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Evaluating the Deterioration Behaviour of Mild Steel in 2 M Sulphuric Acid in the Presence of *Butyrospermum parkii*

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ABSTRACT

Mild steel coupons of dimension 4 by 1.5 cm were examined for the purpose of understanding its deterioration behavior in 2 M sulphuric acid solution in the presence of *Butyrospermum parkii* at a temperature of 60°C. The gasometric technique was used and a number of mild steel coupons were systematically submitted to uninhibited test solutions and those containing extract quantities of 60, 100, 140 cm^3. The volume of hydrogen gas evolved data was recorded for 60 min and thereafter analyzed. The results revealed that though extract quantity was increasing, H_2 evolution and corrosion rate decreased, while only %I.E increased. The reduction in corrosion rate was observed to follow in order of increasing extract quantity. The phytochemical-metal interaction mechanism was best explained by Freundlich isotherm. The best contact time for the extract phytochemicals to properly adsorb to metal surface at extract quantity of 60 cm^3 was 4 min. Furthermore, an expression that explained the correlation between corrosion rate and BP extract quantity was also obtained. The microstructural studies showed that increasing the extract quantity resulted in scanty dispersion of the third phase without any reduction in the pearlite and ferrite phases especially in the 140 cm^3 extract which corresponds to a reduction in degradation rate.

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

INTRODUCTION

The world continues to encounter critical challenges in the field of corrosion prevention and control, where aging equipment, new product design, environmental constraints and stringent low-priced budgets require corrosion control synopsis that are designed for particular circumstances by highly skilled professionals. The degradation of metals has a negative influence on the populace and is apparently an issue of concern as it causes damage to steel structures, chemical plants, energy production and distribution systems, oil and gas production units, transportation systems and many others. The cost of mitigating this physically occurring phenomenon and costs linked with the destruction it causes is extensive. However, there are various techniques for averting and curbing corrosion, which are affected by the exact material to be protected; ecological concerns such as soil resistivity, humidity and exposure to brackish or industrial environments; the type of product to be handled or conveyed and many other issues. The most frequently used techniques include organic and metallic protective coatings; corrosion resistant alloys, plastics and polymers; corrosion inhibitors and cathodic protection technique which are used on pipings, underground storage cisterns and offshore facilities (Ajayi *et al*., 2011a).

In oil exploration for instance inhibitors are used to forestall the effect of the use of highly corrosive acids which are used to improve near-well bore permeability. These acids have been known to remove scale buildup on the inside of casing and tubing, allowing direct attack on bare metal. The acids do not only remove scales in the tubing and casing but gradually reduce the effective wall thickness until it eventually leads to failure. It is therefore, necessary to use inhibitors to flow the well to remove spent acid. The inhibitors are mixed with acid to provide a protective film over exposed completion strings. However, environmental constraints placed on the use of synthetic inhibitors like the highly poisonous benzotriazole and its derivatives due to its deleterious effects on plant and animal life have inspired research (Oguzie, 2008; Okafor *et al.*, 2008; Valek and Martinez, 2007; Singh *et al.*, 2010; Raja and Sethuraman, 2008; Obot and Obi-Egbedi, 2009; Buchweishaija and Mhinzi, 2008; El-Etre, 2003; Saratha *et al.*, 2009; Oguzie, 2006; De Souza and Spinelli, 2009) into the use of organic inhibitors to reduce or control corrosion. These studies (Omotosho *et al.*, 2010; Ajayi *et al.*, 2011a) have indicated that green inhibitors apart from being a genuine source of ecologically friendly and economically available resource are also devoid of additional issues of disposal.

Nevertheless, there seems to be a dearth of articles that have examined the degradation behavior of mild steel in 2 M sulphuric acid in the presence of *Butyrospermum parkii* (BP) at a temperature of 333K amongst the studies conducted hitherto. Consequently, the central point of this investigation is to ascertain the degradation outline and corrosion rate of mild steel at a temperature of 333K and link it with extract quantity, metal-extract adsorption interaction mechanism and microstructural examination of the mild steel coupon. In addition, inhibitor efficiency was determined by the method adopted in literature (Ajayi *et al.*, 2011a; Okafor *et al.*, 2010).

