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Adsorption Integrity of Pharma-ketoconazole on the Corrosion Behaviour of type AA-6063 Aluminium Alloy on High Pressure Gas Cylinders for Oil and Gas Application

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ABSTRACT

The CO_2, air, oxygen and special gases effluence and contamination in compressed gas cylinders during storage and transportation resulting into localised pitting corrosion of the storage and conveying metal is a major challenge in oil and gas sector. In an attempt to address this, the inhibition influence of Ketoconazole (KCZ) drug performance on the electrochemical corrosion behaviour of type AA-6063 aluminium alloy in 1 M H_2SO_4 solutions was studied through weight loss method and potentiodynamic polarization test. The effect of inhibitor concentration was considered from 0.1-1.0% g/v. The results obtained showed that the drug compound performed effectively in acid solutions with average ketoconazole drug inhibition efficiency above 50% in H_2SO_4 acid from weight loss and potentiodynamic polarization test respectively. Furthermore from corrosion propagation it was revealed that the adsorption of ketoconazole drug onto the AA-6063 aluminium was through chemisorption and mixed type system whereby the redox activity initiating corrosion and the electrolytic transport of corrosion propagation were concurrently intimidated by the absorbed molecules and interferences of the species atoms. The structural properties examined by high resolution scanning electron microscope equipped with energy dispersive spectrometer [SEM/EDX] indicate a passive and less deterioration of AA-6063 aluminium alloy. The adsorption characteristics of the compound were determined to obey the Langmuir and Frumkin isotherm model.

Keywords: Adsorption, Corrosion, AA-6063 aluminium, Ketoconazole drug

INTRODUCTION

Aluminum is an attractive material for engineering applications due to its low cost, light weight, high thermal and electrical conductivity as well as high resistance to corrosion in a wide variety of corrosive environments [1-3]. The corrosion resistance of aluminium in corrosive environments may be attributed to the formation of a protective tightly adhered invisible oxide film on the metal surface. The film reduces or prevents the corrosion, this film is stable in the solutions of pH ranges of about 4.5-8.5 (in acids and bases) [2-5]. Due to the solubility of the film in strong acidic or alkaline solutions, the metal shows high rate of corrosion and dissolution in these conditions.

AA 6063 is an aluminium alloy, with magnesium and silicon as the alloying elements. Research by Elewady et al.; Fayomi et al. [6,7] showed that AA 6063 series aluminium has generally good mechanical and corrosion properties. It is typically produced with very smooth surfaces fit for anodizing. The presence of magnesium and silicon within the aluminium microstructure significantly enhances their corrosion resistance in service especially at ambient temperature [8-10]. The major challenge of aluminium alloy in oil and gas services is its susceptibility at high temperature, impunity emitted from CO_2, air, oxygen and special gases contamination in compressed gas cylinders during storage and transportation resulting into localised pitting corrosion.

Corrosion is a naturally occurring phenomenon commonly defined as deterioration of metal surfaces caused by the reaction with the surrounding environmental conditions, it undergoes rusting easily in humid atmosphere and its rate of corrosion is quite high in acidic media and is a natural process that cannot be prevented, but intervention with the correct measures can control it [9,10]. Without intervention, corrosion progresses and becomes damaging causing economic consequences in terms of repair, replacement, product losses, safety and environmental pollution.

Inhibition of metal corrosion by organic compounds occurs through adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media [9-11]. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of Al dissolution in such solutions. Thus, many studies concerning the inhibition of Al corrosion using organic substances are conducted in acidic and basic solutions [11-13].

In recent time, anti-corrosion drug has been attested by researcher to give meaningful retardation against excessive penetration of aggressive medium on metals lattice. The knowledge of the cause of corrosion inhibitor is essential to develop a control technology and to improve the means of protection [14].

Several anti-corrosion drugs have been studied on the mitigation of metals by Obot and Obi-Egbedi; Abdallah [14-16] with positive influence on the metals. The interfacial behaviour of Fluconazole (FLC) and Ketoconazole (KCZ) as anti-corrosion inhibitive drug between aluminium and hydrochloric acid was studied [15]. The results showed that fluconazole is an excellent corrosion inhibitor for aluminium in acidic medium. Inhibition efficiency increased with increase in the concentrations of fluconazole but decreased with rise in temperature. The adsorption of the inhibitor on the aluminium surface is found to accord with Temkin adsorption isotherm whereby the driving force for the adsorption process being the increase in the adsorption enthalpy rather than the reduction in the adsorption entropy.

