Acid Failure of Mild Steel in 2 M Sulphuric Acid in the Presence of *Vernonia amygdalina*

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Abstract

The degradation of mild steel in 2 M sulphuric acid solution in the presence of *Vernonia amygdalina* extract was investigated using gasometric technique. Mild steel coupons of dimension 4 cm by 1.5 cm were immersed in test solutions of uninhibited acid and also those containing extract concentrations of 60,100 and 140 cm^3 at a temperature of 333K for 60 minutes. The volumes of hydrogen gas evolved from the reaction were recorded and examined. The results showed that while extract concentration was increasing, H_2 evolution and % I.E increased, with a reduction in corrosion rate. The reduction in corrosion rate was observed to follow in order of increasing extract concentration. Also, phytoconstituent-metal interaction mechanism was best explained by Freundlich isotherm, with the 4 minutes curve becoming the best contact time for the extract phytochemicals to properly adsorb to metal surface across all concentrations used. Furthermore, an expression suitable for estimating corrosion rate values once concentration is known was also obtained. The microstructural studies however, revealed that increasing the extract concentration led to considerable reduction in the dominant coarsening of the oxide of iron phase, while the pearlite and ferrite phases were highly dispersed.

Key words: Environmentally induced failure, green inhibitors, hydrogen evolution, mild steel, regression analysis, adsorption isotherm.

Introduction

Universal concern about the direct and indirect cost associated with corrosion or degradation of metals across all sectors has been aggravated by the result of a study in the U.S which showed that a whopping \$552 billion representing 6 % of the nation's Gross Domestic Product (GDP) has already been expended on corrosion related issues between 1999 and 2001. These direct costs are the costs incurred by owners and operators of structures and manufacturers of products while indirect costs include such factors as lost productivity because of outages, delays, failures and litigation [1]. In addition, the issue of environmental pollution resulting from corrosion control measures involving the use of synthetic inhibitors in conjunction with acid solutions for the removal of rust and scale in industrial processes is also another source of anxiety. Acids are widely used in the industrial operations of pickling, descaling, oil well acidizing and cleaning of steel and ferrous alloys [2-9]. These operations ensure that machine components come in contact with these hostile species leading to metal loss or depletion in form of reduction in effective size of the component which may inevitably lead to catastrophic failure [9].

Several tested methods for preventing and controlling corrosion are influenced by the specific material to be protected; environmental concerns such as soil resistivity, humidity, and exposure to marine or industrial environments; the type of product to be processed or transported; and many other factors. The most commonly used methods include organic and metallic protective coatings; corrosion resistant alloys, plastics, and polymers; corrosion inhibitors; and cathodic protection technique which is used on pipings, underground storage cisterns, and offshore facilities that creates an electrochemical cell in which the surface to be protected is the cathode and corrosion reactions are abated [1]. It is well known that in developed countries corrosion mitigation management has improved over the past several decades, but more and better ways to encourage, support, and implement optimal corrosion control practices should be sought out.

In a bid to inspire and sustain these efforts, practical attempts have been made by several researchers to investigate the effect of using green inhibitors to combat corrosion of metals in acid media [10-21]. These investigations have shown that green inhibitors represent a veritable source of environmentally friendly, cheaply available and easily applicable resource [5, 7]. Amongst the studies conducted so far there seems to be a paucity of literature that has examined the failure behavior of mild steel in 2 M sulphuric acid in the presence of *Vernonia amygdalina* (VA). Thus, this article is used to focus on establishing the deterioration pattern and corrosion rate of mild steel at a temperature of 333K as it relates to extract concentration, metal-extract adsorption interaction mechanism and microstructural studies of the candidate metal before and after the experiment. Also, inhibitor efficiency (I.E) was determined by the method adopted in literature [22]. The technique adopted in this study was based on the premise in literature [9] that stated that the rate at which metal 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.

Experimental details

Mild steel specimens with dimension 4 x 1.5 cm were employed for the determination of corrosion inhibition of VA extract in 2 M sulphuric acid (H_2SO_4). Specimens were prepared by degreasing in ethanol and cleaning in acetone. It was then allowed to dry. The composition of the mild steel samples was analyzed using Optical Emission Spectrometer (OES) and the result obtained is presented in Table 1.

