Investigating the Acid Failure of Aluminium Alloy in 2 M Hydrochloric Acid Using *Vernonia amygdalina*

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Abstract. The acid failure of aluminium alloy in 2 M hydrochloric acid solution in the presence of *Vernonia amygdalina* extract was investigated using gasometric technique. Aluminium alloy coupons of dimension 4 cm by 1 cm were immersed in test solutions of free acid and also those containing extract volumes of 2, 3, 4 and 5 cm^3 at ambient temperature for 30 minutes. The volumes of hydrogen gas evolved as a result of the rate of reaction were recorded and analyzed. Analysis revealed that maximum inhibitor efficiency which corresponds to the lowest corrosion rate was obtained at optimum inhibitor volumes of 5 cm^3, with reduction in the corrosion rate observed to follow in order of increasing extract volumes. Adsorption study revealed that Temkin isotherm best described the metal surface interaction with the extract phytochemicals, with 12 minutes becoming the best exposure time for the phytochemicals to adsorb to the metal surface at all volumes. Statistical modelling of the corrosion rate yielded an important relationship suitable for estimating corrosion rate values once volumes of the extract is known. Microstructural studies, showed an indirect relationship between crack growth rates and extract volumes, while consistency of the irregular intermetallic phases increases with increasing extract volumes.

1   Introduction

The susceptibility of metallic materials to deterioration in acidic environment is an issue of concern and has assumed worldwide significance because of the losses resulting from such damages. The serious consequences of these corrosion processes are presented in the form of metals degradation, plant shutdowns, waste of valuable resources, loss or contamination of product/environment, reduction in efficiency and costly maintenance representing approximately 3.1% of worlds GDP [1]. However, the use of suitable materials or alloys is one of the most commonly used method and aluminium (Al) alloys are often deployed in this respect. The superior properties of Al-alloy have made it a material of choice in most engineering application.

Industrial operations of oil well acidizing, cleaning and acid pickling involve the exposure of metals to aggressive agents. In oil well acidizing various volumes of hydrochloric acids are used to dissolve carbonate deposits or scales which interfere with oil passage in the tubing. However, the lines and tubing must be protected during this operation from corrosive attack which induces cracks, by the acid, by high temperatures and pressures, and by the potential for a sour environment resulting from the high hydrogen sulphide and carbon dioxide contents.

Studies [2-6] have shown that several synthetic inhibitors are often used for the purpose of combating damage of metals in service. These inhibitors have been found to be toxic to the environment by harming aquatic and plant life in the ecosystem. Increasing awareness for a clean, sustainable and green environment that is devoid of the use of substances that are environmentally damaging has encouraged the use of inhibitors from plant sources. This group of inhibitors have been found to be cheap, easily accessed and replenished, non toxic and equally effective in action. Numerous studies have been reported on the protective action of green inhibitors on metals in acidic and alkaline solutions [7-14], with a few of them focusing on the Al-alloy [15-17]. Of all the previous studies conducted so far, none yet has worked on investigating the acid failure of Al-alloy in 2 M hydrochloric acid using *Vernonia amygdalina* leaf extract. Also, in contrast to previous studies that deduced corrosion rate from weight loss measurements, the uniqueness of the approach adopted in this study was to employ the rate of evolution of hydrogen (H_2) gas as a measure of the rate at which the alloy is corroding in the presence of *Vernonia amygdalina* (VA). The basis for using this technique was based on the theory that the rate at which metal is depleted after exposure corresponds to the rate of evolution of H_2 gas since it was discovered that increased metal loss resulted in rapid rate of evolution of hydrogen gas.

