Omotosho et al.

Environment Induced Failure of Mild Steel in 2 M Sulphuric Acid Using Chromolaena odorata

Omotosho, O.A.[1], Ajayi, O.O [1*], Ajanaku, K.O.[2], Ifepe, V.O.[1]

[1]*Mechanical Engineering Department, Covenant University, P.M.B. 1023, Ota, Nigeria*
[2]*Chemistry Department, Covenant University, P.M.B. 1023, Ota, Nigeria*

Abstract
Failure investigation of mild steel sample in 2 M sulphuric acid solution in the presence of *Chromolaena odorata* extract was conducted using the gasometric method. Mild steel coupons, each measuring 4 cm by 1.5 cm were completely immersed in test solutions of free acid and also those containing extract quantities of 60, 100 and 140 cm^3 at a temperature of 333K for 60 minutes. The volumes of hydrogen gas evolved from the experiment were recorded and analyzed. The result showed that maximum inhibitor efficiency which has a relationship with lowest corrosion rate was obtained at the highest inhibitor concentration of 140 cm^3, with reduction in the corrosion rate observed to follow in order of increasing extract volume. Temkin isotherm best described the metal surface interaction adsorption mechanism. Once concentration of the acid is known, an expression for estimating corrosion rate values in the presence of the extract was obtained. Also, the photomicrograph study showed a direct relationship between the extract quantity and the extent of corrosion. Sample immersed in the 140 cm^3 extract quantity showed no trace of the third phase but rather the presence of a finely distributed pearlite phase indicating that increased inhibitor concentration led to a reduction in the deterioration of the metal.

Keywords: Environmentally induced failure, *Chromolaena odorata*, hydrogen evolution, regression analysis, mild steel, surface coverage.

Introduction
Sound corrosion mitigation techniques have been linked to increased productivity in a variety of industrial concerns. Although, corrosion mitigation techniques are multifarious, the use of inhibitors is one of the widely used methods representing about $ 2.1 billion in the food processing industry in the U.S [1]. The use of toxic inhibitors has been known to contribute immensely to the environmental pollution challenges facing the world today. Industrially, operations of oil well acidifying, cleaning and pickling involve the use of aggressive species. The resultant effect is the reduction in the effective size of the component and its eventual catastrophic failure [2]. The introduction of inhibitors like chromates into such systems does not only reduce the effect of the acids on the metal but also increases environmental problems and the burden of disposal due to its damaging effect on humans, plants and animals [3].
Environmental and safety issues associated with corrosion inhibitors coupled with the need to stimulate and continue these research efforts have resulted in concerted efforts to combat the deleterious effects of these toxic inhibitors. Thus, several studies [4-19] have been undertaken to investigate the effect of using green inhibitors on metals in acidic media. These studies show that green inhibitors represent a genuine source of biodegradable, inexpensive and appropriate resource. Of the several studies, two [17, 18] utilized

Chromolaena odorata (CO) and focused on the effect of this inhibitor on aluminum in Hydrochloric acid. However, this article focuses on the failure behavior of mild steel in 2 M sulphuric acid in the presence of CO. The study was conducted to add to the body of knowledge that already exists as there is a dearth of literature that has examined this inhibitor amongst the studies conducted so far and also, in furtherance of the works that have already been done. Thus, the article dwelt on the deterioration behaviour and corrosion rate of mild steel at a temperature of 60 ^{o}C in relation to extract quantity, metal-phyto-constituent adsorption interaction mechanism and micrograph studies of mild steel before and after the experiment. The efficiency of the inhibitor was also determined by the technique adopted elsewhere [19].

Experimental

The procedure adopted in this study is similar to the method used elsewhere [2, 18]. Mild steel bars were cut into specimen size with a dimension of 4 x 1.5 cm and thereafter degreased in ethanol and acetone. The metal coupons were then allowed to dry. Analysis of the elemental composition of the mild steel sample was done using Optical Emission Spectrometer and the result of the examination is presented in Table 1.

Table 1: Composition of mild steel employed for the study

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

The fresh leaves of *Chromolaena odorata* (CO) were harvested and air-dried until it became completely dried. The dried leaves were then pulverized until it became completely powdered. 200 cm^3 of 2 M H$_2$SO$_4$ solution was introduced into a flat bottom flask together with 10g of the powdered leave. The resulting solution was then refluxed for 2 hours and left over night before it was filtered. Extract volumes of 60, 100 and 140 cm^3 obtained by serial dilution was then employed for the study. The metal coupons were then dropped into the Mylius cell containing the test solution at a temperature of 333K. The experimental set up is available in literature [2, 18]. 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 graph of volume against the time interval were plotted as represented in Figure 1. The inhibition efficiency was subsequently determined, using the method described elsewhere [2, 5, 20] represented by Equation (1):

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

Where, V_H is the volume of hydrogen evolved without inhibitor (i.e. control experiment) and V_{H1} is the volume of hydrogen evolved with inhibitor.