Table 1. Chemical composition of mild steel sample utilized for the investigation

Element	%Content	Element	% Content	Element	% Content
C	0.131	Cu	0.035	Sn	< 0.001
Si	0.028	Co	0.0057	Zn	0.022
Mn	0.397	Ti	0.001	As	0.0059
P	0.0066	Nb	0.0046	Bi	0.0024
S	0.018	V	0.0075	Ca	0.017
Cr	0.0075	W	< 0.010	Ce	< 0.0040
Ni	0.025	Pb	< 0.0020	Zr	0.0016
Mo	< 0.0020	Mg	0.002	La	0.0018
Al	0.125	B	0.0009	Fe	99.4

The acidic extracts of VA were prepared from its fresh leaves by drying the leaves and grinding into powder. The dried grounded powder was weighed, such that 10g of the powder was introduced into a 200 cm^3 flat bottom flask containing 100ml of 2 M H_2SO_4 solution. The resulting solution was refluxed for 2 hours and left over night before it was filtered. Extract concentration of 60,100 and 140 cm^3/l were prepared by serial dilution and then employed for the investigation. The experimental set up and procedure followed the method adopted in literature [9], where each specimen was dropped into the mylius cell containing 50 cm^3 of test solution system. However, the experiments were performed at a temperature of 333K. The volume of H_2 gas evolved per 240 seconds interval was recorded for 60 minutes in a calibrated tube by downward displacement of water and the plot of volume against time interval was carried out and represented in Figure 1. The inhibition efficiency was then determined using Equation 1 below obtained from literature [9, 22]:

$$\text{I.E}(\%) = \frac{(V\text{-}V_I)}{V} \times 100 \tag{1}$$

where, V is the volume of H_2 evolved without inhibitor (i.e. control experiment) and V_1 is the volume of hydrogen evolved with inhibitor.

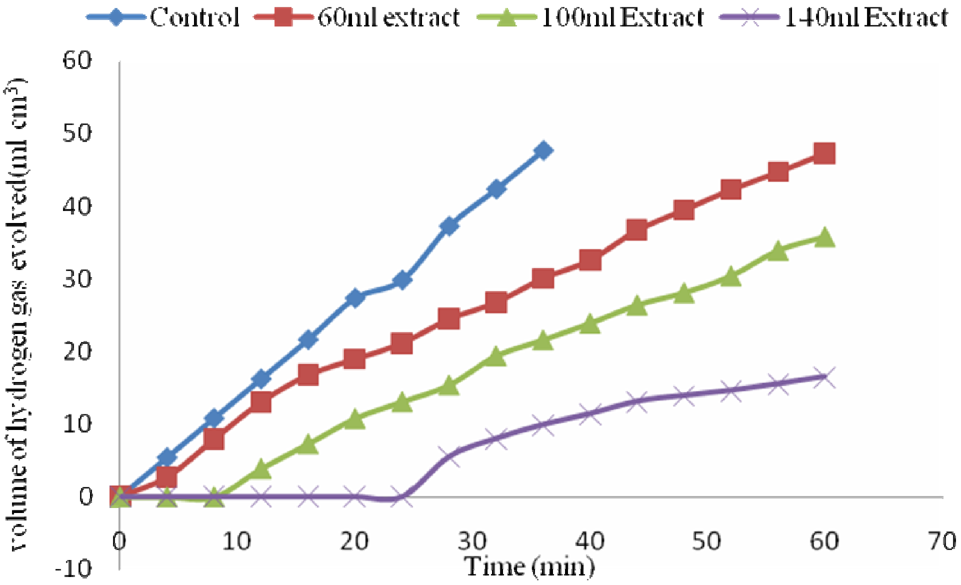


Figure 1: Relationship of volume of H_2 (cm^3) evolved with time (minutes) of mild steel coupons for different concentrations of VA extract in 2 M H_2SO_4 at a temperature of 333K.

It is known that hydrogen is given when metals react with acids, therefore, since H_2 gas is given off as one of the products of reaction when mild steel reacts with H_2SO_4, it is appropriate to predict the rate of reaction by determining the rate of H_2 gas evolution from the system. Subsequently by inference, the rate of reaction relates to the rate of corrosion damage of the mild steel in H_2SO_4 in the presence of VA extract. Thus, the rate of corrosion corresponding to the rate of H_2 evolution was modeled based on the approach adopted elsewhere [9] which articulates 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. Consequently, 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. From these analogies Equation 2 was obtained [9]:

$$R \ \alpha \ \frac{dWm}{dt} \ \alpha \ \frac{dVol}{dt} \tag{2}$$

where α = proportionality sign.
Vol = volume of H_2 gas evolved
Wm = metal weight loss due to corrosion
R = Rate of corrosion
t = time