VA leaves are green with a characteristic odour and a bitter taste. No seeds are produced and the tree has therefore to be distributed through cutting. VA is commonly called ewuro and edidot or bitter leaf in Ibadan and Cross River State in South West and South – South Nigeria respectively [18,19]. The present study therefore seeks to investigate the inhibitive effect of this extract on the environmentally assisted cracking of Al-alloy in 2.0 M hydrochloric (HCl) using the gasometric technique at ambient temperature. It is well known that when metals in service corrode in the presence of acids, H_2 gas is constantly evolved. The rate at which the H_2 gas is evolved corresponds to the rate of metal dissolution in the environment, depicted by weight loss. Thus, if there is a way to measure the volume of H_2 gas evolved as a relationship with the metal mass loss, the rate of corrosion of the metal within the environment can directly be simulated without necessarily shutting down the system or plant.

This will enable the engineers to have a pre-knowledge of the situation and know when to carry out particular type of maintenance. The focus of this study therefore is to establish the relationship between corrosion rate and the rate of evolution of H_2 gas as well as determine other necessary parameters that relate to metal surface phenomenon in a particular environment. Furthermore, inhibitor efficiency was determined by the method adopted by Okafor et.al [20-23] and the corrosion rate modeled statistically. The investigation further goes on to analyze the adsorption mechanism of the extract and also its effect on the microstructure of the alloy.

2   Materials and Methods

Rectangular specimens of Al metal coupon of dimension 4 x 1 cm were employed for the determination of corrosion inhibition of VA extract. Specimens were prepared by degreasing in ethanol and acetone. It was then allowed to dry. The composition of the Al samples was analyzed using Optical Emission Spectrometer (OES) and the result as obtained is presented in the table below.

Table 1   Composition of aluminium alloy employed.

S/N	Element	wt %
1.	Silicon	0.157
3.	Cadmium	0.0005
4.	Iron	0.282
5.	Calcium	0.0011
6.	Copper	0.0025
7.	Cobalt	<0.0010
8.	Manganese	0.024
9.	Lithium	<0.0002
10.	Magnesium	0.51
11.	Sodium	0.0005
12.	Zinc	<0.0010
13.	Phosphorous	<0.0010
14.	Nickel	<0.0010

Table 1 (*continued*) Composition of aluminium alloy employed.

S/N	Element	wt %
15.	Lead	<0.0005
16.	Chromium	0.023
17.	Tin	<0.0010
18.	Titanium	0.0049
19.	Strontium	<0.0001
20.	Silver	<0.0001
21.	Vanadium	0.0035
22.	Boron	0.0007
23.	Zirconium	0.0020
24.	Beryllium	<0.0001
25.	Al	99
26.	Bismuth	<0.0010

The acidic extracts of VA were prepared from its fresh leaves after it has been air dried and ground into powder. Ten grams (10g) of the powder was then put into a flat bottom flask containing 200 cm^3 of 2 M HCl solution. The resulting solution was refluxed for 2 hours and left over night before it was filtered. Extract quantity of 2, 3, 4, and 5 cm^3 obtained by serial dilution were employed for the investigation and the experimental set up is as presented in Figure 1. Each specimen was dropped into the mylius cell containing 50 cm^3 of test solution system at room temperature. The volume of H_2 gas evolved per 120 seconds interval was recorded for 30 minutes in a calibrated tube by downward displacement of water and the plot of volume against the interval was carried out and represented in Figure 2. The inhibition efficiency was then determined using the technique adopted elsewhere [20-23]:

$$I.E\left(\%\right) = \frac{\left(V_H\text{-}V_{HI}\right)}{V_H} \times 100 \tag{1}$$

