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Comparative Evaluation of *Pterocarpus osun* and *Hibiscus sabdariffa* Plant Extracts as Eco-Friendly Corrosion Inhibitors for Mild Steel in Hydrochloric acid

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Abstract

The study is a comparative analysis to evaluate the inhibition efficacies of two plant extracts; *Pterocarpus osun* (PO) and *Hibiscus sabdariffa* (HS), to mitigate the corrosion rate of mild steel in hydrochloric acid. The solutions used for the tests were prepared by extraction through refluxing the ground plant parts in ethanol, and using the extracts to prepare solutions of 100-3000 mg/dm^3 concentrations. The corrosion inhibition performance was tested on mild steel coupons using weight-loss and potentiodynamic polarization techniques in 0.1 M and 1.0 M HCl media. The corrosion experiments spanned for a period of 120-hour at 24-hour interval of suspension, retrieval of the metal coupon and re-weighing to measure weight loss, and subsequently calculating the inhibition efficiencies were carried out. Results indicate that both PO and HS significantly reduced corrosion rates, with inhibition efficiencies reaching up to 98.9% for PO and 96.9% for HS at higher concentrations. The results showed decreased weight loss and reduced corrosion rates in the company of PO and HS at higher concentrations. The polarization results showed that both extracts functioned as mixed-type inhibitors. The study confirms PO and HS as effective, renewable and sustainable inhibitors for the corrosion of mild steel in acidic system: and can be utilized in industrial settings for economic benefits.

Keywords: Corrosion inhibition, gravimetric, *Hibiscus sabdariffa*, mild steel, potentiodynamic polarization, *Pterocarpus osun*

Introduction

Natural plants which are rich in bioactive components, consisting of heteroatoms [1] are likely to be accountable for their corrosion inhibitory potent ability. Corrosion in nature converts mild steel to its original, most stable oxide state, which has been of major concerns to industrialists [2]. Plant extracts have proven as better alternatives than conventional inhibitors with regards to their cost effectiveness, renewability, readily available nature, sustainability and safety to the eco-system [3. The literature has widely reported the potential of plant extract, which serves as corrosion inhibitors by actually blocking the active sites on the surface of the metal through adsorption of their bioactive components, thus isolating the metal from the corrosive substances [4]. The usage of plant extracts as green and efficient corrosion inhibitors has been studied for corrosion protection as coatings, nanoparticles and chemical inhibitors [5]. Besides, the preview carried out by Prabu et al. [6] portrayed green inhibitors to have better inhibition efficiencies than synthetic inhibitors, using methods such as computational studies, electrochemical measurements, and scanning electron microscopy techniques. Sani et al. [7] studied the potential of *Senna occidentalis* to inhibit the corrosion of mild steel in hydrochloric and sulphuric acid media using gravimetric method and adsorption isotherm studies. The inhibition efficiency increased with increase in concentration of the inhibitor, and the adsorption on the mild steel obeyed Langmuir adsorption isotherm. Ade [8] reviewed the ability of organic inhibitors to inhibit the corrosion of carbon steel in hydrochloric acid, nitric and sulphuric acid media using weight loss method. Corrosion inhibition mechanism was by adsorption of the carboxylic, nitro and hydroxide groups of the organic inhibitors, on the surface of the metal through bonding with the lone pair electrons to push away the corrosive species from the metal. Guar gums and Arabic gums were studied as green inhibitors by Claudia and Horatiu [9] for comparative inhibition efficiencies for mild steel corrosion in concentrated hydrochloric acid using gravimetric and electrochemical methods. The findings revealed that guar gum gave a better inhibition efficiency than Arabic gums and the inhibition efficiency increased alongside the concentration of inhibitor, with the best performance at 3.3 g/l.

Therefore, there is the need for further study as part of the expanding research in green chemistry. This study reported the comparative assessment of the corrosion inhibition efficiencies of two natural dyes namely: *Pterocarpus osun* and *Hibiscus sabdariffa* on mild steel in acidic medium.