Equation 2 was determined by developing a correlation between volume evolved and the time of evolution. This was done by a polynomial regression analysis of the volume of H_2 gas evolved against time leading to Equation 3 [9]:

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

Thus,

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

For measurements relating to 60 cm^3 extract concentration, the corrosion rate model is presented as Equation 6. This was obtained after adapting Equation 3 and 4 in line with the approach in literature [9]:

$$Vol= 0.501 + 0.938t - 0.002t^2 \quad (5)$$

$$\frac{dVol}{dt} = 0.938 - 0.004t \quad (6)$$

Results and discussion

An analytical look at Figure 1 revealed that the corrosion rate of mild steel as indicated by the amount of H_2 evolved decreased in the presence of VA when compared to the control. The amount of H_2 evolved also decreased with increasing concentration of the extract. This indicates that the VA extract in the solution has an inhibitive effect on the corrosion of mild steel in H_2SO_4 and that the extent of inhibition depends on the amount of VA extract present. This same behavior was also observed in Figure 2 which shows the percentage inhibition efficiency (% I.E). However, the % I.E. readings for samples in the 100 and 140cm^3 extract were very closely related at the beginning of experiment but became distant as the experiment progressed. Also the readings for 60 and 100 cm^3 extract were observed to be far apart at the beginning, with the distance being maintained till the end of the experiment, thus pointing to the fact that there was significant improvement in the performance of the extract when concentration was increased.

The % I.E. values in Figure 2 for the 140 cm^3 extract concentration showed the best performance, followed the by 100 cm^3 extract and then by the 60 cm^3 extract. The 140 cm^3 concentration maintained its optimum % I.E. value for most part of the experiment. All extract concentrations had peak % I.E. values at 4 minutes, this indicates that 240 seconds is best exposure time for all the extract concentration. However, the inhibitive effects depreciated after 4 minutes for all extract concentration.

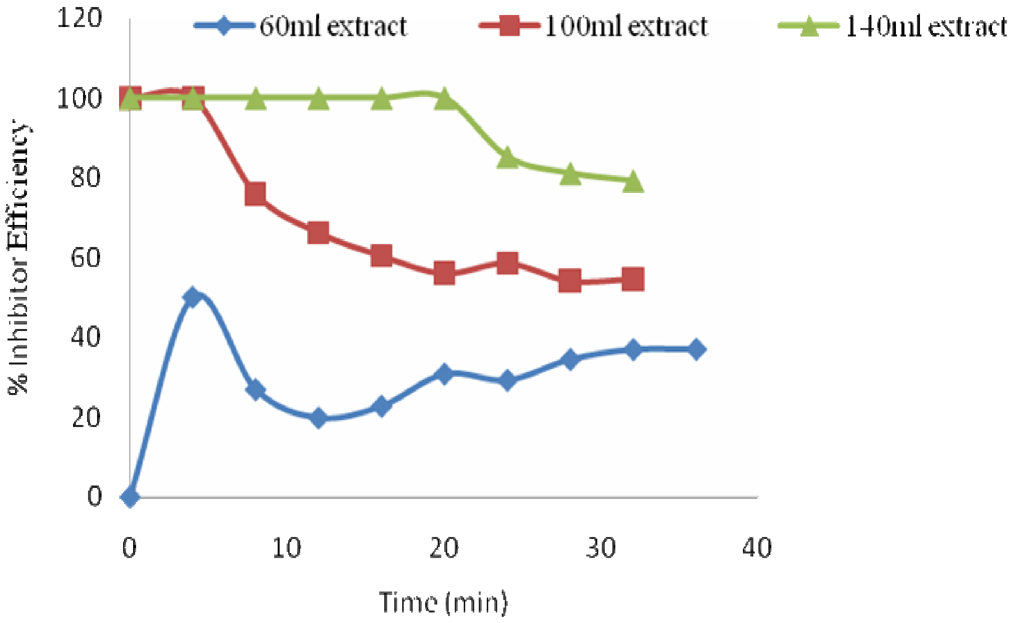


Figure 2: Percentage inhibition efficiency of varying concentrations of VA extracts with time (minutes) on mild steel coupons in 2 M H_2SO_4 solution at a temperature of 333 K.