By adopting a similar technique used elsewhere [2, 18], it was possible to do a modeling of the rate of corrosion from the rate of H$_2$ gas evolved. This is implicitly a way to model the rate of material loss when the correlation between the weight loss and H$_2$ gas evolution is known. The basis for this is as represented in Equation (2) which can also be found in literature [2, 18]:

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

Where α = proportionality sign.
ΔV = volume of hydrogen gas evolved
ΔW = metal weight loss due to corrosion
R = rate of corrosion
t = time (s)

A polynomial regression analysis of the volume of H_2 gas against time obtained by developing a relationship between volume evolved and time was used to evaluate Equation 2. This however resulted in Equation 3 similar to the approach adopted in literature [2, 18]:

$$V = c + bt + at^2 \qquad (3)$$

Thus,

$$R = \frac{dV}{dt} = b + 2at \qquad (4)$$

A precise illustration of this study will involve modifying equations 3 and 4 to the volume-time measurement for individual concentration. Thus, the corrosion rate model for measurements relating to 140 cm^3 extract volume is presented as equation (6):

$$V = -0.2952 + 0.2043t + 0.0014t^2 \qquad (5)$$

$$\frac{dV}{dt} = 0.2043 + 0.0028t \qquad (6)$$

Results and discussion

The illustration in Figure 1 of volume hydrogen evolved with time for the control solution as well as extract quantities of 60, 100, 140 cm^3 shows that CO extract in the solution has an inhibitive effect on the corrosion of mild steel in H_2SO_4 and that the degree of inhibition depends on the amount of CO extract present, since the amount of H_2 evolved decreased with increasing concentration of the extract.

Figure 2 shows the relationship between percentage inhibition efficiency (% I.E) and time. It depicted a pattern that was similar to what was observed in Figure 1. The highest inhibitor efficiency was shown by the 140 cm^3 extract throughout the experiment. The highest % I.E was attained at the start of the experiment and at 4 minutes by samples immersed in the 100 and 140 cm^3 extract quantity. The curves of % I.E readings for samples in the 100 and 140 cm^3 extract were observed to be closely related throughout the experiment while that of the 60 cm^3 extract was far apart from the 100 and 140 cm^3 extract showing that increased extract quantity increased inhibition efficiency. However, sample immersed in the 60 cm^3 extract had its highest % I.E value of 56.72 at 28 minutes.
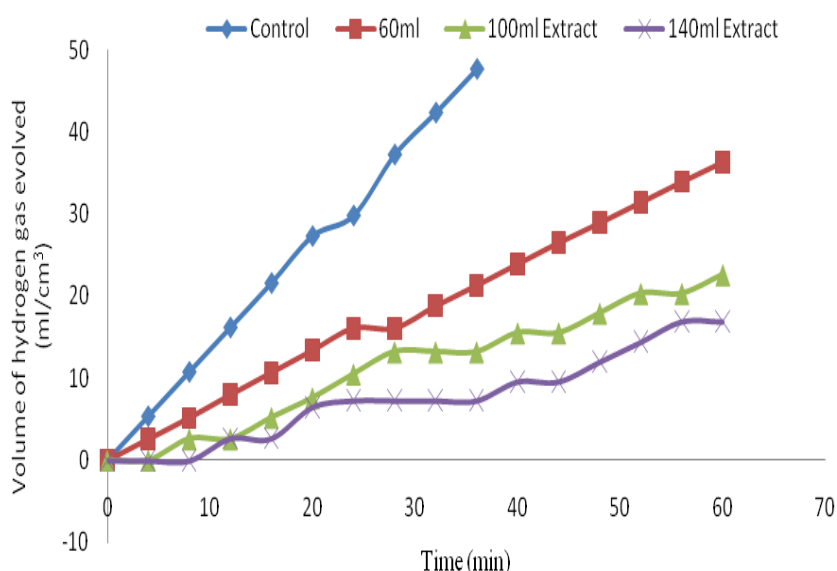