MATERIALS AND METHODS

The determination of corrosion inhibition of mild steel specimens with dimensions 4 by 1.5 cm in 2 M sulphuric acid (H_2SO_4) in the presence BP extract is exactly the same as in the earlier article (Ajayi *et al.*, 2011b) except that here the measurements were carried out at extract quantities of 60, 100 and 140 cm^3 obtained by serial dilution and a temperature of 60°C, while the volume of H_2 gas evolved per 240 sec interval was recorded for 60 min in a calibrated tube by downward displacement of water. The mild steel sample employed for the study was analyzed using Optical Emission Spectrometer (OES) and the composition is presented in Table 1. The inhibition efficiency was then determined using Equation 1 obtained from literature (Ajayi *et al.*, 2011a; Okafor *et al.*, 2010).

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

However, based on the assumptions in literature (Ajayi *et al.*, 2011a, b) the following relationships were also obtained:

$$R \propto \frac{dWm}{dt} \propto \frac{dV_{H_2}}{dt} \tag{2}$$

Table 1: Chemical composition of mild steel coupon employed for the study

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

Where:

α = Proportionality sign
V_{H2} = Volume of H_2 gas released
W_m = Metal weight loss due to chemical reaction
R = Corrosion rate
t = Time

Consequently, Eq. 2 was determined by modeling the rate of corrosion from the direction of rate of H_2 gas evolved which is incidentally a way to model the rate of material loss when the connection between the weight loss and H_2 gas evolution is known. Equation 3 was obtained 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 (Ajayi *et al.*, 2011b):

$$V_{H2} = c+bt+at^2 \tag{3}$$

Therefore,

$$R = \frac{dV_{H2}}{dt} = b+2at \tag{4}$$

For measurements relating to 100 cm^3 extract quantity, the corrosion rate model is presented as Eq. 6. This was obtained after relating Eq. 3 and 4, an approach similar to what was done in earlier article (Ajayi *et al.*, 2011b):

$$V_{H2} = 0.0003t^2+0.6781t-1.2169 \tag{5}$$

$$\frac{dV_{H2}}{dt} = 0.006t+0.6781 \tag{6}$$

RESULTS AND DISCUSSION

It is obvious by observing Fig. 1 that the corrosion rate of mild steel as indicated by the amount of H_2 evolved decreased in the presence of BP when compared to the control. As the concentration of the extract increased the amount of H_2 evolved decreased. This infers that the BP extract in the solution has a retarding effect on the deterioration of mild steel in H_2SO_4 and that the degree of retardation depends on the amount of BP extract in solution. A trend similar to Fig. 1 was also

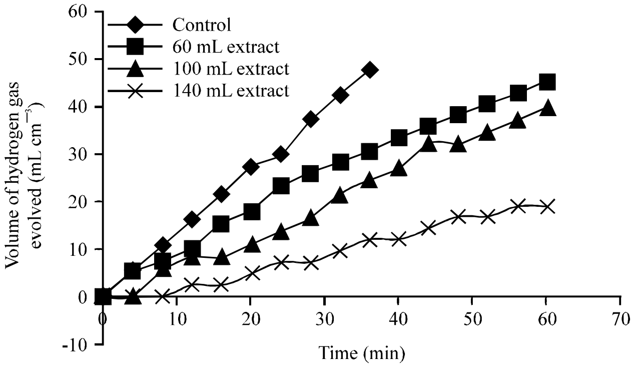

Fig. 1: Plots of volume of H_2 (cm^3) evolved with time (min) of mild steel coupons for different concentrations of BP extract in 2 M H_2SO_4 at a temperature of 333K