In addition, from Figure 3 it was noted that the corrosion rate at a temperature of 333K, largely decreases in the presence of VA extract when the values obtained for the inhibited solutions are compared to the control. Amongst the extract concentrations considered, the 60 cm^3 extract of VA showed the lowest effect of reducing the corrosion rate of mild steel, as the values began at 0.16 cm^3/s and ranged between 0.015 and 0.0105 cm^3/s from 4 minutes till the experiment ended. This was followed by the 100 cm^3 extract which began at a value of 0.0109 cm^3/s and ranged between 0.0108 and 0.0107 cm^3/s from 4 minutes till the end. Also, the 140 cm^3 extract began at 0.0028 cm^3/s and ranged between 0.003 and 0.0008 cm^3/s, showing a slowing down of the corrosion rate, but as the experiment progressed corrosion rate values became near constant until the experiment ended. The reduction in corrosion rate in the presence of VA extract at different concentrations according to Figure 3, was observed to follow the order; 60 cm^3 extract < 100 cm^3 extract < 140 cm^3 extract.

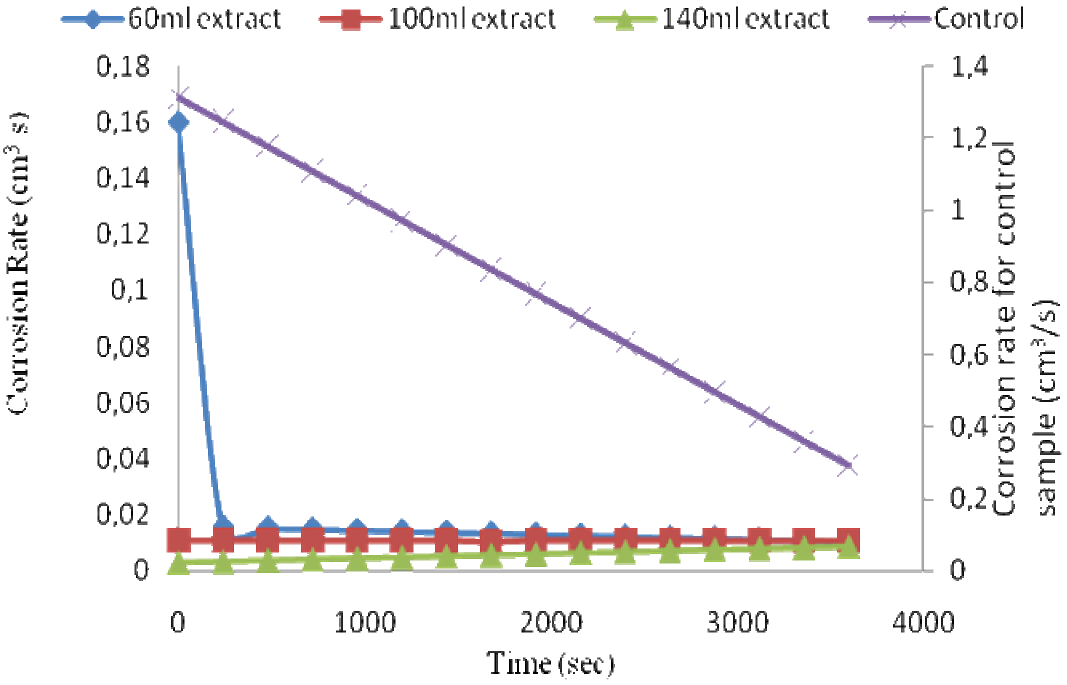


Figure 3: Corrosion rate of varying concentrations of VA extract with time (minutes) on mild steel coupon in 2M H_2SO_4 solution at a temperature of 333 K.