In this study, the use of Ketoconazole is envisaged on the corrosion retardation of aluminium in acidic environments since the knowledge of the cause of corrosion is essential to develop a control technology and to improve the means of protection. KCZ is an antifungal drug with a brand name of Nizoral was found to be a heterocyclic compound containing N, O and aromatic rings containing several π bonds which could possibly serve as active sites for the adsorption process [15,16]. Besides, KCZ is very cheap and easily available. For this research study KCZ drug was selected as organic inhibitors from different concentration to examine its potential performance to mitigate excessive deterioration of AA-6063 aluminium in acidic solution by using weight loss method and linear polarization measurement.

MATERIALS AND METHODS

Material

Type AA-6063 aluminium alloy obtained commercially from the aluminium rolling mill in Ota, Nigeria was analysed and the nominal chemical composition (mass fraction) of: 0.20% Si, 0.42% Fe, 0.11% Cu, 0.027% Mn, 99.8% Al was obtained.

Inhibitive admixed

A 5 mg white powder of KCZ was obtained from Pharma-chemical laboratory in South Africa. It was prepared in volume concentrations of 0.1, 0.3, 0.5 and 1.0 ml per 25 ml of 1.0 M H_2SO_4 acid. The obtained KCZ was diluted with distilled water to make 2 ml concentrated solution. The structural formula is shown in Figure 1, with the molecular formula of $C_{26}H_{28}Cl_2N_4O_4$ and molar mass of 531.43 g/mol.

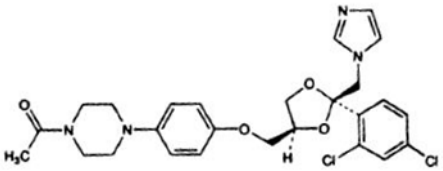

Figure 1: Chemical structure of ketoconazole

Test media

98% analytical grade H_2SO_4 was prepared with deionized water to obtain a dilute concentration of 1 M H_2SO_4 which serves as corrosive test medium.

Specimens preparation

Rectangular aluminium specimen were mechanically cut to size of 15 × 15 × 2 mm with the area of 3 cm^2 was used for study of the mass loss, and for electrochemical study. The surfaces of the specimens were mechanically polished with different grades (400, 600 and 1200 µm) of emery papers, then rinsed with distilled water and allow to dry [5].

Weight loss experiment

Aluminum samples of dimension 15 × 15 × 2 cm were cut to size with area of 3 cm^2 and the hole 3 mm diameter drilled at one end of the coupon samples and polished with abrasive paper rinsed with distilled water and allowed to dry. The pre-cleaned and weighed samples were suspended in beakers using glass hooks and rods containing the test solutions of different concentrations of 0.1, 0.3, 0.5 and 1.0 ml. Tests were conducted under total immersion conditions in 25 ml of the solution. Immersion time was varied from 1-21 days (504 h). The samples were retrieved from test solutions after every 72 h, appropriately cleaned, dried and reweighed. The weight loss was taken to be the difference between the weight of the samples at a given time and its initial weight.

Plots of weight-loss (mg) and corrosion rate (mm/y) versus exposure time (h) for the two test media and those of percentage inhibition efficiency (%IE) versus exposure time (h). The corrosion rate (R) values are obtained by using the following equation [13]:

$$R = \frac{87.6\,W}{DAT} \qquad (1)$$

Where, W is the weight loss in milligrams, D is the density in g/cm^2, A is the area in cm^2 and T is the time of exposure in hours. The %IE was calculated from the relationship:

$$\% \text{ Inhibition Efficiency} = \left(\frac{w1-w2}{w1}\right) \times 100 \qquad (2)$$

Where, W1 and W2 are the weight loss (in the absence and presence of KCZ). The %IE was calculated for all the inhibitors every 72 h during the course of the experiment, while the surface coverage is calculated from the relationship:

$$\theta = [1 - \frac{wi}{w2}] \qquad (3)$$

Where, θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent. W1 and W2 are the weight loss of aluminium sample in free and inhibited acid solution respectively.