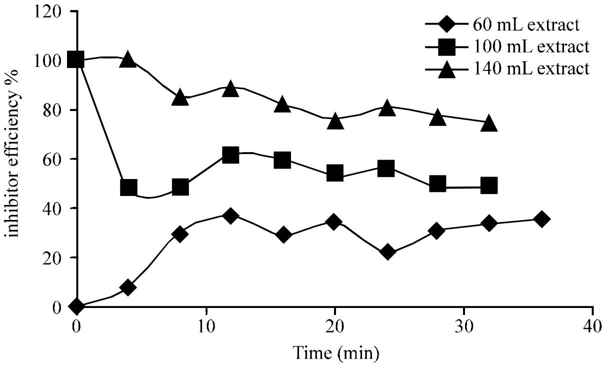

Fig. 2: Percentage inhibition efficiency of varying concentrations of BP extracts with time (min) on mild steel coupons in 2 M H_2SO_4 solution at a temperature of 333K

observed in Fig. 2 which shows the percentage inhibition efficiency (%I.E). Though, the %I.E readings for samples in the 100 and 140 cm^3 extract were very closely related as the experiment began, it however, 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, but eventually came relatively close on the 8th min and even closer on the 32nd min. Thus, the behavior of the mild steel samples in the three extract quantities employed for the study shows that there was appreciable improvement in the performance of the BP extract when concentration was increased.

For the 100 and 140 cm^3 extract quantities in Fig. 2 the %I.E values showed the best performance at the beginning of the experiment, while the 60 cm^3 extract quantity had the least value at the commencement of the experiment. It however, attained its highest value on the 12th min of experiment. %I.E values decreased for the 100 and 140 cm^3 extract quantities as the experiment progressed. It could be that the corrosion products formed during the reaction prevented the inhibitors from performing. However, the 140 cm^3 concentration maintained its maximum %I.E value throughout the experiment.

From Fig. 3, it was clearly shown that the corrosion rate values at a temperature of 60°C, decreased evidently in the presence of BP extract when the values obtained for the inhibited solutions were compared to the uninhibited solution (Fig. 4). Average corrosion rate values for the

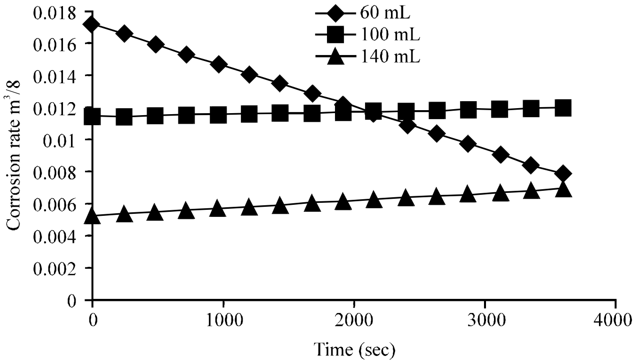

Fig. 3: Corrosion rate of varying concentrations of BP extract with time (sec) on mild steel coupon in 2 M $H_2 SO_4$ solution at a temperature of 333K

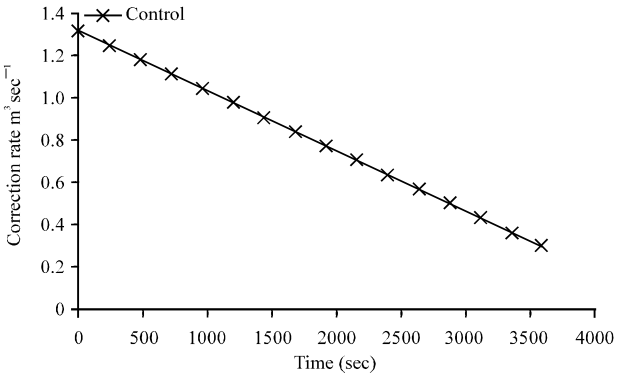

Fig. 4: Plot of corrosion rate of mild steel coupon with time (secs) in 2 M $H_2 SO_4$ solution at a temperature of 333K

extract quantities of 60, 100, 140 cm^3 and the control were 0.01241, 0.0115, 0.00602 and 0.8048 cm^3 sec^{-1}, respectively. This values showed that Fig. 3 is in agreement with Fig. 2 therefore, the reduction in corrosion rate in the presence of BP extract at different concentrations according to Fig. 3, was observed to follow the trend; 60 cm^3 extract <100 cm^3 extract <140 cm^3 extract. In spite of the fact that corrosion rate values of the 100 cm^3 extract shifted higher than the 60 cm^3 extract quantity at the 40th min of the experiment and remained there till the end of the experiment, the overall average corrosion rate values still showed that the 100 cm^3 extract performed better.