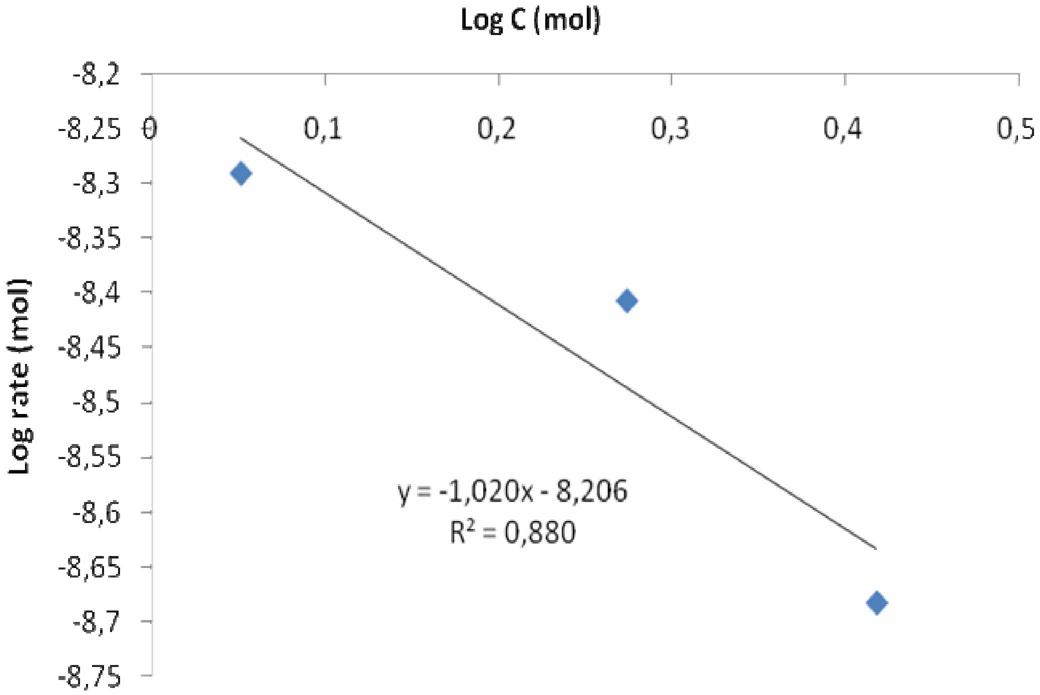


Figure 4: Plot of Log of corrosion rate against log of the acid extract concentration

The investigation of the connection between corrosion rate, R, and the varying concentration to obtain reaction constant and also the specific reaction constant for the H_2SO_4-corrosion of mild steel in the presence of VA extract involved performing a regression analysis of the values of R against those of concentration. This same approach was adopted elsewhere [9]. Following this same approach it was also found out that corrosion rates can be correlated with acid concentration with Equation 7 [9, 23-24]:

$$\text{Log } R = \text{Log}k + B\text{Log } C \tag{7}$$

where R = corrosion rate,
k = reaction constant,
B = specific reaction constant and
C = concentration.

By using the same technique adopted elsewhere [9], a conversion to same unit (mol min^{-1}) is necessary to determine reaction constant and this was done by assuming that hydrogen evolution took place at 1.01325 x 10^{-5} Pa. Figure 4 shows the relationship between Log R and Log C for the Al-alloy coupon sample. The straight line in the graph correlates all the points with a correlation coefficient of 0.94. The estimated k and B values were 6.216 x 10^{-9} mol min^{-1} and -1.0208 respectively. The negative value of B obtained in this study is quite different from other studies when no inhibitors were used [23-24] and it was indicated by a decreasing slope which appreciably portrayed the inhibitive action of the VA extract on the mild steel corrosion. Therefore, the precise connection can be expressed as:

$$\text{Rate} = 6.216 \times 10^{-9}\, C^{-1.0208} \tag{8}$$

This viewpoint is in accord with Figure 3, where a well-defined disparity was shown between the uninhibited and inhibited media.

Adsorption Studies

The metal-extract interface interaction mechanism can be explained using various adsorption isotherms such as Langmuir, Freundlich, Boris-Swinkels and Temkin. The degree of surface coverage, θ, for the different inhibitor concentrations were analyzed based on volume of H_2 gas evolved measurements. A bid was then made to fit the θ values with the different adsorption isotherms and the Freundlich isotherm was found to be best fitted to the θ values. The Freundlich isotherm has been established in studies [9, 25] as an experiential equation having the ability to fit nearly all experimental adsorption data. It is also amongst the most widely used isotherms for the description of adsorption equilibrium and capable of describing the adsorption of organic compounds. The Freundlich equation is expressed as [9]:

$$\theta = A_c C^{1/F} \tag{9}$$

and in linearized logarithm as:

$$\log\theta = \log A_c + \frac{1}{F}\log C \tag{10}$$

where
θ = surface coverage
A_c = characteristic constant related to the adsorption capacity
C = concentration
F = characteristic constant related to adsorption intensity or degree of favourability of adsorption.

A graph of logθ versus logC has a slope value of 1/F and an intercept magnitude of $\log A_c$ as shown in Figure 5. The value of $\log A_c$ is equivalent to log θ when C equals unity. From the plot and equation of the straight line obtained, the estimated value of F and A_c is 1.072 and 3.062, while a good correlation coefficient of 0.99 was also obtained. The value of f obtained in this study shows a favourable adsorption which is defined by a Freundlich constant that has a value between 1 and 10 [9, 25]. 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 a physical adsorption process where a bond is formed between the phytochemicals and mild steel surface.