Where, V_H is the volume of H_2 evolved without inhibitor (i.e. control experiment) and V_{HI} is the volume of hydrogen evolved with inhibitor.
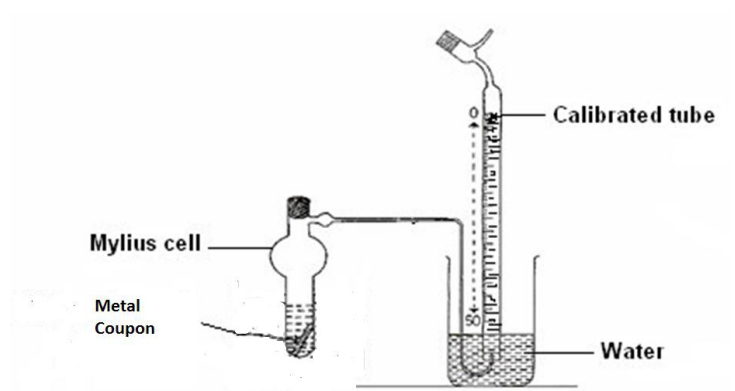
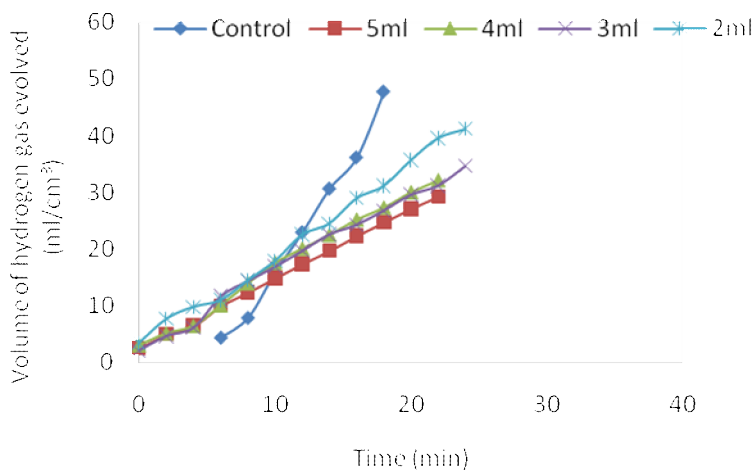**Figure 1**   Schematic diagram of the experimental set up [20-23].

Figure 2   Variation of volume of H_2 (cm^3) evolved with time (minutes) of Al coupons for different volumes of VA extract in 2M HCl at room temperature.

Since the Al-alloy reacts with HCl in such a way that H_2 gas is given off as one of the products of the reaction, it is therefore, suitable to predict the rate of reaction by determining the rate of H_2 gas evolution from the system. By inference, the rate of reaction corresponds to the rate of corrosion damage of the Al-alloy in HCl in the presence of VA extract. Thus, the rate of corrosion corresponding to the rate of H_2 evolution was modeled based on the idea that the rate of H_2 gas evolution is directly proportional to the rate of corrosion, which will also be directly proportional to the rate at which the weight of the metal is lost. This therefore means that, modeling the rate of corrosion from the direction of rate of H_2 gas evolution is indirectly a way to model the rate of

material loss when the relationship between the weight loss and H_2 gas evolution is known. The basis for this is as represented in Eq. 2 [21-23]:

$$\Delta V \; \alpha \; \Delta W$$

$$\frac{d\Delta V}{dt} \; \alpha \; \frac{d\Delta W}{dt}$$

$$\text{But } R \; \alpha \; \frac{d\Delta W}{dt} \; \alpha \; \frac{dV}{dt} \tag{2}$$

where,

α = proportionality sign
ΔV = volume of H_2 gas evolved
ΔW = metal weight loss due to corrosion
R = rate of corrosion
t = time (minutes)

Thus to determine Eq. 2, it is necessary to develop a relationship between volume evolved and the time of evolution. This was arrived at by a polynomial regression analysis of the volume of H_2 gas against time leading to Eq. 3 [21-23]:

$$V = c + bt + at^2 \tag{3}$$

Thus,

$$R = \frac{dV}{dt} = b + 2at \tag{4}$$

A particular case of this study will involve adapting Eq. 3 and 4 to the volume-time measurement for individual volume of extract. For instance, for measurement relating to 5 cm^3 extract, the corrosion rate model is presented as Eq. 6 [21-23]:

$$V = -3.247 + 1.227t + 0.00197t^2 \tag{5}$$

$$\frac{dV}{dt} = 1.227 + 0.0394t \tag{6}$$

3   Results and Discussion

Examining Figure 2 revealed that the corrosion rate of Al-alloy as indicated by the amount of H2 evolved decreased in the presence of VA when compared to the control. The amount of H2 evolved also decreased with increasing volume of the extract. This indicates that the VA extract in the solution has an inhibitive effect on the corrosion of Al in HCl and that the extent of inhibition depends on the amount of VA extract present. However, 2 cm3 extract became effective after the 12th minute when compared to the control, while the 3 and 4 cm3 extract became effective between the 10th and 12th minute and then the 5 cm3 extract became effective just on the 10th minute of the experiment duration. This same trend was observed in Figure 3 which shows the percentage inhibition efficiency (% I.E).
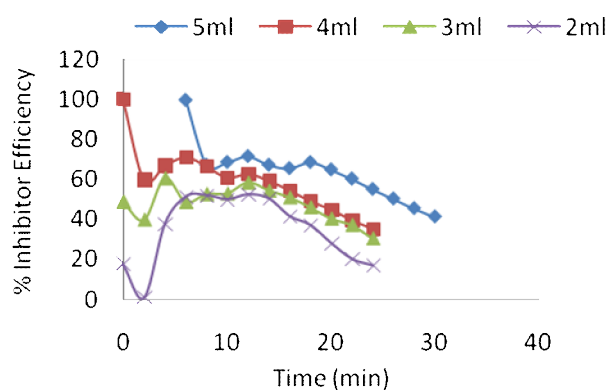

Figure 3 Percentage inhibition efficiency of varying volumes of VA extracts with time (minutes) on Al coupon in 2M HCl solution at ambient temperature.

Thus, at the beginning of the reaction, % I.E. dipped for all the extract volumes, while % I.E. attained the highest values and became stable between the 8th and 14th minute of the experimental duration, showing that a relationship might exist between this particular times and % I.E. In a way it suggests that a complex formation might have resulted from the reaction between HCl, Al-alloy and the extract phytochemicals. However, for all extract volumes the % I.E. values began to drop after about the same time (16th minute) with 2 and 5 cm^3 extract showing the highest and lowest drop respectively.

It was observed furthermore, from Figure 4 that the rate of corrosion generally decreases in the presence of VA extract. The 2 cm^3 extract of VA shows the lowest effect of reducing the corrosion rate of Al followed by the 3 cm^3 extract. The 5 cm^3 extract however began by slowing down the rate but towards the latter part of the reaction, the rate tends to increase above the 3 cm^3 extract

volumes, though only marginally. The reduction in corrosion rate in the presence of VA extract at different volumess was observed to follow the order; 2 cm^3 extract < 3 cm^3 extract < 4 cm^3 extract < 5 cm^3 extract.
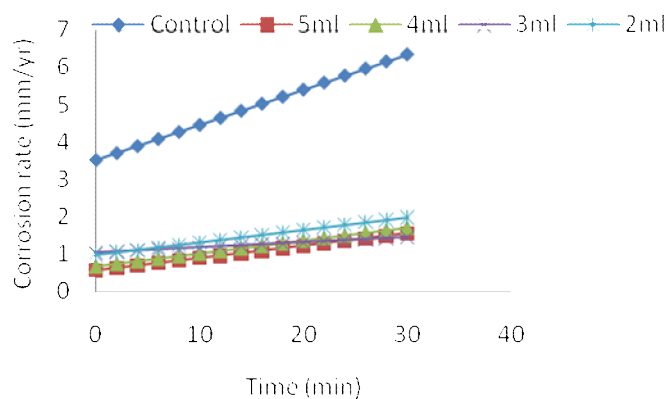

