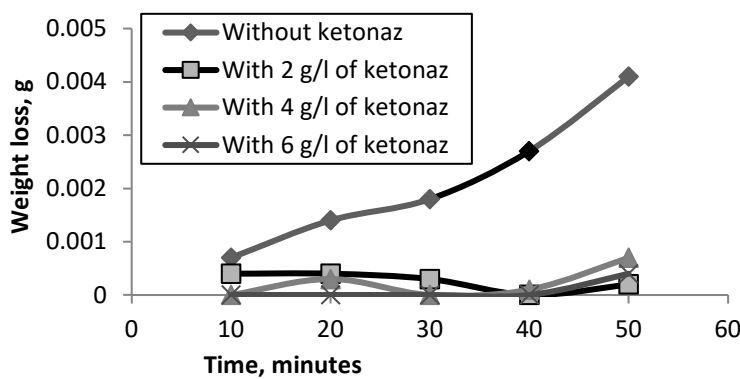


Fig. 3. Weight loss vs. time with and without the presence of different amount of ketonaz.

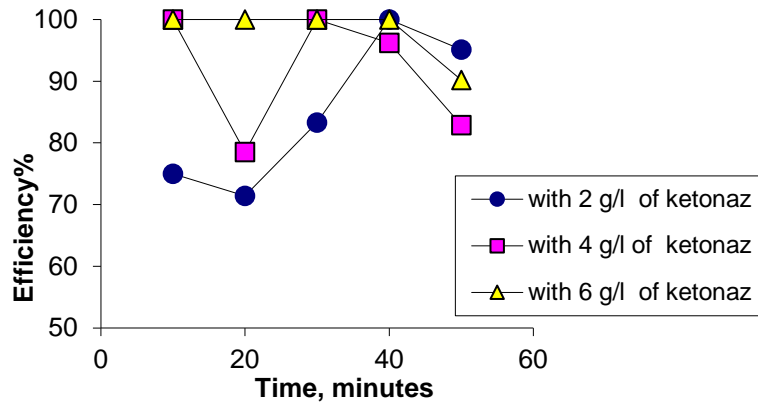


Fig. 4. Inhibition efficiency vs. time at different amount of ketonaz.

In Fig. 4. and Table 2 above the inhibition got maximum after 10 minutes (ranged from about 75% at 2g/l of ketonaz to 100% at 4 and 6g/l) of exposure and this figure gave no clear indication at what time the inhibition was started within this period of 10 minutes which represents too much time of exposure. Also, it can be clearly shown that at 6g/l of inhibitor the efficiency values were stabilized around 100% during the progress of exposure time, only at 50 minutes all the values of efficiency were reduced, it could be due to the increasing effect of HCl with time or in another way due to instability of the formed film on aluminium specimen. In the coming paragraph by electrochemical means the statements of inhibitor actions will be presented from the beginning of immersion.

To detect the mode of Ketonaz action, both anode and cathode current-time were drawn as shown in Fig. 5. and Fig. 6. below (6g/l of ketonaz was used because it gave the best inhibition action). It can be shown that ketonaz works as an inhibitor only on the anode at -600 mV (corrosion potential E_{corr} is -773 mV) where the current before the addition was approximately 0.4 mA and after 5 minutes, i.e., starting dosing of ketonaz to the solution, it was reduced to about -1 mA and then it is stabilized at around, ~ -0.92 mA. This can reflect the potent role of the inhibitor in which it eliminates the anodic sites, reversing polarity to the cathode sites where it gives additional cathodic reaction stabilized at about -0.36 mA with the minimum current while by regarding the cathode current at -900 mV, Fig. 6. in which the dosage of ketonaz was started after an elapsed of 5 minutes where the current slightly fluctuated around -90 mA. Since the corrosion is free without any external driving force-imposed voltage, therefore, the inspection must be done at the corrosion potential which it had the value of -773 mV in this study and by doing so, Fig. 7. was obtained, at which the current was reduced to about 81 mA which refers to efficiency of about 50 %, i.e., after an elapsed of 900 seconds of dosing.