Linear polarisation and open circuit potential

The corrosive environment of 1.0 M H_2SO_4 was simulated in a beaker by adding 25 ml of each component. The organic inhibitor prepared and added at varying concentrations for each sample. The conducting wire was attached to the polished surface of the sample using aluminum tape and connected to the working electrode, graphite counter electrode immersed in solution and reference electrode placed on sample surface. The nova software was used with Linear Polarization (LR) resistance and the current was set to 10 mA (max) and 10 nA (min). LSV staircase parameter start potential of -1.5 v, step potential 0.001 m/s and stop potential of 1.5 v set. New separate samples of each type of metal were again used to conduct an Open Circuit Potential (OCP) test by adding varying concentration of organic again and the same simulated media. The OCP ran to 60 min. Applied potential *vs.* current density was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants ' ba' and 'bc' respectively. According to the Stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$\text{Icorr} = \frac{(ba \times bc)}{(2.303(ba \times bc) \times Rp)} \qquad (4)$$

Where, Rp is the polarization resistance. The values were calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curve at E_{corr}. The Inhibition Efficiency (*IE*) was calculated using the following equation:

$$\text{I.E}\ (\%) = [\frac{(Icorr - Icorr(1))}{Icorr}] \times 100 \qquad (5)$$

Where, I_{corr} is corrosion current without inhibitor and I_{corr} (1) is corrosion current with inhibitor.

Structural properties

The structural evolution was characterized on Joel JSM6510 Scanning Electron Microscope (SEM) built with Energy Dispersive Spectroscopy (EDS) and Olympus BX51M.

RESULTS AND DISCUSSION

Weight loss measurements

The results of the weight-loss examination of type AA-6063 aluminium alloy at various time intervals, in the absence and presence of ketoconazole concentrations in 1 M H_2SO_4 are presented in Figure 2. The variation of weight loss, corrosion rate and percentage inhibition efficiency versus exposure time at specific KCZ concentrations were examined in Figures 2-4. The aluminium sample immersed in the medium with 0.1% (ml) inhibitor concentration lost the most weight at 504 h (21 days) of the experiment with a weight loss of 2.500 g. The value for the as-received experiment without inhibitor addition is 3.0002 g at the end of the experiment and hence recorded the most deformed within this period. However a changed occur at 1%, 0.5% and 0.3 (ml)% of inhibitor concentrations with the lowest weight loss values of 1.200 g, 2.100 g and 1.800 g (504 days) of the experiment respectively. A sharp resistance to the activity of the SO_4^- and H^+ could be seen reason been that there was a slow progression of weight loss in every inhibited samples as compared to the control samples over time. Interestingly one could link the positive slow influence of sulphide on the degradation behaviour to the effect of ketoconazole activities at the metal/solution interface of the samples. On the other hand, the functional groups, molecular structure, and the chemical interaction of its heteroatoms with the aluminium at the metal lattice could also could suitable inhibitive action seen. The aluminium was seen to passives with increase in KCZ concentration due to increase in the presence of networking inhibitive molecules.

In Figure 3, the recorded corrosion rate values also decreased with time as the inhibitor concentration increases. As at 21 days of the experiment, the 0.1 ml% KCZ concentration apart from the control had the highest corrosion rate value of 0.4191 mm/y. The control sample has a corrosion rate of 0.503 mm/y. The corrosion rate values decreased progressively with the increase in inhibitor drug concentration with 0.2012, 0.352, 0.3018 mm/y for 1 ml%, 0.5 ml% and 0.3 ml% inhibitor concentrations respectively.

In Figure 4, a high percentage of inhibitor efficiency was noticed at the initial of the experiment at 72 h with 0.1 ml% inhibitor possessing 90% inhibition performance and 80% for sample with 1.0 ml%. This high inhibitor efficiency pointed out the potential of KCZ adsorbed drug. Invariably at the end of the experiment (504 h) a recorded 60% inhibitive performance was seen with 1.0 ml% induced sample. This implies that firstly adsorption take place but impede over time based on % concentration. Secondly it is good to state that the inhibitor drug affects the redox process, thereby influencing the cathodic regions of the Al surface through physiochemical interaction between the molecules of the inhibitor and the acid solutions. More so with KCZ retarding the hydrogen penetration, its influence was seen as a mixed type inhibitive compound.