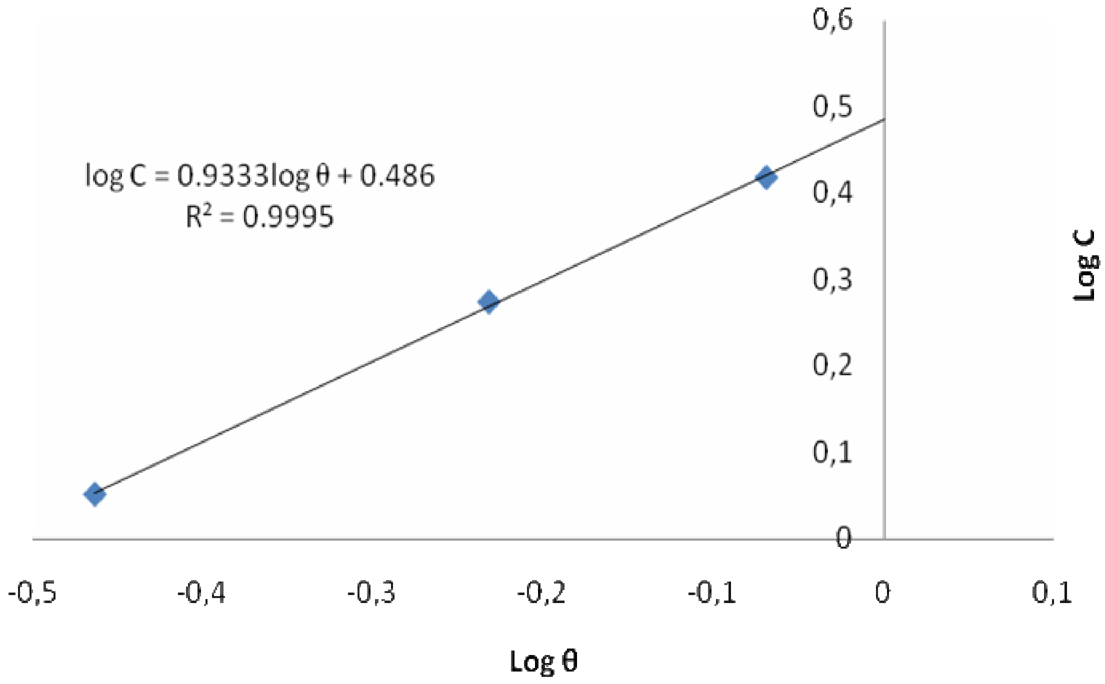


Figure 5: Variation of logarithm of surface coverage with logarithm of concentration of acid extract showing compliance with Freundlich isotherm.

The process of adsorption is normally known to take place easily when the value of the free energy change is negative. By using the Gibbs equation the adsorption free energy can be obtained [9, 26]:

$$\Delta G = -RT\int_0^a F\frac{da}{a} \tag{11}$$

The Gibbs equation (Eq. 11) can therefore be expressed as:

$$\Delta G = -FRT \tag{12}$$

The terms ΔG, F, R and T are the free energy change, parameter of the Freundlich equation, gas constant and temperature respectively. Accordingly, the adsorption of VA extract on the mild steel is a spontaneous process since the value of ΔG is negative (-2.968 KJ mol^{-1}).

Also, the degree of surface coverage, θ, for the extract at different concentration was plotted for different time intervals of 4, 8, 12, 16, 20, 24, 28, 32 and 36 minutes as shown in Figure 6 to investigate if there are any contribution of times of exposure to the relationship between θ and C. The 12 minutes curve had the lowest surface coverage value at extract concentration of 60 cm^3, while at this same concentration the 4 minutes curve had the highest θ value. The highest overall θ value of 1 was attained by the 4 and 8 minutes curve at a concentration of 100 cm^3.