When one considers the inhibition evolution with time as in Fig. 8. below it can be seen that after elapsed 1000s (700seconds after dosing) there will be about 52% inhibition. This period 1000 seconds of the appearance of a moderate inhibition efficiency of 52% represents a very long period to give reasonable protection.

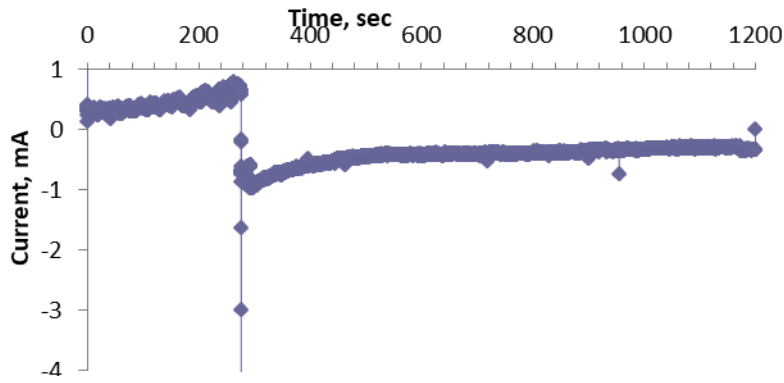


Fig. 5. Current evolution at 600 mV in the anodic region with the addition of 6 g/l ketonaz after about 300 seconds of aluminium immersion in 18% HCl.

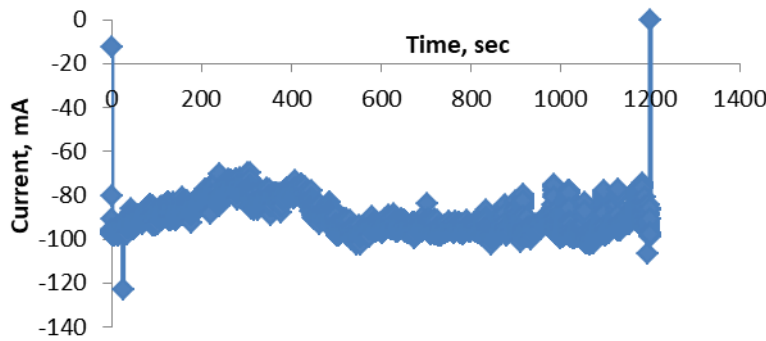


Fig. 6. Current-time evolution at 900 mV in the cathodic region with the addition of 6g/l ketonaz after about 300 seconds of aluminium immersion in 18% HCl.

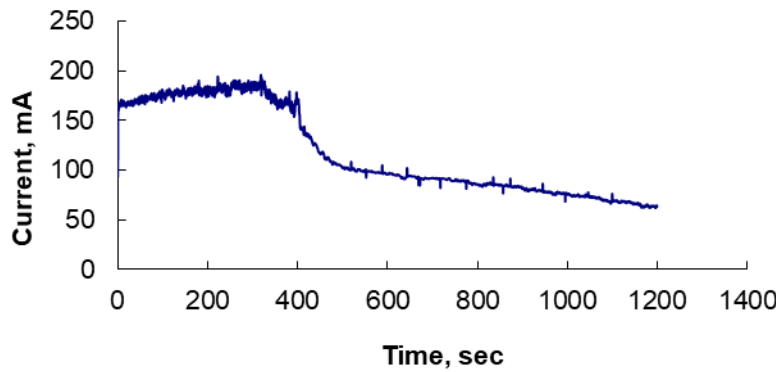


Fig. 7. Current behaviour at E_{corr} of 773 mV with the addition of 6 g/l of ketonaz after 300 seconds of aluminium immersion in 18% HCl solution.