Figure 1. Graph of volume of hydrogen (cm^3) evolved against time (minute) of mild steel coupons for different concentrations of CO extract in 2 M H_2SO_4 at a temperature of 333K.
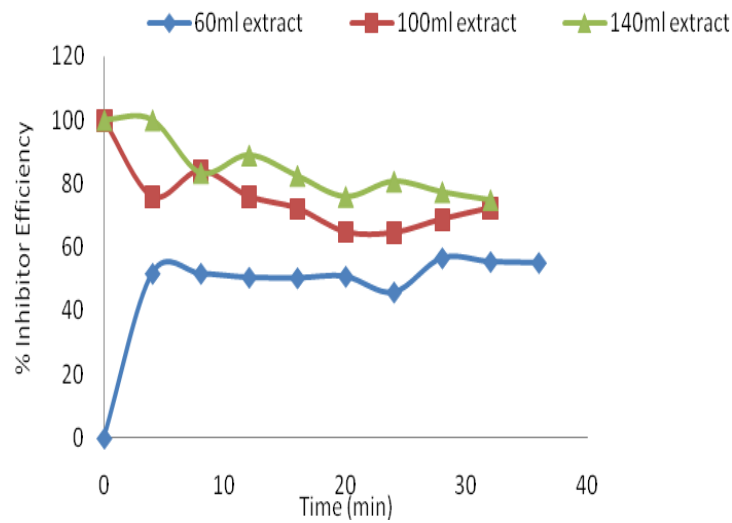
Figure 2. Percentage inhibition efficiency of varying concentrations of CO extracts with time (minutes) on mild steel coupon in 2M H_2SO_4 solution at a temperature of 333K.

Figure 3 shows that corrosion rate values basically decreases in the presence of CO extract when compared to Figure 4 where the plot of the corrosion rate of the control specimen with time at a temperature of 333K is shown. The 60 and 140 cm^3 extract of CO shows the least and best effect of reducing corrosion rate respectively amongst the extract quantity used. However, at the 52nd minute corrosion rate values of the 140 cm^3 extract shifted higher than the 100 cm^3 extract until the experiment ended. Corrosion rate values for the 60 cm^3 extract remained almost constant with values ranging between 0.00995 and 0.00977 cm^3/s from the beginning to the end of the experiment. By analyzing corrosion rate data to obtain average values it was possible to categorize corrosion rate values for extract quantity in the following order; 60 cm^3 extract < 100 cm^3 extract < 140 cm^3 extract.
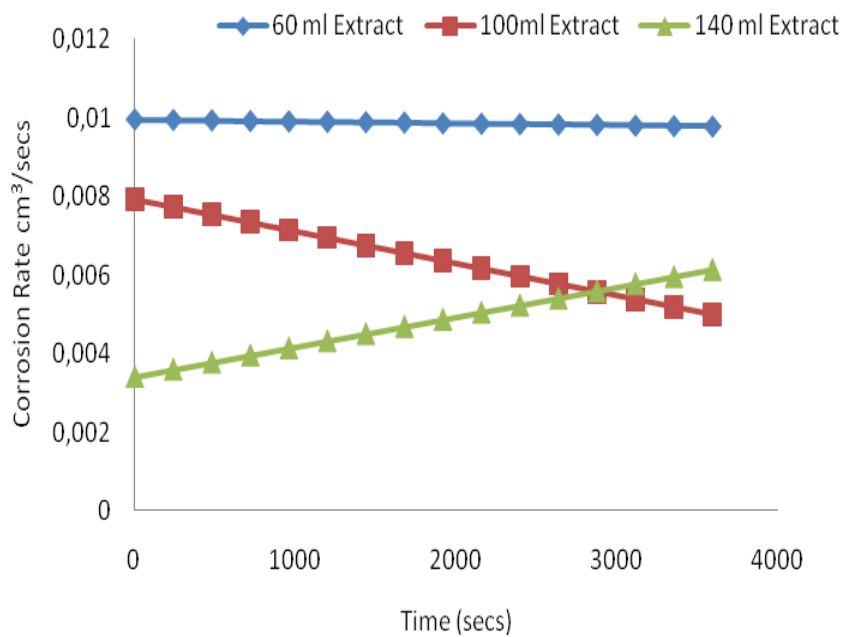