Materials and Methods

Materials

Plants

The dried, ground stem of *Pterocarpus Osun* (PO) and dried leaves of *Hibiscus sabdariffa* (HS) were obtained from local market and validated at Department of Crop Science and Technology, Federal University of Technology, Owerri, Nigeria.

Metal specimen (mild steel)

The mild steel specimen used for this study was mechanically cut into coupons using Bridgeport milling machine, each with dimensions 3 X 3 X 0.14cm. The percentage composition were determined through elemental analysis techniques and shown as follows (wt %) : C (0.30, Mn (0.30), P (0.045), S ().050), Cr (0.064), Cu (0.040), Ti (0.04), the rest is Fe. Each coupon was degreased in acetone, rinsed with distilled water and then, dried in warm air before being stored in a moisture free dessicator [10].

Experimental Investigation

Preparation of Plant Extract

Thirty (30) grams of the ground leaves of Hibiscus sabdarifa (HS) were added to 400ml of ethanol contained in a 500ml round-bottomed flask, the resulting solution was heated under reflux for 3 hours, and then filtered after allowing it to cool down at room temperature, the ethanol content of the filtrate was evaporated with the aid of rotary evaporator and the obtained slurry was stored in air tight container and kept away from the sun, thereafter, it was used for the experiment.

The same procedure was repeated for the ground stem of *Pterocarpus osun* (PO), the concentrations of 100 mg/L, 500 mg/L, 1000 mg/L, 2000 mg/L and 3000 mg/L were prepared from the stock solution [10]. All experiments were carried out at 30 ± 1 ^{O}C and non-deaerated solutions. The corrosive media used were 0.1 M and 1.0 M HCl solutions

Weight loss (gravimetric) method

Mild steel coupons with dimensions 3 x 3 x 014 cm were polished, degreased in absolute ethanol, dried in warm air and then weighed. The weighed mild steel coupons were then hanged in beakers containing the test solutions using rods and glass hooks. The tests were conducted ensuring that the mild steel coupons were immersed completely into the test solutions which were 300 ml at 30 ^{O}C. The mild steel coupons were removed after 24 hrs consecutively for 120 hrs, cleaned, each experimental set was dried and re-weighed. Weight loss was then calculated as the difference between the previous weights and the final weights, which was put in record. The results were then reported, the tests were repeated to get averages of triplicate determinations [10]. The inhibition efficiency, (I. E), degree of surface coverage (θ) together with the rate of corrosion, (CR), were calculated for mild steel in 0.1 M and 1 M concentrations of HCl, this was done for *Pterocarpus Osun* and *Hibiscus Sabdariffa* using the equations below [11].

$$\Delta W = W_1 - W_2 \quad (1)$$

$$\%I = \left(1 - {W_1}/{W_2}\right) \ X100 \quad (2)$$

$$\theta = 1 - {W_1}/{W_2}$$
(3)

$$CR = {\Delta W}/{AT}$$
(4)

W_1= Weight of mild steel before exposure to the corrosive media

W_2 = Weight of mild steel after exposure to the corrosive media

θ = Degree of surface coverage

ΔW = weight loss of metal coupons in mg

T = the exposure time in hours

A = exposed area of metal coupon in cm^2

Electrochemical studies

A three electrode corrosion cell having PAR 263 potentiostat/galvanostat was used for the electrochemical assessment, the metal specimen were encapsulated in expoxy resin such that the exposed area was 1 cm^2, the exposed area were smoothen with emery papers of different grades ranging from 200-1000, mild steel was used as the working electrode, graphite rod was used as the counter electrode while saturated calomel electrode was used as the reference electrode, the solution was left unstirred and the readings were taken after 0.5 hr immersion at 303 K, potential range was ±250 mv while scan rate was 0.333 mv/s during the assessment, triplicate measurements were taken to ensure reproducibility [10].