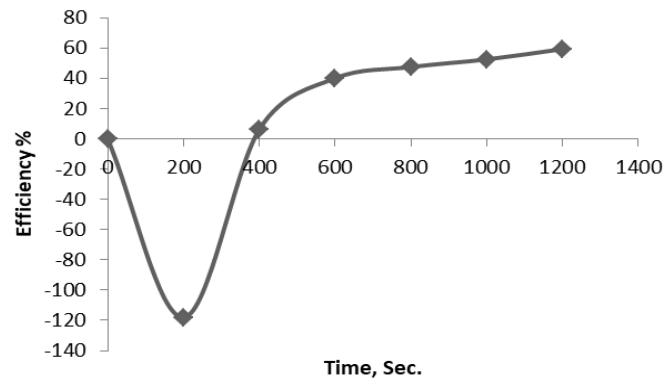


Fig. 8. Evolution of inhibitor efficiency with time*based on Fig. 6.

It can be seen that the protection increased as the time went on especially after about 550 second and this represents too much time for inhibition to give useful performance. Since the inhibitor action is improved with the progressing of time, therefore, it is anticipated that the mode of action is through dissolution of aluminium to give Al^{+3} that combined with HCl-keonaz solution forming $AlCl_3$ -keonaz as a reaction product (see below), then precipitation mechanism takes place when the concentration of this product exceeds some limits.

By focusing on Fig. 9. in which keonaz was added before immersion of aluminium, it is concluded that there is approximately no current as soon as the piece is immersed meaning that the efficiency is 100% which resembles the results of the weight loss given in Table 2. This current is changed to a cathodic one in accordance with Fig. 5. assuring that keonaz is instantaneously blocked the surface of aluminium by forming a film barrier which retards HCl attack without any time delay meaning that the mechanism of keonaz action is by adsorption (see below) and not by solubility effect of the corrosion product. This gives the answer to the questioning about the efficiency curve of Fig. 4. Therefore, keonaz protects aluminium efficiently when it added at the start of operation (before aluminium immersion).

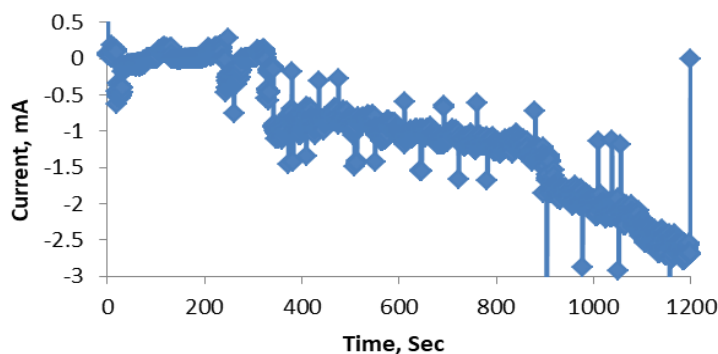


Fig. 9. Current time in the presence of 6g keonaz added before aluminium immersion at 773 mV.

3.1. Mechanism of Ketonaz Action

Excellent corrosion inhibitor is not that one which gives electrons to the unfilled orbitals of the metal (HUMO energy) but also accepts free electrons from the metal (LUMO energy) [12]. When ketonaz comes in contact with the surface of aluminium, an electrostatic interaction (physisorption) takes place. This mechanism explains the high value of inhibition process (especially at the early stages) when ketonaz is added initially and the surface of aluminium is still clean before immersion. In other direction, when ketonaz is added after 300 seconds of immersion process, the aluminium is reacted with HCl to form AlCl_3 which could propagate with time on the surface of aluminium giving a weak protection due to continuous attack of the environment and it could interfere with ketonaz.