Figure 3. Corrosion rate of varying concentrations of CO extract with time (secs) on mild steel coupon in 2M H_2SO_4 solution at a temperature of 333K.
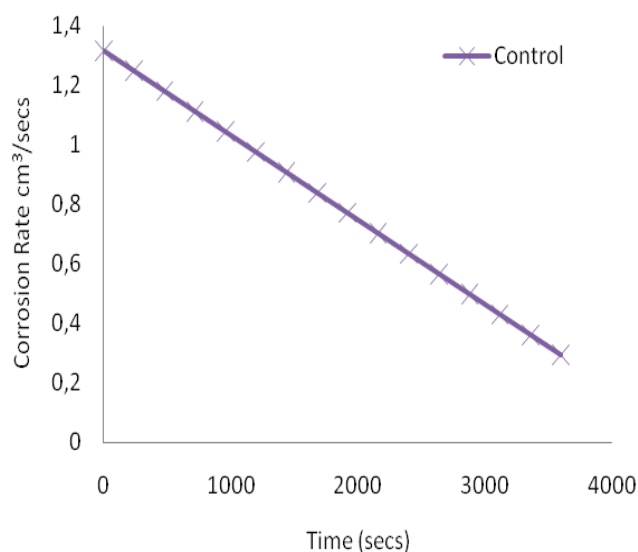
Figure 4. Plot of corrosion rate of mild steel coupon with time (secs) in 2M H_2SO_4 solution at a temperature of 333K.
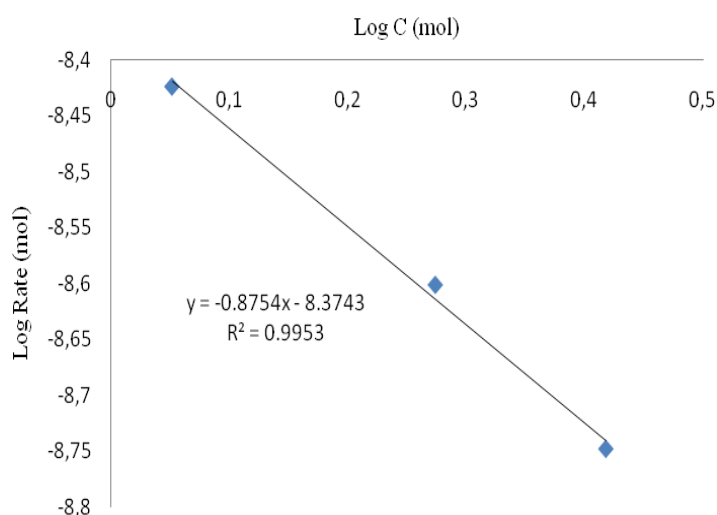

Figure 5. Plot of log of corrosion rate against log of the acid extract volume.

Analyzing the correlation between corrosion rate, R, and varying concentration of acid in the presence of different extract volume to obtain reaction constant and also the specific reaction constant for the acid-corrosion of mild steel in the presence of CO extract was done according to literature [2, 18] through a statistical regression analysis of the values of R against those of concentration. Also, it is well known from literature [2, 18, 21, 22] that acid concentration and corrosion rates can be linked with the equation represented as:

$$logR = logk + BlogC \qquad (7)$$

Where R = corrosion rate,
K = reaction constant,
B = specific reaction constant and
C = concentration of the acid.
The corrosion rates obtained from H_2 evolution method must be converted to the same unit (mol min^{-1}) to obtain reaction constant, by assuming that H_2 evolution reaction occurred at 1.01325×10^{-5} Pa. The relationship between Log R and Log C for the mild steel coupon sample is shown in Figure 5. A good

correlation coefficient of 0.9976 was obtained through the straight line in the graph that correlates all the points. The estimated k and B values obtained were 4.223×10^{-9} mol min^{-1} and -0.8754. The negative value of B obtained in this study is a departure from the positive value of B obtained in other studies [21, 22] which did not involve the use of inhibitors and is depicted by the decreasing slope which suggestively illustrates the inhibitive action of the CO extract on corrosion of the mild steel coupon. The exact relationship for the corrosion of mild steel by the acid in the presence of CO extract is consequently expressed as:

$$R = 4.223 \times 10^{-9} \ C^{-0.8754} \tag{8}$$

By observing Figures 3 and 4, it is clear that this perspective is in accord with the results obtained where a distinct disparity was shown between the uninhibited and inhibited solutions.