Scanning electron microscopy studies (SEM)

Super facial examinations of the mild steel coupons were carried out by SEM examinations of the mild steel surfaces exposed to different test solutions using XL-30FEG scanning electron microscope, mild steel specimens of dimensions 15 x 15 x 2 mm were cleaned as previously described Okore *et al.* [10] and immersed for 24 hrs in the blank solutions (hydrochloric acid) without and with the inhibitors under study at 30 ± 1^0C. The metals were washed with distilled water, dried in warm air before subjecting them to surface examination.

Results and Discussions:

Pontentiodynamic Polarization

The electrochemical results are represented in Table 1 and in Figure 1 as shown below.

Table. 1 Potentiodynamic polarization result for mild steel corrosion in 1 M and 0.1 M HCl in the presence and absence of the inhibitor

System	E_{corr}	I_{corr}	Θ	IE (%)
1 M HCl	**-500.4**	**183**		
100 mg/L PO	-474.9	121.8	0.334	33.4
1000 mg/L PO	-466.9	27.2	0.851	85.1
100 mg/L HS	-458.2	123.7	0.324	32.4
1000 mg/L HS	-472.8	35.4	0.807	80.7
0.1 M HCl	**-496.2**	**145.7**		
100 mg/L PO	-486.4	92.3	0.449	36.7
1000 mg/L PO	-491.2	18.4	0.874	87.4

100 mg/L HS	-485.3	100.7	0.308	30.8
1000 mg/L HS	-474.2	28.2	0.806	80.6

Table 1 shows that the I_{corr} values for 1 M HCl and 0.1 M HCl are 183 μA/cm^2 and 145.7 μA/cm^2 respectively, that is the corrosion rates in the absence of inhibitors, with 0.1 M HCl having a lower I_{corr}, which indicates less aggressive corrosion compared to 1 M HCl system. The introduction of PO and HS to the corrosive system reduced the I_{corr} significantly to 27.2 μA/cm^2 and 35.4 μA/cm^2 respectively for 1 M HCl at concentration of 1000 mg/l, showing that PO and HS are effective corrosion inhibitors, with PO exhibiting better performance than HS at higher concentration.

3.2 Gravimetric Results

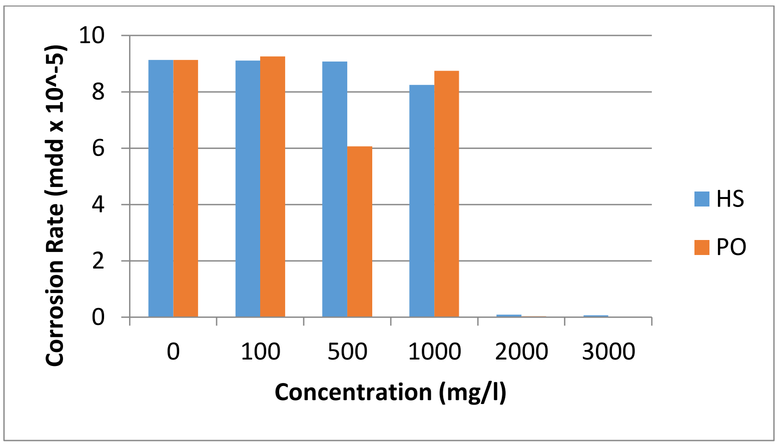


Figure 2:Weight loss against concentration for mild steel coupons in 0.1M HCl with or without *Pterocarpus osun* and Hibiscus sabdariffa at 303K