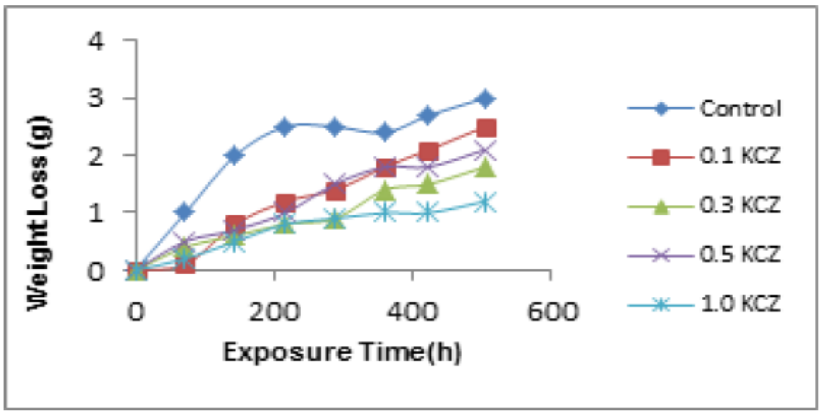

Figure 2: Variation of weight loss with exposure time in the presence and absence of KCZ in 1 M H_2SO_4

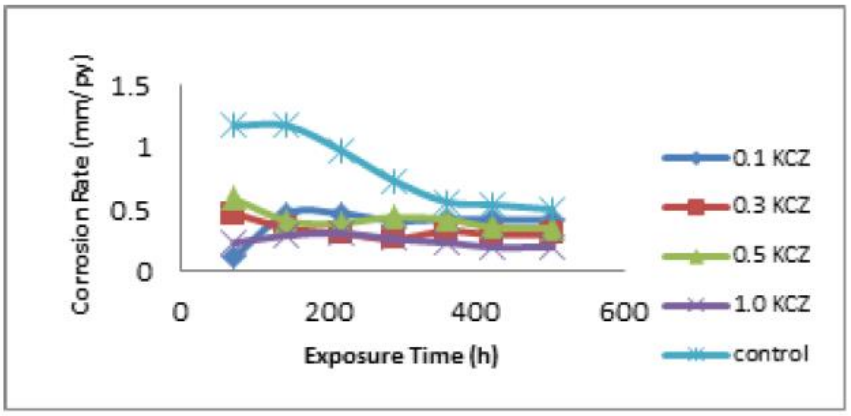

Figure 3: Effect of concentration of KCZ inhibitor on corrosion rate of aluminium 1 M H_2SO_4

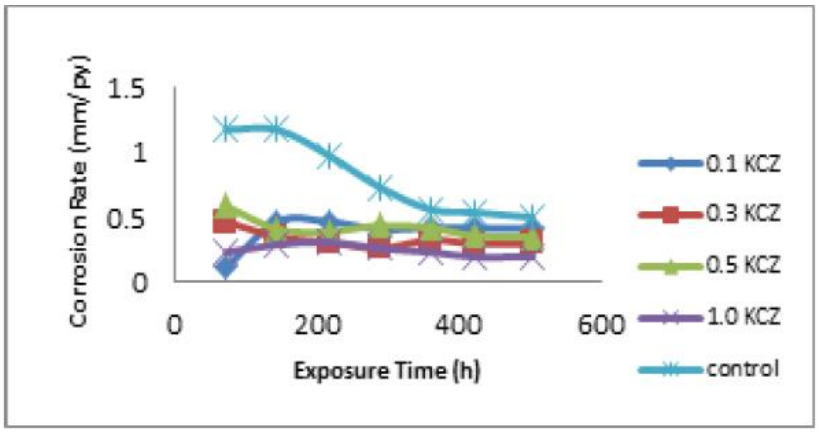

Figure 4: **Plot of inhibition efficiency of KCZ inhibitor in 1 M H_2SO_4 during the exposure time**

Linear potentiodynamic polarization

The polarization result of KCZ on the anodic and cathodic curve for mild steel in the acid media was investigated. Observation of Figure 5 depicts the polarization curves with and without KCZ addition. KCZ expressively influenced the corrosion behaviour of the aluminium alloy in 1 M H_2SO_4 solution in all volume fraction of KCZ concentration. Data observed from the Tafel plot correlate with the observed polarization curve. The result obtained from the polarization study was also in conformity with the weight loss experiment which indicates the spontaneous improvement from 0.1-1.0 ml%. Obviously protective film from aluminium matrix and the adsorbed molecules of KCZ were seen to cultivate the progression of corrosive resistance species. The amount KCZ molecule at increasing level was noticed to compete and inhibit the active site by blocking the lattice pole invaded by acid solution. The corrosion potential as observed in Figure 5 deviates to more positive potentials with increase in KCZ concentration, thus protecting the aluminium from severe hydrogen evolution impediment (Table 1).