A study of the relationship between corrosion rate, R and the varying concentration to determine reaction constant and also the specific reaction constant for the corrosion of mild steel in 2 M H_2SO_4 in the presence of BP extract involved performing a regression analysis of the values of R against those of concentration. This method was also adopted in literature (Ajayi *et al.*, 2011b) and it was discovered that corrosion rates and acid concentration can be correlated with the following equation (Ajayi *et al.*, 2011b; Mathur and Vasudevan, 1982; Noor and Al-Moubaraki, 2008):

$$\text{Log Ra} = \text{Log } k_i + \text{ELog C} \qquad (7)$$

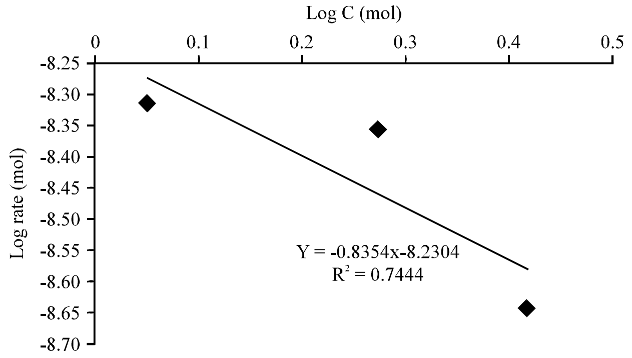

Fig. 5: Plot of log of corrosion rate against log of the acid extract quantity

Where:
Ra = Corrosion rate
k_i = Reaction constant
E = Specific reaction constant and
C = Concentration

A change to same unit (mol min^{-1}) is required to determine reaction constant and this was done by assuming that hydrogen evolution took place at 1.01325×10^{-5} Pa. Figure 5 illustrates the relationship between log Ra and log C for the mild steel coupon sample. The straight line in the graph correlates all the points with a correlation coefficient of 0.86. The calculated k_i and E values were 5.88×10^{-9} mol min^{-1} and -0.8354, respectively. The negative value of E obtained is distinct from other studies where no inhibitors were used (Mathur and Vasudevan, 1982; Noor and Al-Moubaraki, 2008) and it was indicated by a decreasing slope which quite clearly depicted the inhibitive action of the BP extract on mild steel corrosion. Therefore, the specific correlation can be expressed as:

$$\text{Ra} = 5.88\times10^{-9}\ C^{-0.8354} \qquad (8)$$

This line of thought is in agreement with Fig. 3 and 4, where a well-defined disparity was shown between the inhibited and control media.

The adsorption studies were also carried out by studying the metal-extract interface interaction mechanism which can be explained using various adsorption isotherms such as Freundlich, Langmuir, Temkin and Boris-Swinkels. The extent of surface coverage, θ, for the different inhibitor concentrations were analyzed based on volume of H_2 gas evolved measurements. The θ values were then fitted with the different adsorption isotherms and it was discovered that the Freundlich isotherm was the best fitted. The Freundlich isotherm has been established in studies (Ajayi *et al.*, 2011a, b; Febrianto *et al.*, 2009) as a practical equation with the capacity to fit virtually all experimental adsorption data. It has also been described in literature (Ajayi *et al.*, 2011a, b) to be one of the most extensively used isotherms for the explanation of adsorption equilibrium with the capability of describing the adsorption of organic compounds. The Freundlich equation is expressed as (Ajayi *et al.*, 2011a, b):