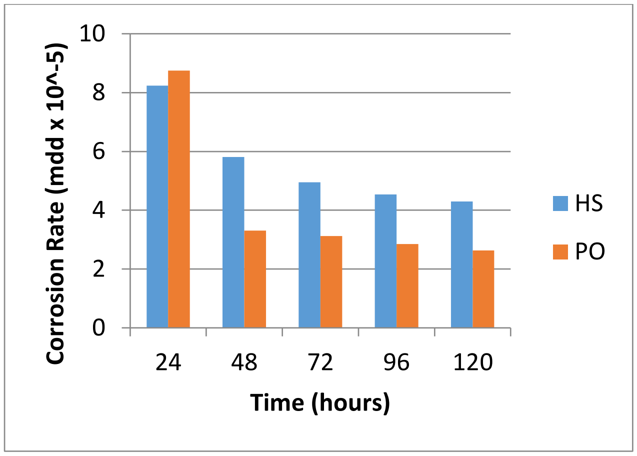


Figure 3: Weight loss against time for mild steel corrosion in 0.1M HCl with or without *Pterocarpus osun* and *Hibiscus sabdariffa* at 303K

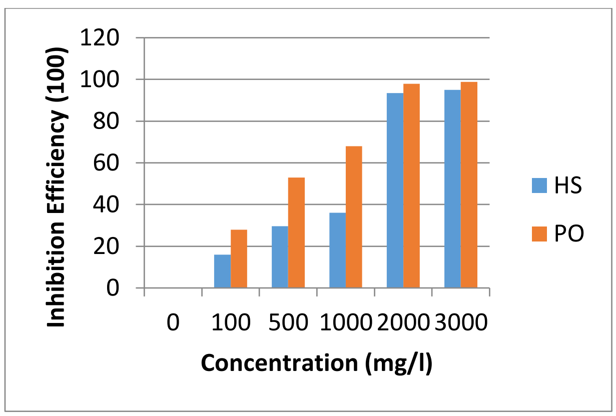


Figure 4: Inhibition Efficiency against concentration of *Pterocarpus osun* and *Hibiscus sabdariffa* for mild steel corrosion in 0.1M HCl at 303K

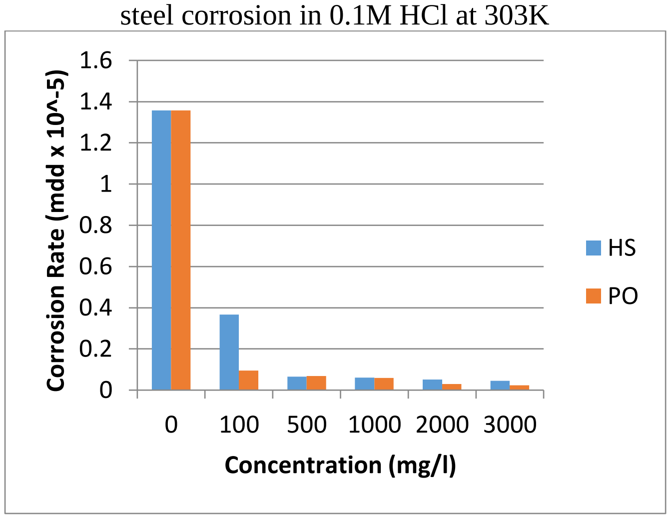


Figure 5: Weight loss against concentration for mild steel coupons in 1M HCl with or without *Hibiscus sabdariffa* and *Pterocarpus osun* at 303K

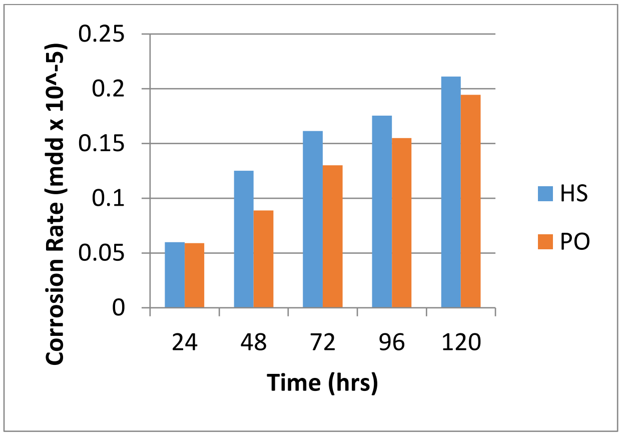


Figure 6: Weight loss against time for mild steel coupons in 1M HCl with or without *Hibiscus sabdariffa* and *Pterocarpus osun* at 303K