Figure 4 Corrosion rate of varying volumess of VA extract with time (minutes) on Al coupon in 2M HCl solution at room temperature.
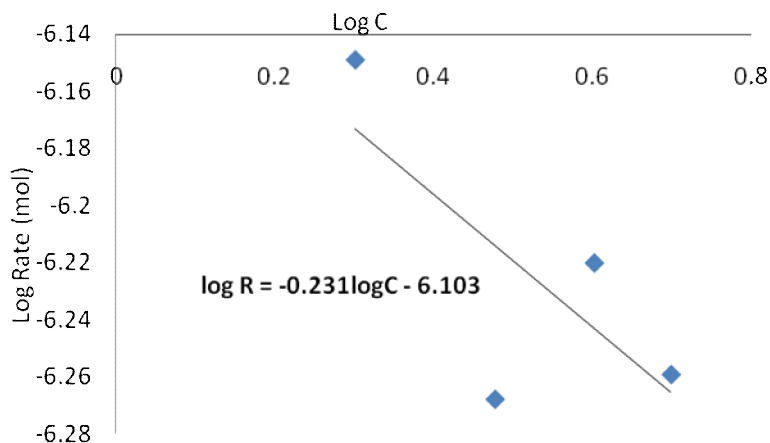

Figure 5 Plot of Log of corrosion rate against log of the acid extract volumes.

In addition, investigating the relationship between corrosion rate, R, and the changing volumes to the determine reaction constant and also the specific reaction constant for the HCl-corrosion of Al-alloy in the presence of VA extract involved carrying out a statistical regression analysis of the values of R against those of concnetration. However, it has been proven [21-25] that corrosion rates can be linked with acid volumes with the equation:

$$LogR = Logk + BLogC \qquad (7)$$

where,

R   = corrosion rate
k   = reaction constant
B   = specific reaction constant and
C   = volumes.

Therefore to obtain reaction constant, the corrosion rates obtained from H_2 evolution method must be converted to the same unit (mol min^{-1}) by assuming that H_2 evolution reaction occurred at 1.01325×10^{-5} Pa. Figure 5 shows the relationship between LogR and LogC for the Al-alloy coupon sample. The straight line in the graph correlates all the points with a correlation coefficient of 0.73. The estimated k and B values were 7.89×10^{-7} mol min^{-1} and -0.231. This is divergent to the positive value of B obtained in other studies [24-25] when no inhibitors were used, therefore, the negative value of B indicates a decreasing slope which significantly depicts the inhibitive action of the VA extract on the Al-alloy corrosion. Thus, the exact relationship can be described as:

$$R = 7.89 \times 10^{-7} \; C^{-0.231} \qquad (8)$$

This perspective is in accord with Figure 4, where a clear cut distinction was observed between the control and inhibited solutions.

3.1   Adsorption Studies

The mechanism of interaction between the phytochemicals in the VA extract and the metal surface can be explained using various adsorption isotherms. The degree of surface coverage, θ, for the different inhibitor volumess were evaluated based on volume of H_2 gas evolved measurements. Efforts were then made to fit the θ values using the correlation coefficient with different adsorption isotherms namely, Langmuir (0.978), Freundlich (0.984), Frumkin (0.329) and Temkin (0.99). However, the Temkin isotherm was found to be best fitted to the θ values as it showed the highest coefficient of correlation. This was expected, as the method has been reported to be superior in the prediction of gas phase equilibra [26]. The plot of θ as a function of logarithm of volumes of VA is shown in Figure 6.

This result therefore confirms the assumption that the corrosion inhibition of the VA extract is attributed to the adsorption of molecules of phytochemicals on the metal surface by the process of chemisorption where a covalent bond is formed