Adsorption Studies
The systematic interaction between the phytochemicals in the CO extract and the metal surface is easily expounded by utilizing several adsorption isotherms such as Langmuir, Freundlich, Boris-Swinkels, Frumkin and Temkin. Surface coverage values, θ, for the varying extract volumes were assessed based on the measurement of the volume of H_2 gas evolved while efforts were made to fit the θ values with the different adsorption isotherms and the Temkin isotherm was thus found to be best fitted to the θ values at different time intervals. The Temkin isotherm has been reported [23] to be superior in the prediction of gas phase equilibra. The graph of θ as a function of logarithm of concentration of CO is shown in Figure 6.
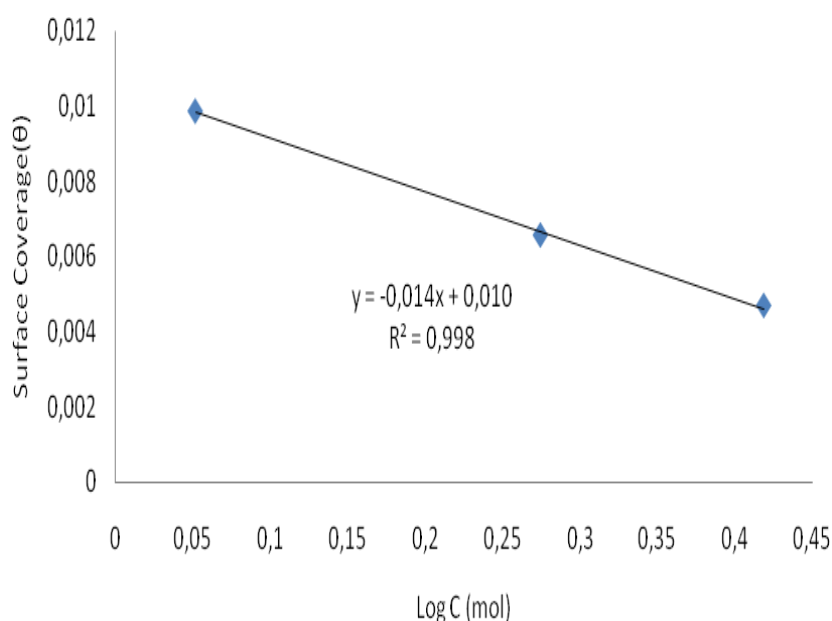

Figure 6. Plot of surface coverage (θ) with logarithm of concentration of acid extract at a temperature of 333K in accordance with Temkin isotherm.

Thus, this result validates the theory that the corrosion inhibition of the CO extract is attributed to the adsorption of phytochemical molecules on the metal surface by the chemisorption process where covalent bond is formed between phytochemicals and mild steel which is a known tribological consideration in metal surface preparation.
Also, the surface coverage intensity for different extract volume was plotted for different time intervals of 4, 8, 12, 16, 20, 24, 28, 32 and 36 minutes as shown in Figure 7 to evaluate if there are any contribution of times of exposure to the correlation between θ and C.
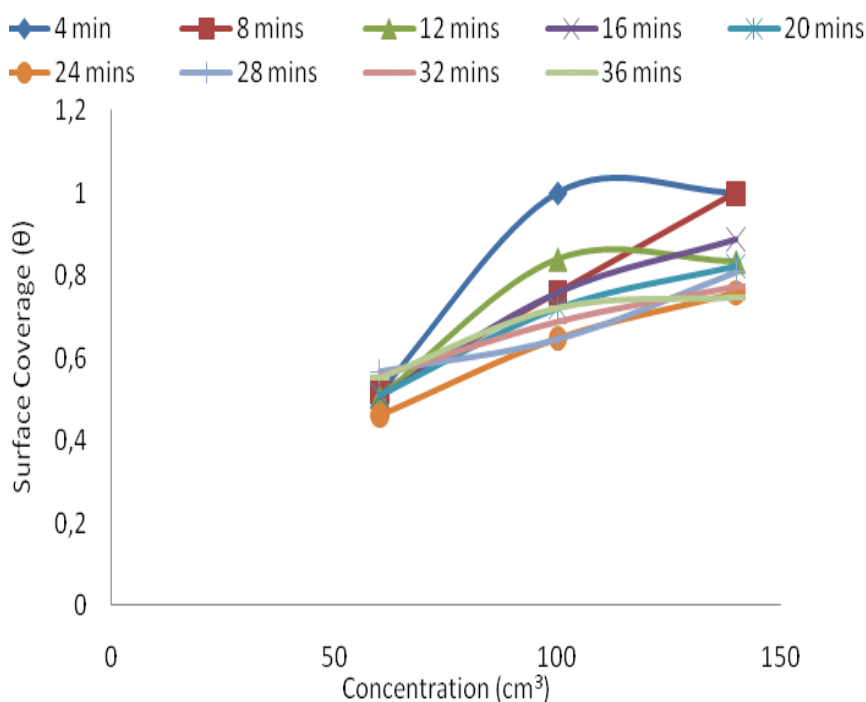
Figure 7. Variation of surface coverage (θ) with extract volume (cm^3) at a temperature of 333K for different time intervals.