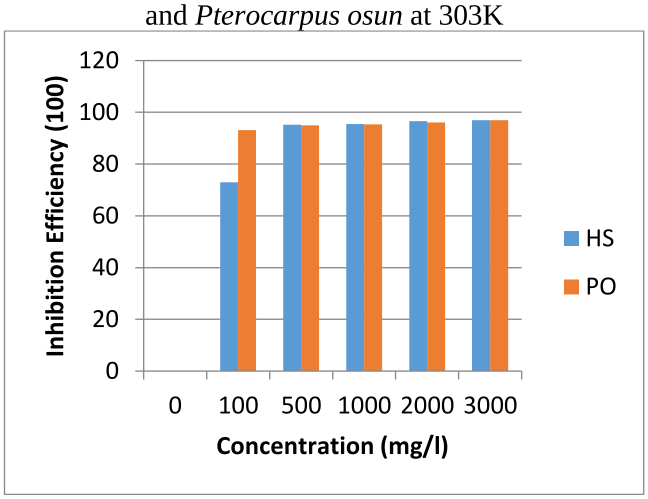


Figure 7: Inhibition Efficiency against concentration of *Pterocarpus osun* and *Hibiscus sabdariffa* for mild steel corrosion in 0.1M HCl at 303K

The analysis of the results in Figures 2 to 7 is presented as follows. The weight loss reduced as the concentration of PO and HS increased, with PO producing greater reduction at concentrations of 100 mg/L and above. Besides, PO and HS reduce weight loss within the exposure time, thus showing their ability to reduce corrosion rate within the time interval of the experiment.

PO showed better effectiveness than HS, with time. In addition, PO outperforms HS, with inhibition efficiency out shining even at lower concentration of the inhibitors: Inhibition efficiency reached maximum values of 98.9 % and 95 % respectively at 3000 mg/l for 0.1 M HCl. Chaubey *et al*. [12] carried out comparative analysis of *Cannabis sativa*, *Rauwolifia serpentine*, *Cymbopogon* *citrates*, *Annona squamosa* and *Adhatoda vasica*, for aluminium surface, and found *Rauwolifia serpentine* to exhibit the highest inhibition efficiency of 97% at 200 mg/l. Sivakumar and Srikanth [13] studied the inhibitive effect of leaves, bark, seed and fruit extracts of *Mimusaps elongi* on mild steel corrosion in hydrochloric acid, and found the leaf extract to give the maximum inhibition efficiency of 98.5 % at 200 mg/l. Temperature studies showed reduction in inhibition efficiency with elevation in temperature. Chugh et al. [14] studied the corrosion behaviour of some schiff bases and found them to exhibit mixed-type behaviour. Janati *et al*. [15] studied comparative corrosion inhibition of 1,4-diallyl-6-chloroquinoxaline-2,3-(1 H ,4 H)-dione (1a) and 1,4-diallyl-6-nitroquinoxaline-2,3-(1 H ,4 H)-dione (1b), and discovered inhibition efficiencies of 95 5 and 89 % respectively at 10^{-3} M concentration and temperature of 308 K

Adsorption Isotherms

Langmuir isotherm suggest that each site holds one adsorbed species [16] and can be represented by