From Figure 6, the open circuit potential curve was presented with aim of observing the polarization trend against time. The nature of the OCP in the presence of inhibitor was different from that of the blank which is assumed expected if the inhibitor performs efficiently. At 1 M H_2SO_4 and varied addition of concentrations of KCZ drug compound. The sample without KCZ inhibitor in the acid media shows massive degradation of the Al samples compared to the inhibited samples as observed from the potential time curve. The curve shifted towards positive potentials, attesting that metal degradation is inactive in the presence of KCZ.

With this, appreciable corrosion inhibition as a result of the electrochemical activities of KCZ indicated less corrosion deterioration rate. From general view one can attest that the cations of the inhibitor molecules effectively offset the corrosive influence of SO_4^{2-} and H^+ ion in the test medium. Although, the differential mechanism of inhibition in most organic compound often performed in Al were often recorded to perform well due to diffusion activity of organic molecules from organic inhibitive compounds at the metal surface layer therefore leading to less corrosion failure.

Table 1: Polarization data for inhibited aluminium in acid media

Sample	I_{corr} (A/cm^2)	R_P (Ω)	E_{corr} (V)	Corrosion Rate (mm/yr)
Control	5.52E-08	6.01E + 06	-0.9728	2.9085
0.1 KCZ	2.10E-09	2.14E + 07	-0.9660	1.9455
0.3 KCZ	9.19E-10	3.19E + 07	-0.8321	1.8756
0.5 KCZ	5.37E-12	3.69E + 07	-0.8522	1.7659
1.0 KCZ	2.44E-11	4.51E + 07	-0.6735	1.5632

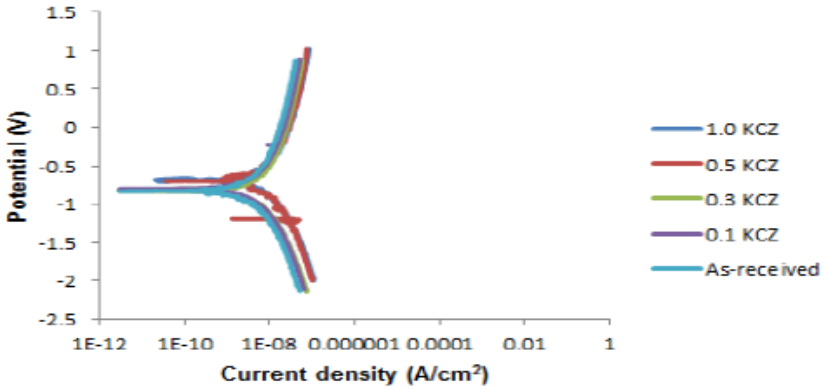

Figure 5: Cathodic and Anodic polarization scans for aluminium substrate with and without KCZ in 1 M H_2SO_4

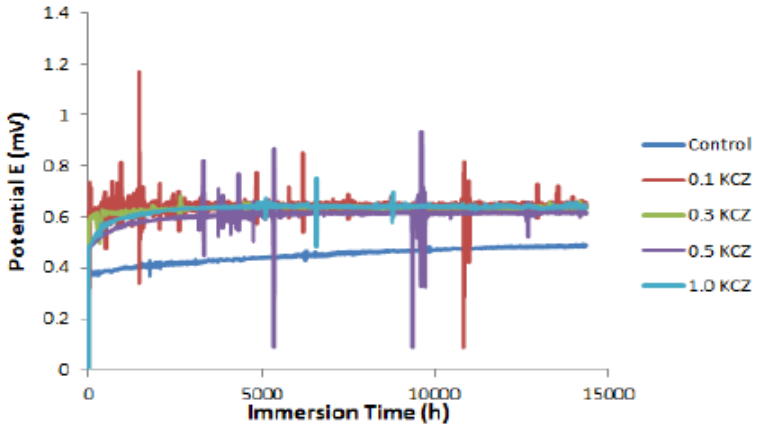

Figure 6: Open circuit potential curves for potential measurements in the presence and absence of KCZ in 1 M H_2SO_4