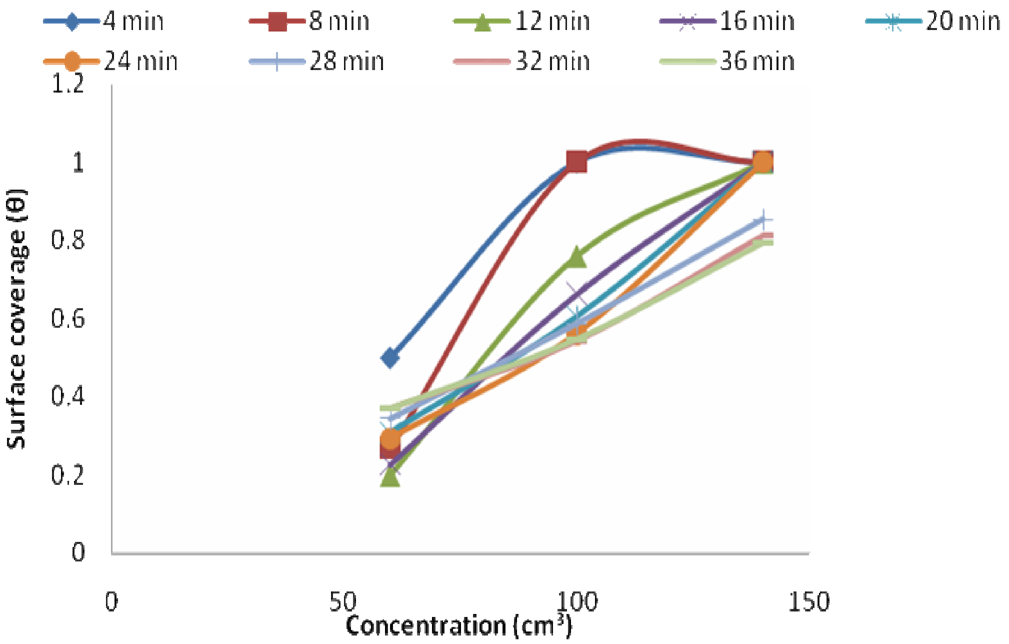
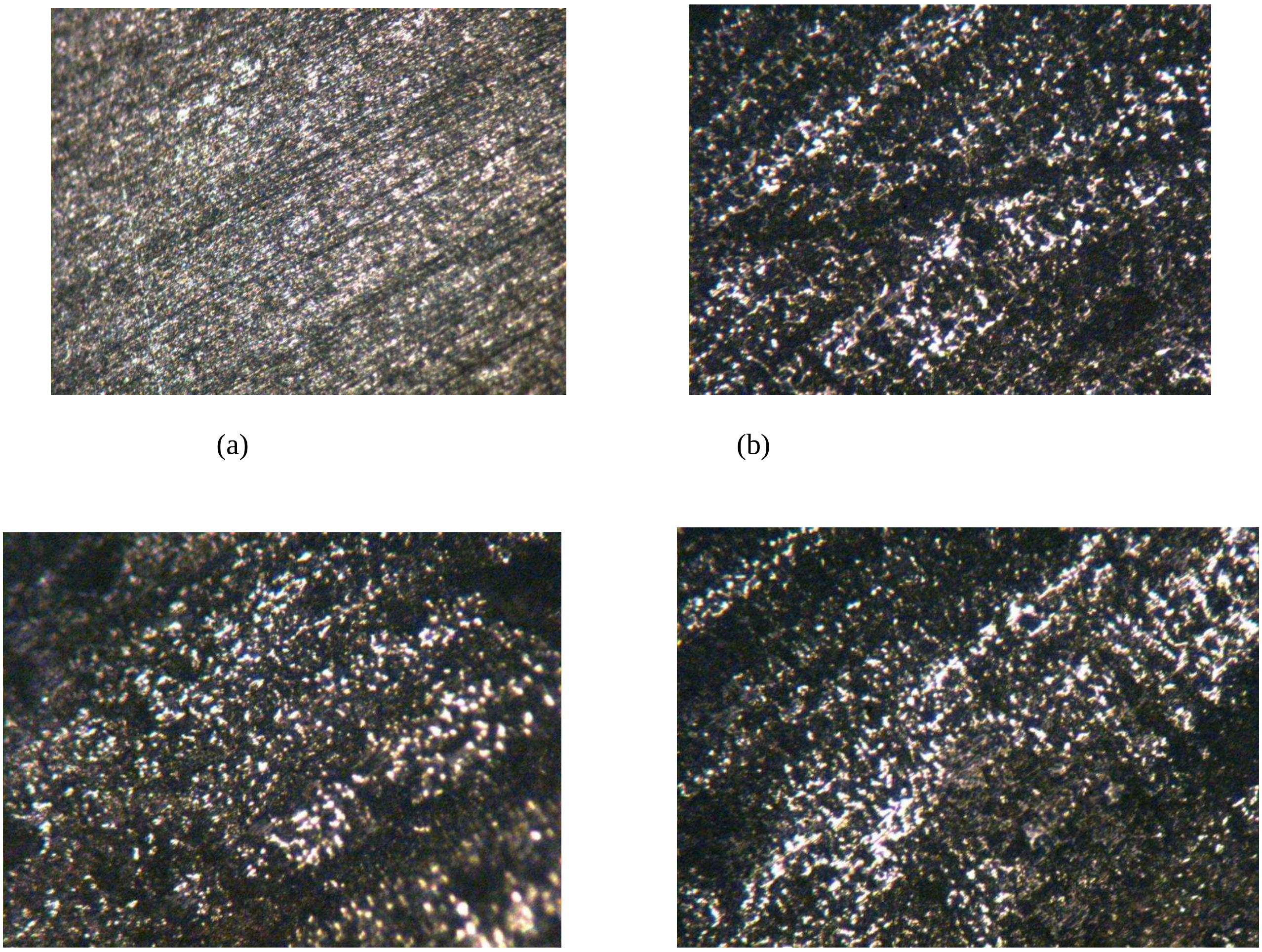