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (5)$$

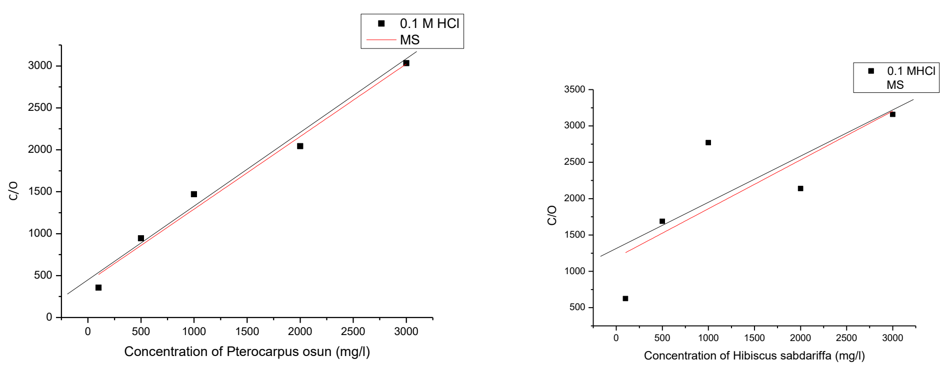
C = concentration of the inhibitor,

θ = degree of surface coverage

K = the equilibrium constant.

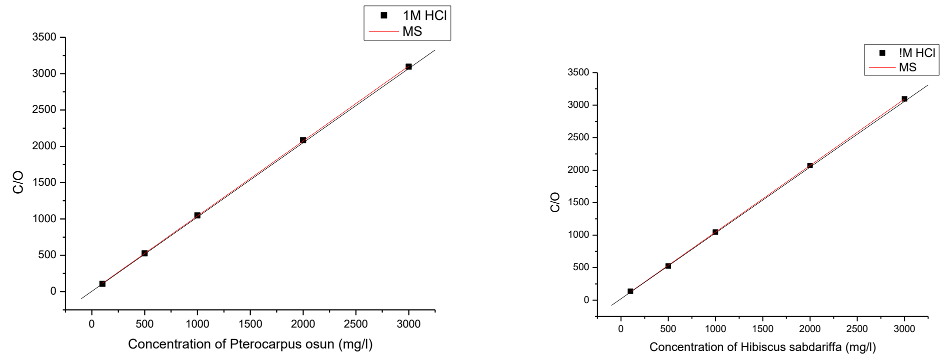
The plot of $\frac{C}{\theta}$ against C represents Langmuir adsorption isotherm, and it is expected to be linear with a positive intercept on $\frac{C}{\theta}$ axes and a slope of unity

Data for the Langmuir adsorption isotherm are presented in Figures 8 and 9 below.



[a] [b]

Figure 8: Langmuir isotherm for mild steel in 0.1M HCl containing [a] *Pterocarpus Osun* and [b] Hibiscus sabdariffa at 303K



[a] [b]

Figure 9: Langmuir isotherm for mild steel in 1M HCl containing [a] *Pterocarpus osun* and [b] *Hibiscus sabdariffa* at 303K

Linear Regression Analysis

Standard free energy (ΔG_{ads})values were determined from the values of K_{ads} using the equation below.

$$\Delta G_{(ads)} = -RTLn\, K_{ads} \quad (6)$$

$\Delta G_{(ads)}$= the standard free energy of the adsorption process

K_{ads} = adsorption equilibrium constant

R = Gas constant

= 8.314J/K/mol

T = Temperature

= 303K

K_{ads} and ΔG_{ads} are presented in Tables 4 and 5 as shown below.

Table 4: Langmuir Adsorption isotherm parameters obtained from the corrosion data for mild steel coupons in 0.1M HCl containing *Pterocarpus osun* (PO) and *Hibiscus sabdariffa* (HS)

Inhibitor	**Intercept**	**Slope**	**K**	**Ln K**	**R^2**	ΔG_{ads} (KJmol^{-1})
PO	426.8754	0.8659	0.0023	6.075	0.9758	-15.303
HS	1189.7984	0.6716	0.0008	7.132	0.5196	-17.966

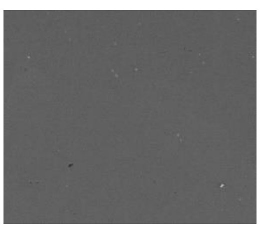
Table 5: Langmuir Adsorption isotherm parameters obtained from the corrosion data for mild steel in 1M HCl containing *Pterocarpus osun* (PO) and *Hibiscus sabdariffa* (HS)