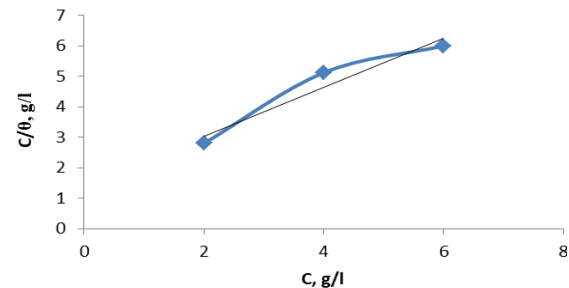
3.2. Adsorption isotherm

The main step in the action of inhibitor in acid solution is the adsorption onto the surface of the metal [12]. Adsorption depends on many factors; inhibitor concentration, pH, temperature, type of surfaces, and type of anions [9, 12].

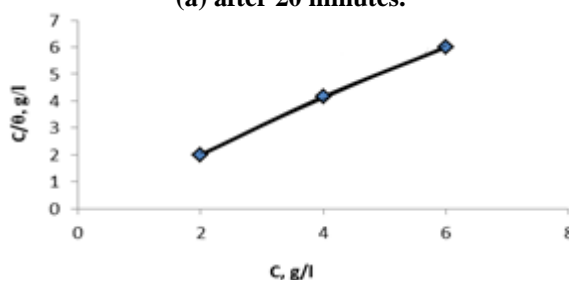
It was found that the best applicable isotherm in this study is Langmuir isotherm Eq. (2) in which a plot of C/θ versus C gives a straight line of the slope of about unity (C stands for inhibitor concentration and θ inhibitor coverage which equals inhibition efficiency% / 100) [14-16]. Figure 10 shows the Langmuir relation, it was selected for best fitting, in which 20, 40 and 50 minutes of exposure were selected in order to check the progressing of time effect on the isotherm;

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad (2)$$

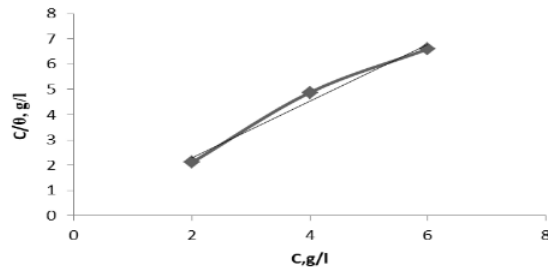
$$K_{ads} = 1/55.5e(-\Delta G_{ads}/RT) \quad (3)$$



(a) after 20 minutes.



(b) after 40 minutes.



(c) after 50 minutes.

Fig. 10. Langmuir adsorption isotherm for aluminium in 18% HCl solution in presence of 6 g/l of ketonaz, (a) after 20 minutes of exposure (b) after 40 minutes of exposure and (c) after 50 minutes of exposure.

From Fig. 10. and Table 3, the values of the isotherm parameters at early stages of the inhibition process, i.e. after 20 and, 40 minutes indicate that the physisorption of ketonaz interaction with aluminium occurs spontaneously, moreover, the strength of interaction is increases with the time. On other hand, the energy of adsorption after 50 minutes decreases and it was transformed into the non-spontaneous case this means that the inhibition is decreased or even stopped as can be assured by returning back to Fig. 4.

Table 3. Adsorption energy values at different temperatures

| Time, min | Adsorption energy $-\Delta G_{ads}$, kJ/mol | Correlation factor, R^2 |
|-----------|---|---------------------------|
| 20 | 8.88 | 0.940 |
| 40 | 11.912 | 0.886 |
| 50 | -18.214 | 0.988 |

4. Conclusions

In this study: some concluding observations from the investigation are given below:

- From experimental work, ketonaz works as an inhibitor for the corrosion of aluminium in a 18% HCl solution.
- As the concentration of inhibitor increases the inhibition efficiency increases.
- The adsorption process of ketonaz is spontaneous at early stages of immersion giving excellent protection.
- Ketonaz adsorption on the aluminium surface in 18% HCl solution obeys Langmuir adsorption isotherm.
- As the time of the process goes beyond 40 minutes the inhibition is decreased which is attributed to the effect of HCl in attacking the formed film by ketonaz at earlier stages.