Surface coverage and adsorption isotherm

Presented in Figures 7-9 are the curves of the surface coverage and mechanism of adsorption isotherm of the KCZ concentrations for corrosion inhibition of type AA-6063 aluminium alloy in 1 M H_2SO_4. The mechanism of adsorption on aluminium is a surface interaction phenomenon through which KCZ ionized atoms are attracted to the aluminium surface and adsorbed. From Figure 7, the interactive coverage is between 0.8 at the beginning of the experiment and 0.6 at the end of the experiment in (504 h). The linearity effect (R^2) ranges is 0.82. This implies that the adsorption process is influenced by the nature of the adsorbate, surface charge of the metal, the aggressiveness of the electrolyte and by the chemical structure of the inhibitors. This is in par with study by Umoren et al. that charge molecule and chemical structure built up surface active species at metal/solution interaction. The measured data are also seen to obey Langmuir and Frumkin adsorption isotherm as observed in Figures 7 and 8 showing values of degree of linearity (R^2) ranges from 0.92-0.96. More so, it is noteworthy to mention that the inhibitor are term as adsorption and mixed type on the metal surface. This are assumed to be adsorbed by the interaction between the lone pair of the electrons of the chemo-adsorbed species and activity of oxygen and nitrogen atoms respectively from ketoconazole drugs.

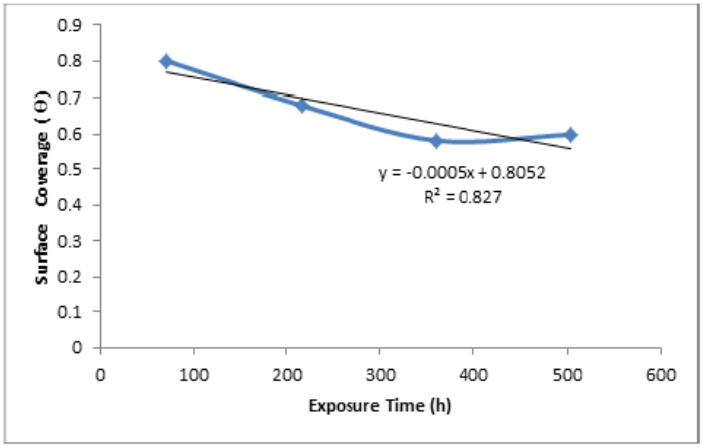

Figure 7: Surface coverage against exposure time

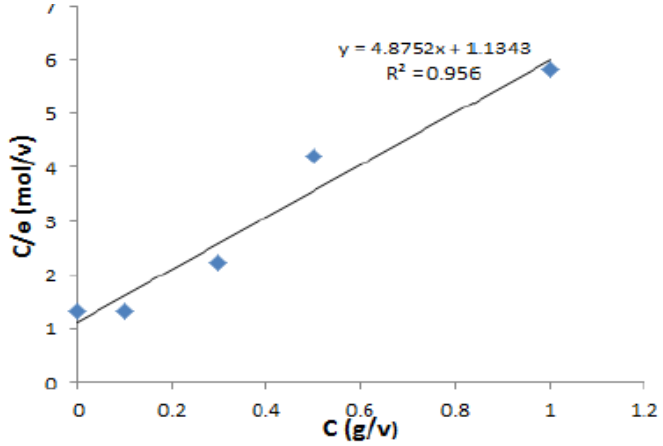

Figure 8: Langmuir isotherm for adsorption of KCZ inhibitor onto aluminium surface in 1 M H_2SO_4