The 4 minute time curve showed the highest θ value at extract volume of 100 cm^3 while the 24 minute curve showed the least value at extract volume of 60 cm^3. However, all the time curves showed an uptrend from the beginning to the end of the experiment as concentration of the extract increased. This is in accordance with Figure 3 where inhibitor efficiency increased as extract volume increased. An analysis of the average of the θ values shows that 24 minutes curve had the least θ value throughout the experiment while the 4minutes curve had the highest value. Using the average value analysis it is straightforward to conclude that the surface coverage trend at different times can be depicted in the following order, 24 min < 32min < 28min < 36min < 20min < 16min < 12min < 8min < 4min. The θ values displayed by the 4 minutes time curve was the highest across all the concentrations utilized. Thus, showing that this time frame was the best for the phytochemicals to adsorb to the mild steel surface and retard corrosion effactully as well as supporting the claim in Figure 3 which evidently signifies that the peak I.E (%) value was at 4 minutes.

Furthermore, the values of θ were also plotted against ln C and presented in Figure 8. The studies on the adsorption phenomenon involved relating θ against ln C (i.e natural logarithm of concentration) using Equation 8 [24]:

$$\theta = \beta + \gamma \ln C \qquad (8)$$

Figure 8 Plot of Surface Coverage (θ) with natural logarithm of concentration (cm^3) at a temperature of 333K.

Where; β (ml/ml) = $\dfrac{RT}{b}$ lna

$\gamma = \dfrac{RT}{b}$

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

R and T are the gas constant (8.314 J mol^{-1} K^{-1}) and temperature (333 K) respectively. By extending the analysis, it was possible to estimate the values of the energy of adsorption, b, and the maximum adsorption capacity, a, in terms of volume of hydrogen evolved to be 10,186.02 J mol^{-1} and 0.13 respectively.