between phytochemicals and Al-alloy. This phenomenon is an important tribological consideration in metal surface preparation.
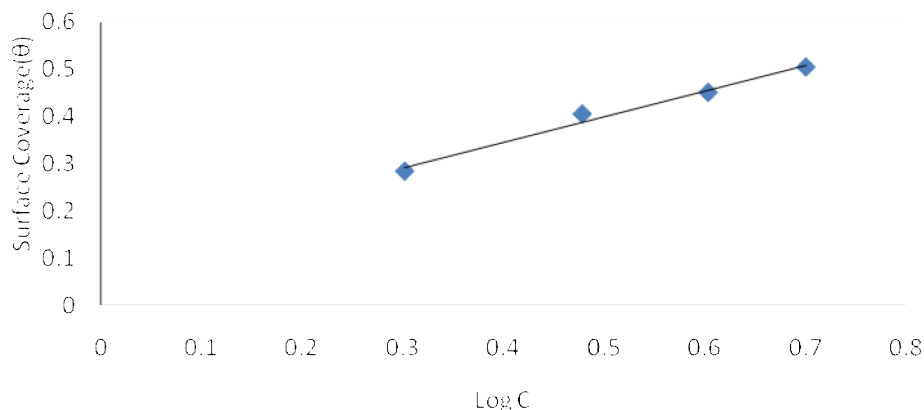

Figure 6 Variation of surface coverage (θ) with logarithm of volumes of acid extract showing compliance with Temkin isotherm.

Furthermore, the degree of surface coverage, θ, for the extract at different volumes was plotted for different time intervals of 8, 12, 16, 20, 24, 28 and 30 minutes as shown in Figure 7 to investigate if there are any contribution of times of exposure to the relationship between θ and C.
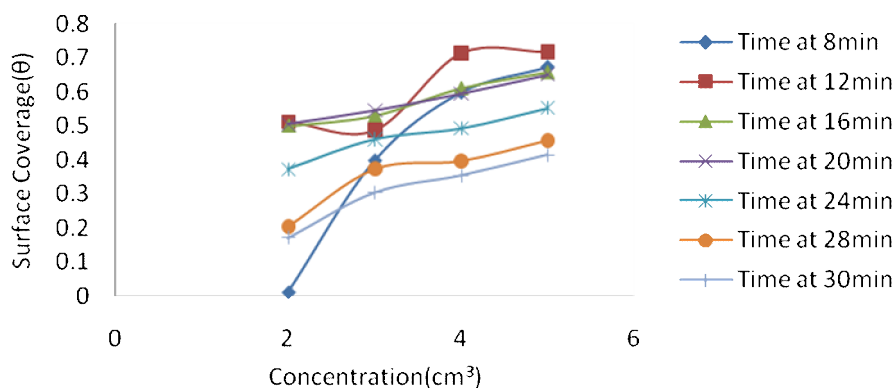

Figure 7 Variation of surface coverage (θ) with extract volumes (M) at different time intervals.

For the 8 minutes curve, the surface coverage, θ, was very low at extract volumes of 2 cm^3, but the rate of surface coverage during this time frame increased rapidly after 3 cm^3 volumes until it reached the optimum level of 0.0652 at extract volumes of 5 cm^3. The θ values for the 24, 28 and 30 minutes curve were quite low across all volumes, when compared to the others from the

beginning to the end of the experiment. However, for the 12 minutes curve which is closely followed by the 16 and 20 minutes curve, the θ values were high throughout the experiment even as extract volumes increased, showing that this is the best exposure time for the phytochemicals in the extract to adsorb to Al-alloy surface. This further validates the assertion in Figure 3 that clearly indicates that the peak I.E (%) value was between the 8th and 14th minutes for all extract volumes employed in the study.

The values of θ were also plotted against lnC and presented in Figure 8. Further study on the adsorption phenomenon required correlating θ against lnC (i.e natural logarithm of volumes) as shown in Figure 8, in such a way that [27]:
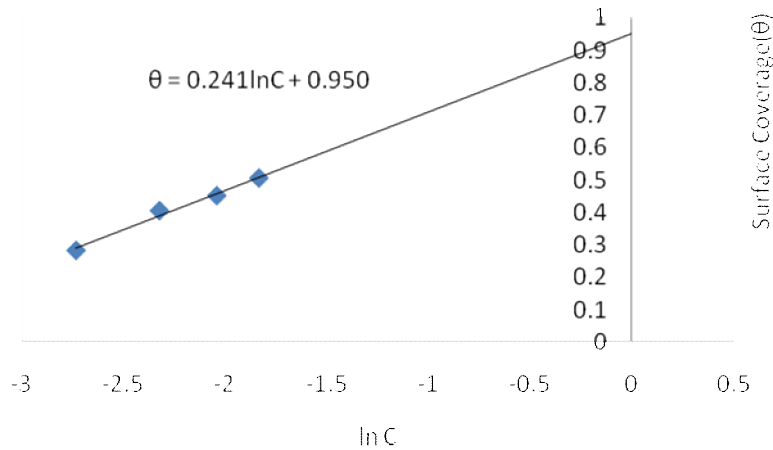
$$\theta = \beta + \gamma \ln C \tag{9}$$