Figure 6: Relationship of surface coverage (θ) with extract concentration (M) at different time intervals.

At a concentration of 140 cm^3, the 36 minutes curve showed the lowest θ value while the 4, 8, 12, 16, 20 and 24 minutes curve had the highest values. For the other time frames of 28, 32 and 36 minutes changes in θ were very similar and the values were closely related throughout the experiment. The overall best surface coverage was displayed during the 4 minutes time frame across all concentrations used, showing that this time frame was the best for the phytochemicals to adsorb to the mild steel surface and retard corrosion efficiently.

Superficial effects of the H_2SO_4 action on the metal in the presence of VA extract were investigated using optical microscope. Also, the photomicrograph studies were performed on these samples so as to examine the state of the mild steel surface and grain structure. The investigations were however, carried out on three metal samples which comprise that of the control experiment (having no inhibitor present), sample from the least inhibitor concentration (sample from 60 cm^3 extract) and sample from the highest extract concentration (sample from 140 cm^3 extract). These were chosen to study all the occurences on the case scenario of exact 2.0 M H_2SO_4 attack, the least and highest inhibitive effect scenarios, knowing that all others will fall within these bounds. Superficial analysis was carried out and the micrograph of the metal before immersion is shown in Figure 7a. It was observed that the microstructure of mild steel comprised of three phases, these were; the first phase (ferrite) which is white, the second phase (pearlite) which is grey and the third phase (oxide of iron) which is black in colour. Figure 7a shows that the ferrite and pearlite are evenly dispersed while the pearlite phase is observed to be more dominant. Figure 7b shows the mild steel in the H_2SO_4 without any inhibitor (control). The observation of the microstructure showed a dominant coarsening of the third phase. This is obviously a clear indication of corrosion. The third phase in Figure 7c is scarcely dispersed and even more scarcely dispersed in Figure 7d, while the pearlite and ferrite phases are highly dispersed in Figs. 7c and 7d. This is a result of the inhibitive action of the VA extract. The phytochemicals in the extract were responsible for this action. Thus, a relationship existed between corrosion inhibition and VA extract concentration which infers that increased extract concentration is directly proportional to reduction in corrosion rate. This essentially means that by increasing the extract concentration, metal degradation is reduced because the time of initiation of crack is prolonged. This in effect extends the useful life of the metal.



(a) (b)

(c) (d)

Figure 7: Micrographs for mild steel sample surface (a) before the experiment (b) after immersion in 2M H_2SO_4 for 60 min (c) after immersion in 60 cm^3 of VA extract for 60 min (d) after immersion in 140 cm^3 of VA extract for 60 min. All the immersions were done at a temperature of 333 K.

Conclusion

The study analyzed volume of hydrogen evolved data that resulted from the gasometric experiments at a temperature of 333K to ascertain if any relationship existed: between H_2 evolved and time; inhibitor efficiency and concentration; corrosion rate and time; surface coverage and time; and adsorption mechanism with concentration. Several indices that portrayed the performance of the metal in the medium at different inhibitor concentrations were pinpointed and an expression detailing the connection between corrosion rate and VA extract concentration was also obtained. The results showed that whereas extract concentration was increasing, H_2 evolution and corrosion rate reduced, while only inhibitor efficiency increased. The phytoconstituent-metal surface interaction mechanism was best described by the Freundlich isotherm which is a practical equation, having the ability to fit nearly all experimental adsorption data. The 4 minutes curve was also revealed, as the best contact time for the phytochemicals across all concentrations deployed to appropriately adsorb to metal surface. The microstructural studies showed that increasing the extract concentration led to considerable reduction in the dominant coarsening of the oxide of iron phase, while the pearlite and ferrite phases were highly dispersed, which is an indication of a reduction in degradation rate that clearly suggests that the inhibitor was more effective as concentration increased.

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