$$\theta = H_c C^{1/e} \qquad (9)$$

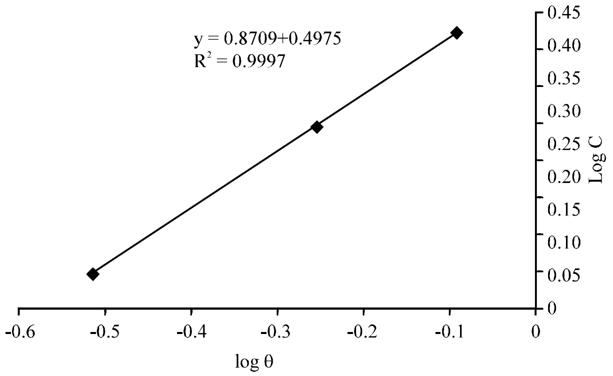

Fig. 6: Plot of logarithm of surface coverage with logarithm of concentration of acid extract showing compliance with Freundlich isotherm

and as a logarithm relationship in linear form as:

$$\log\theta = \log H_c + \frac{1}{e}\log C \tag{10}$$

Where:

θ = Surface coverage
H_c = Characteristic constant related to the adsorption capacity
C = Concentration
e = Characteristic constant related to adsorption intensity or degree of favourability of adsorption

From Fig. 6, it is clear that the graph of log θ versus log C has a slope value of 1/e and an intercept size of log H_c. The value of log H_c is equivalent to log θ when C equals unity (Ajayi *et al.*, 2011a; Ajayi *et al.*, 2011b). The calculated values of e, H_c and correlation coefficient obtained from the plot and equation of the straight line are 1.15, 3.144 and 0.99. The value of e obtained in this study shows a favourable adsorption which is defined by a Freundlich constant that has a value between 1 and 10 (Ajayi *et al.*, 2011a, b; Febrianto *et al.*, 2009). The corrosion inhibition of the BP extract is thus, attributed to a straightforward physisorption process, which is 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.

Adsorption is normally initiated easily when free energy change has a negative value, thus, by using the Gibbs equation the adsorption free energy can be obtained as (Ajayi *et al.*, 2011a, b; Yang *et al.*, 2009):

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

Equation 8 can therefore be re written as:

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

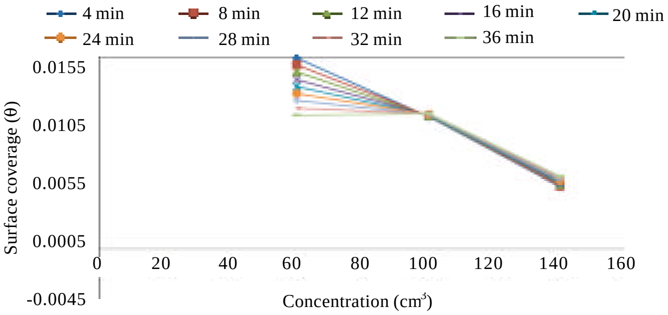

Fig. 7: Relationship of surface coverage (θ) with extract quantity (M) at different time intervals.

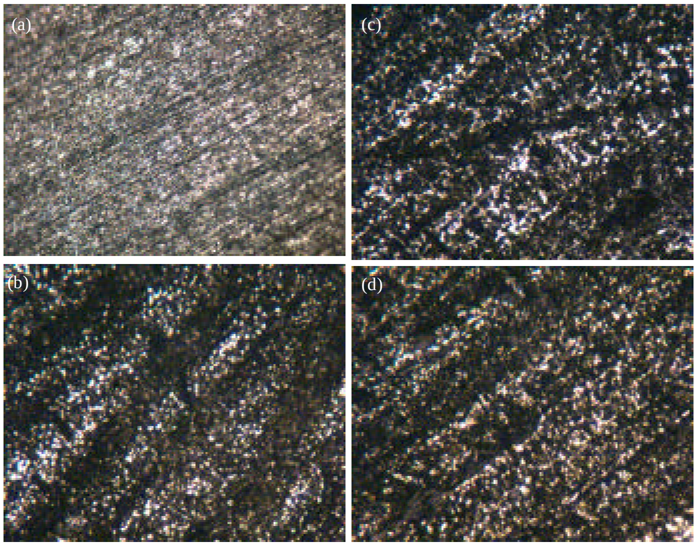

Fig. 8(a-d): Micrographs for mild steel sample surface, (a) Before the experiment, (b) After immersion in 2 M H_2SO_4 for 60 min, (c) After immersion in 60 cm^3 of BP extract for 60 min and (d) After immersion in 140 cm^3 of BP extract for 60 min. All the immersions were done at a temperature of 333K

The terms ΔG, e, R and T are the free energy change, parameter of the Freundlich equation, gas constant and temperature, respectively. Hence, the adsorption of BP extract on the mild steel can be said to be impulsive or a spontaneous process since the value of ΔG is negative (-8.704 kJ mol^{-1}).