Figure 8 Variation of Surface Coverage (θ) with natural logarithm of volumes (M).

where:

$$\beta \ (ml/ml) = \frac{RT}{b} \ln a \tag{10}$$

$$\gamma \ = \frac{RT}{b} \tag{11}$$

a = Temkin constant related to the maximum adsorption capacity
b = Temkin constants related to the energy of adsorption.
θ = Surface coverage
C = Volumes

R and T are the gas constant (8.314 J mol^{-1} K^{-1}) and temperature (298 K) respectively. From further analysis, the values of the energy of adsorption, b, is estimated to be 10,322.72 J mol^{-1} while the maximum adsorption capacity, a, in terms of volume of H$_2$ evolved is estimated to be 52.36. The estimated value of a, shows that bonding energy exists between the phytochemical and the metal. However, since bonding energy range for ion-exchange is reported [28] to be in the range of 8-16, the value of b indicate that the process cannot be physisorption, as its value is quite high. The values of b, as low as 0.073, is reported elsewhere [28] to depict weak ionic interaction.

The surface effects of the HCl action on the metal in the presence of VA extract were investigated using optical microscope. Also, the photomicrograph studies were performed on these samples in order to evaluate the condition of the Al-alloy surface and grain structure. However, the investigation were carried out on three metal samples which include that of the control experiment (having no inhibitor present), sample from the lowest inhibitor volumes (sample from 2 cm^3 extract) and sample from the highest extract volumes. These were chosen to study the phenomenon on the case scenario of direct 2 M HCl attack, the least and highest inhibitive effect scenarios, knowing that all others will fall within these limits. Superficial analysis was carried out and the micrograph of the alloy before immersion as observed in Figure 9a, indicate the presence of three phases,which were the α-Al (white) phase, the Mg$_5$Al$_8$ (grey) phase and the thick spotted coarse Mg$_2$Si (black) phase. The first two mentioned phases were observed to be finely dispersed. In Figure 9b, which is the control sample, the micrograph indicate the presence of irregular flakes of the intermetallic phase along the grain boundaries which eventually resulted in intergranular cracks (depicted by the red hexagon) with evidence of pittings (illustrated by the red circle). The influence of 2 and 5 cm^3 acid extract of VA for 30 minutes on the aluminium specimen as shown in Figs. 9c and 9d, respectively indicate reduction in intergranular cracks and pittings, there were however evidence of conspicous grain coarsening and/or rearrangement. The appearance of surface flakes was apparently lowered with increasing volumes of inhibitors than without. It was also discovered that the irregular intermetallic phases were more uniform after exposure to increasing volumes of inhibitors due to the adsorption efficiency of the VA extract which controls the acidic and cathodic reaction that may affect the grain structure. Immersion in 2 and 5 cm^3 of extract volumes reduces the corrosion attack with the attack being more prominent in 2 cm^3 than the 5 cm^3 extract. Samples in the 2 cm^3 extract show no major cracks and few pitting along the second, alpha and widely dispersed inter-metallic phase, while samples in the 5 cm^3 extract present a finely dispersed alpha and second phase with no major cracks. Thus, by comparing Figs. 9c and d, it is observed that the addition of VA extract has apparently slowed down the crack growth rate, and