The effects of the H$_2$SO$_4$ action on the metal in the presence of CO extract were analyzed by using optical microscope. The photomicrograph studies were performed on these samples so as to examine the condition of the mild steel surface and grain structure. The investigations were conducted on three metal samples which comprise that of the control experiment (having no inhibitor present), sample from the least inhibitor content (sample from 60 cm^3 extract) and sample from the highest extract volume (sample from 140 cm^3 extract). These were selected to study all the occurences on the case scenario of exact 2.0 M H$_2$SO$_4$ attack, the least and highest inhibitive effect scenarios, knowing that all others will fall within these limits. Surface analysis was carried out and the micrograph of the metal before immersion is shown in Figure 9a. It was noted that the microstructure of mild steel consisted of three phases, these were; the first, second and third phases which were the ferrite which is white, the pearlite which is grey and the oxide of iron which is black in colour respectively.
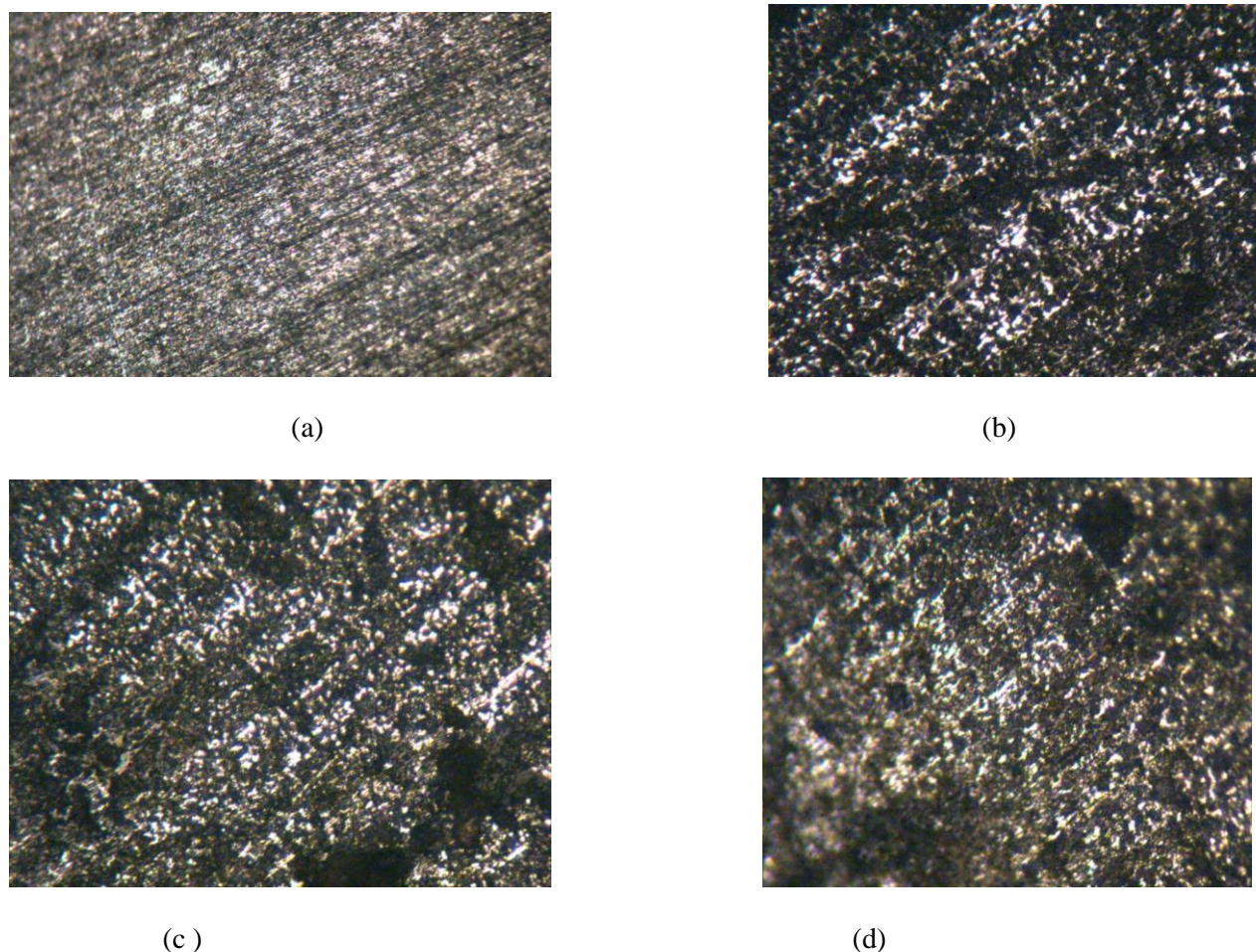.

(a)   (b)

(c)   (d)

Figure 9. Micrographs for mild steel surface (a) before immersion in 2M H$_2$SO$_4$ solutions (b) after immersion in 2M H$_2$SO$_4$ for 60 min (c) after immersion in 60 cm^3 of CO extract for 60 minutes (d) after immersion in 140 cm^3 of CO extract for 60 minutes.

Figure 9a shows that the ferrite and pearlite are equally dispersed whereas the pearlite phase is observed to have a more cogent manifestation. Figure 9b depicts the mild steel in the H$_2$SO$_4$ without any inhibitor (control). The microstructure is observed to show a dominant coarsening of the third phase which is an apparent indication of general corrosion. In Figure 9c traces of the third phase was observed and this was evident at the edges of the mild steel sample, indicating that the 60 cm^3 extract volume reduced corrosion.

However, Figure 9d shows virtually no trace of the third phase present but rather a finely distributed pearlite phase was observed indicating increased effectiveness of the inhibitor at extract volume of 140 cm^3. This fundamentally indicates a direct relationship between extract volume and corrosion inhibition. Increased extract volume however, leads to reduction in metal degradation rate and in effect extension of the useful life of the metal.

Conclusion

Experimental study of the environmentally induced damage of mild steel by 2 M H_2SO_4 acid in the presence of CO extract was conducted using the gasometric technique. The different indicators that evaluated the performance of the mild steel coupon in the medium were identified and an expression that represents a vital contribution to knowledge was established. The study revealed that the highest % I.E and lowest corrosion rate values were obtained at maximum extract quantity of 140 cm^3. Interaction mechanism between the plant phytoconstituents and mild steel surface was best explained by the Temkin isotherm, indicating its gas phase equilibra predicting capability. The 4 and 28 minutes time curve was revealed, as the best time for the phytochemicals in the 140 and 60 cm^3 extract to suitably adsorb to mild steel surface. A significant expression appropriate for estimating corrosion rate values once acid concentration is known was also obtained. Photomicrograph studies showed that only traces of the oxide of iron phase was left on mild steel sample immersed in 60 cm^3 while the sample immersed in the 140 cm^3 extract showed no trace of the third phase but rather a finely distributed pearlite phase was observed. Thus, indicating that increased inhibitor concentration led to a reduction in the degradation of the metal and by extension prolonging the useful life of the metal.