Furthermore, 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 min as shown in Fig. 7 to investigate if there are any contribution of times of exposure to the relationship between θ and C. Extract phytochemicals was able to attain the highest surface coverage, θ, at 4 min when extract quantity was 60 cm^3, this was followed by the 8, 12, 16, 20, 24, 28, 32 and 36 min time. Interestingly surface coverage values demonstrated a similar behavior at extract quantities of 100 and 140 cm^3. This is clearly different from the behavior of aluminum alloy when immersed in 2 M hydrochloric acid solution in the presence of *Chromolaena odorata* (Ajayi *et al.*, 2011b), which displayed increasing surface coverage values as the extract quantities increased for each time interval. From Fig. 7, it is straight forward to say that the 4 min time frame across all concentrations used displayed the overall best surface coverage, showing that this time frame was the best amongst others considered for the phytochemicals to adsorb to the mild steel surface and inhibit corrosion efficiently.

In addition, the optical microscope was used to investigate superficial effects of the acid action on the metal in the presence of BP extract. Micro-examination was carried out for a number of goals, the most obvious of which was to assess the structure of the material and metallurgical anomalies that might have resulted from the acid action. The examinations were however, carried out on three metal samples which included 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 organic inhibitor concentration (sample from 140 cm^3 extract). These were chosen to study all the occurrences on the case scenario of direct acid attack, the least and highest inhibitive effect scenarios, knowing that all others will be within these limits. Superficial analysis was carried out and the micrograph of the metal before immersion is shown in Fig. 8a. 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 8a shows that the ferrite and pearlite are evenly dispersed while the pearlite phase is observed to be more dominant. Figure 8b shows the mild steel in the acid solution without any inhibitor (control). The inspection of the microstructure showed a dominant coarsening of the third phase which is evidently an indication of corrosion. The third phase in Fig. 8d was scantily dispersed and even more scantily dispersed in Fig. 8c, while there was a reduction in the pearlite and ferrite phases in Fig. 8c. The occurrence of scanty dispersion of the third phase in Fig. 8d is an indication of the inhibitive action of the BP extract. The effect of the phytochemicals in the extract resulted in this response. The difference in the degree of dispersion of the third phase in Fig. 8c and 8d shows that increased concentration of the extract produced a better result, indicating the existence of a relationship between corrosion inhibition and BP extract quantity which simply translates to a direct correlation.

CONCLUSION

The volume of hydrogen evolved as a result of the reaction between the mild steel coupon and 2 M H_2SO_4 in the presence of BP at a temperature of 333K was utilized in plotting graphs of: volume of H_2 evolved against time; %I.E against concentration; corrosion rate against time; surface coverage against time; and adsorption mechanism against concentration. Various indices that represented the deterioration of the mild steel coupon in the medium at different extract quantities were highlighted and an expression that explained the correlation between corrosion rate and BP extract quantity was also obtained. The results revealed that though extract quantity was increasing, H_2 evolution and corrosion rate decreased, while only %I.E increased. The interaction mechanism between metal surface and extract phytochemicals was best explained by the Freundlich isotherm which has the capacity to fit nearly all experimental adsorption data. The 4 min curve was also revealed, as a vital and important interaction time for the phytochemicals across all concentrations employed to properly adsorb to metal surface since it had the highest surface coverage values at extract quantity of 60 cm^3. The microstructural studies showed that increasing the extract quantity resulted in scanty dispersion of the third phase without any reduction in the pearlite and ferrite phases especially in the 140 cm^3 extract which corresponds to a reduction in degradation rate.

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