the higher the extract volumes the slower the crack growth rate and the longer the life of the alloy.
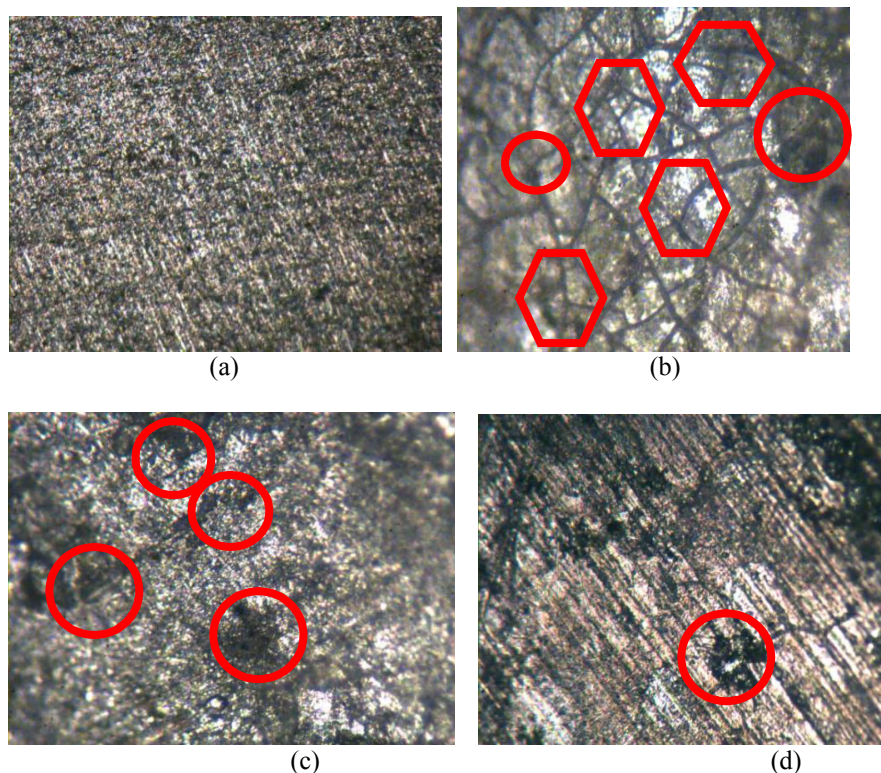

Figure 9 Micrographs for Al surface (a) before immersion in 2M HCl solutions (b) after immersion in 2 M HCl for 30 min (c) after immersion in 2 cm^3 of VA extract for 30 min (d) after immersion in 5 cm^3 of VA extract for 30 min.

4   Conclusions

The study investigated the acid failure of Al-alloy by HCl acid in the presence of VA extract using gasometric technique. The various indicators that characterized the behaviour of the alloy in the medium at different inhibitor volumes were highlighted and a new relationship that represents a vital contribution to knowledge was also obtained. Investigations showed that maximum % I.E and lowest corrosion rate were obtained at optimum extract volumes of 5 cm^3. The mechanism of interaction between the phytochemicals in the plant extract and Al-alloy surface was best described by the Temkin isotherm, showing its capability of predicting gas phase equilibra. The 12 minutes time frame was revealed, as the best time for the phytochemicals across all volumess utilized to suitably adsorb to alloy surface. Statistical modelling of

corrosion rate yielded an important relationship suitable for estimating corrosion rate once volumes of VA extract is known. The microstructural studies revealed that crack growth rate slowed down and irregular intermetallic phases were more even and undeviating as extract volumes increased, which is in agreement with the initial inference of lowest corrosion rate at optimum extract volumes. Based on the results, the authors recommend the development and calibration of a device that measures corrosion rate based on the principle that metal depletion after exposure is directly proportional to the volume of H_2 gas evolved. This may require that a further study be conducted to determine the exact relationship between the volume of H_2 gas evolved and the corresponding amount of metal depleted.

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