Nomenclatures

| | |
|------------|------------------------------|
| C_{inh} | Inhibitor concentration, g/l |
| E_{corr} | Corrosion potential, mV |

| | |
|----------------------|---------------------------|
| G | Activation Energy, kJ/mol |
| K_{ads} | Adsorption Constant, (-) |
| R | Gas constant, kJ/mol.°K |
| T | Temperature, °C, °K |
| W | Weight loss, gm |
| Greek Symbols | |
| θ | Inhibitor coverage |
| η | Inhibition efficiency |

References

1. El-Maksoad, S.A.A. (2008). The effect of organic compounds on the electrochemical behavior of steel in acidic media. A review. *International Journal of Electrochemical Science*, 3, 528-555.
2. Rani, R.B.A.; and Basu, B.B.J. (2012). Green inhibitors for corrosion protection of metals and alloys: An overview. *International Journal of Corrosion*, 2012, 1-15.
3. Fayomi, O.S.I.; Akande, I.G.; and Nsikak, U. (2019). An overview of corrosion inhibition using green and drug inhibitors. *Journal of Physics: Conference Series*, 1378(2).
4. Husin, H.; Solo, B.B.; Ibrahim, I.M.; Chyuan, O.H.; and Roslan, A. (2018). Weight loss effect and potentiodynamic polarization response of 1-Butyl-3-methylimidazolium chloride ionic liquid in highly acidic medium. *Journal of Engineering Science and Technology*, 13(4), 1005-1015.
5. Hussein, W.N.; Bahar, S.S.; Rida, N.M.A.; and Alwan, H.H. (2017). Evaluation of inhibitors blends used in Iraqi markets for automobile cooling system. *Journal of University of Babylon*, 25(5), 1821-1829.
6. Mohd, N.; and Ishak, A.S. (2015). Thermodynamic study of corrosion inhibition of mild steel in corrosive medium by piper nigrum extract. *Indian Journal of Science and Technology*, 8(17), 1-7.
7. Christian, V. (2004). *Corrosion of aluminium* (1st ed.). Amsterdam: Elsevier Ltd.
8. Elewady, G.Y.; El-Said, I.A.; and Fouda, A.S. (2008). Anion surfactants as corrosion inhibitors for aluminium dissolution in HCl solutions. *International Journal of Electrochemical Science*, 3(2), 177-190.
9. Rozenfel'd, I.L. (1981). *Corrosion inhibitors*. New York: Mc-Graw Hill.
10. Devakai, H.; and Priya, P.G. (2016). Corrosion studies using zeolite synthesized from fly ash. *Indian Journal of Science and Technology*, 9(20), 1-10.
11. Verma, C.; Chauhan, D.S.; and Quraishi, M.A. (2017). Drugs as environmentally benign corrosion inhibitors for ferrous and nonferrous materials in acid environment: An overview. *Journal of Materials and Environmental Sciences*, 8(11), 4040-4051
12. Obot, I.B.; and Obi-Egbedi, N.O. (2010). Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole: Experimental and theoretical investigation. *Corrosion Science*, 52(1), 198-204.
13. Drugs.com. (2019). Ketoconazole shampoo. Retrieved August 1, 2019, from <https://www.drugs.com/pro/ketoconazole-shampoo.html>.

14. Perez, N. (2004). *Electrochemistry and corrosion science* (1st ed.). New York: Springer
15. Ali, A.I.; and Fouad, N. (2012). Inhibition of aluminium corrosion in hydrochloric acid solution using black mulberry extract. *Journal Material Environmental Science*, 3(5), 917-924.
16. Bouklah, M.; and Hammouti, B. (2006). Thermodynamic characterization of steel corrosion for the corrosion inhibition of steel in Sulphuric Acid solution by Artemisia. *Portugaliae Electrochemica Acta*, 24, 457-468.