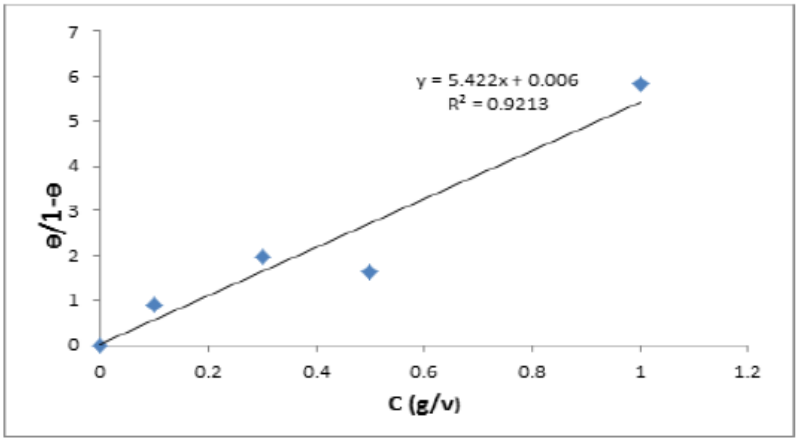

Figure 9: Frumkin isotherm for adsorption of KCZ inhibitor against concentration

Figure 10a-10b shows the scanning electron micrographs of the type AA-6063 aluminium before and after exposure in 504 h, 1.0 ml% of KCZ inhibitor. The surface of the control samples shows severe pits during corrosion metal/medium interaction. The protective layer of aluminium could not resist the threats of SO_4^{2-} and H^+ ion emitted from the solution. In other hands, it can be seen that the dissolution rate of aluminium reduced and better surface appearance were observed due to the formation of protective inhibitor film on the metal surface (Figure 10b). Although, the aluminium surface from the acid medium with KCZ inhibitor possesses inhibitor molecules that fully cover the metal interface, ensuing a sufficient protection of inhibition against corrosion intimidation. This is in par with the major assumption [4]. The EDS confirms the elemental composition of metal/medium-inhibitive activity at metal interface (Figure 10c).

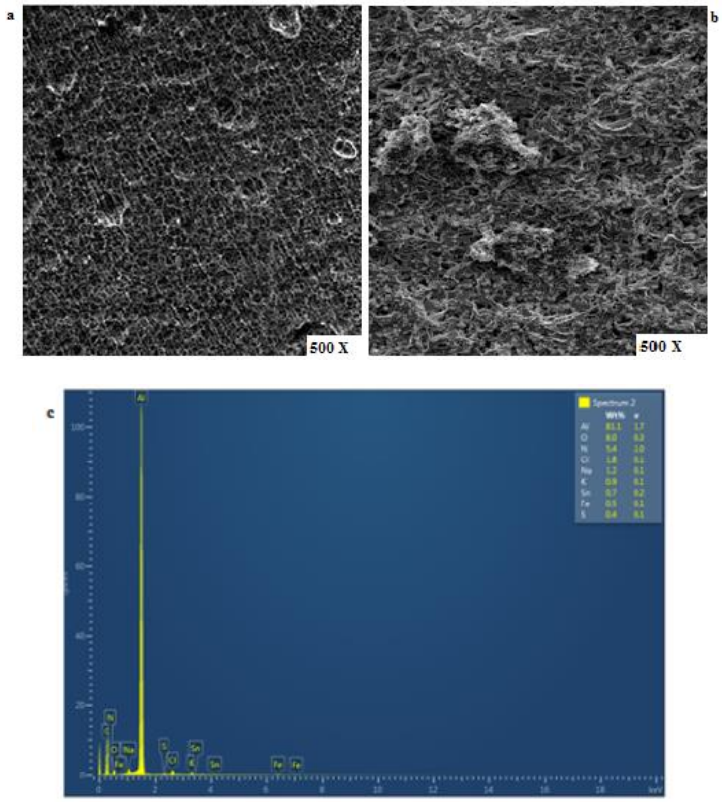

Figure 10: SEM micrographs of (a) Aluminum sample with 0% concentration of KCZ inhibitor. (b) 1.0 Concentration of KCZ inhibitor, (c) EDS of 1.0 concentration of KCZ inhibitor

CONCLUSION

It is clear of the result obtained that the electrochemical properties of KCZ drug on the corrosion inhibition of type AA-6063 aluminium in 1 M H_2SO_4 acid performed well as highly derivative organic drug. It was determined to be mixed type with significant inhibitor efficiency of over 60%. It is ascertained that the inhibitive action are as a results of the activity of the functional groups and sufficient molecules by KCZ compounds. The adsorption isotherm fit favoured the Langmuir and Frumkin adsorption.

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