References

1. Koch, G. H., Brongers, M. P. H., Thompson, N. G., Virmani, P., Payer, J.H. F.HWA-RD-01-156 (2001) [available at http://www.corrosioncost.com/pdf/main.pdf] accessed 22/05/2011.
2. Ajayi, O.O., Omotosho, O. A., Ifepe, V.O., *Journal of Material and Environmental Science,* 2 (2011) 186-195.
3. Sanjay, K. S., Ackmez, M., Essam, K., *Journal of Corrosion Science and Engineering*, 11 (2009) Paper 14.
4. Saratha, R., Priya, S.V., Thilagavathy P., *E-Journal of Chemistry,* 6 (3) (2009) 785-795.
5. Ebenso, E.E., Ekpe, U.J., *West African Journal of Biology and Applied Chemistry,* 41 (1996) 21 – 27.
6. Ebenso, E.E., Ekpe, U.J., Ibok U.J., *Discovery and Innovation,* 10 (1998) 52 – 59.
7. Ebenso, E.E., Ibok, U.J., Ekpe, U.J., Umoren, S., Ekerete, J., Abiola, O.K., Oforka, N.C., Martinez, S., *Transactions of the Society for the Advancement of Electrotechnical Science and Technology,* 39 (2004) 117 –123.
8. Ekpe, U.J., Ebenso, E.E., Ibok, U.J*., Journal of West Africa Science Association,* 37 (1994) 13 – 30.
9. Oguzie, E.E., *Material Chemistry and Physics*, 99 (2006) 441 – 446.
10. Njoku, P.C., Oguzie, E.E., Nwaogu, U.C., *Journal of Chemical Society of Nigeria,* (2006) 89 – 95.
11. Martinez, S., Tagljar, I., *Journal of Molecular Structure THEOCHEM,* 640 (2002) 167-174.
12. Obot, I.B., Obi-Egbedi, N.O., *Portugaliae Electrochimica Acta,* 27 (2009) 517-524.
13. Abiola, O.K., Oforka, N.C., Ebenso, E.E., Nwinuka, N.M., *Anti-Corrosion Methods and Materials*, 54 (2007) 219-224.
14. James, A.O., Akaranta, O., *African Journal of Pure and Applied Chemistry,* 3 (2009) 262-268.
15. Rajendran, S., Jeyasundari, J., Usha, P., Selvi, J.A., Narayanasamy, B., Regis, A.P.P., Rengan, P., *Portugaliae Electrochimica Acta,* 27 (2009) 153-164.
16. Davis, D., Guy, J., Fraunhofer, A., Krebs, L.A., Dacreas, C.M., *Corrosion,* (2001) Paper 1558.
17. Obot, I.B., Obi-Egbedi, N.O., *Journal of Applied Electrochemistry,* 40 (11) (2010) 1977-1984.
18. Ajayi, O.O., Omotosho, O.A., Ajanaku, K.O. Olawore, B.O. *Journal of Engineering Applied Science,* 6 (2011) 10-17.

19. Okafor, P.C., Ebenso, E. E., Ekpe, U.J. *International Journal Electrochemical Science,* 5 (2010) 978.

20. Ebenso, E.E., Eddy, N. O., Odiogenyi, A.O., *African Journal of Pure Applied Chemistry,* 2 (2008) 107-115.
21. Noor, E.A., Al-Moubaraki, A.H., *International Journal Electrochemical Science,* 3 (2008) 806 – 818.
22. Mathur, P.B., Vasudevan, T., *Corrosion (NACE),* 38 (1982) 171-178.
23. Febrianto, J., Kosasih, A.N., Sunarsob, J., Ju, Y., Indraswati, N., Ismadji, S.,   *Journal of Hazardous Materials*, 162 (2009) 616–645.
24. Pandey, P.K., Sharma, S.K., Sambi, S.S., *International Journal of Environmental Science Technology,* 7 (2010) 395-404.

(2012) ; www.jmaterenvironsci.com