Inhibitor	**Intercept**	**Slope**	**K**	**Ln K**	**R^2**	ΔG_{ads} (KJmol^{-1})
PO	11.2804	1.0307	0.0886	2.425	0.9999	-6.109
HS	24.6283	1.0231	0.0406	3.205	0.9995	-8.073

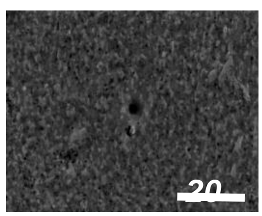
The analysis of the results in Figures 8 and 9 and Tables 4 and 5 are presented as follows. The linearity of the graphs shows monolayer adsorption on a homogeneous surface with no interaction between adsorbed molecules. Higher intercept values of HS: PO= 426.8754, HS= 1189.1984 showing that HS has a higher initial adsorption capacity than PO. PO has a higher slope than HS: PO = 0.8659, HS = 0.6716, thus showing that PO adsorbs faster than HS within the same experimental conditions. Higher Kads values for PO suggests stronger surface adsorption than HS. Besides, HS has a higher ln K value than PO, showing higher energy of adsorption. PO has R^2 values approaching unity (0.9758), which is a better fit to Langmuir adsorption isotherm than HS (0.5196). Moreover, both PO and HS exhibit negative ΔG values, which shows spontaneity; PO is more negative, thus indicating more thermodynamically favoured reaction and stronger adsorption. The mechanism of adsorption from the recorded values of ΔG signifies physiosorption. Sivakumar and Srikanth [13] also concluded physiosorption in similar corrosion work. Janati et al. (2020) observed chemisorptions in their work.

Scanning Electron Microscopy (SEM) Analysis

The surface structure of the products of corrosion on mild steel surface in 0.1 M and 1 M HCl with or without inhibitors was studied and the photographs are presented in Figure 11 as shown below:



a



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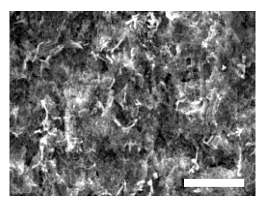

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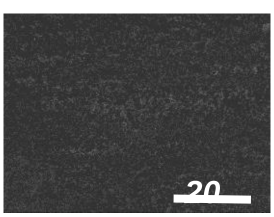

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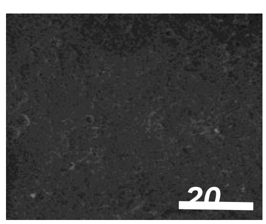

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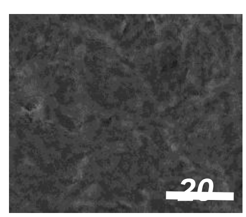

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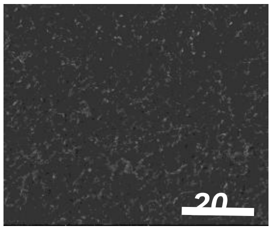

g

Figure 10: (a) SEM pictures for polished mild steel surface; (b), (c) SEM photographs of mild steel surface dipped in 0.1M , 1 M HCl; (d), and (e) SEM pictures for mild steel dipped in 0.1M HCl containing HS and PO; (f) and (g) SEM pictures for mild steel dipped in 1M HCl containing HS and PO

Figure 10 a is the picture of the surface of the polished metal when it had not been dipped in the acid solution; it has a lustrous appearance. Figure 10 b and c are pictures of the surface of the metal after it was dipped in 0.1 M and 1 M HCl respectively; both showed marred appearance, but the effect is greater in 'c'. Figures d, e and f and g are pictures of the metal in the aggressive media with HS and PO; pictures appear even. Chaubey et al. [12] obtained similar result with Scanning Electron Microscopy analysis. Chugh et al. [14] used X-ray diffraction and X-ray photoelectron spectroscopy and discovered that mild steel surface was protected by adsorption.

Conclusion

PO and HS plant extracts have shown to be very effective corrosion inhibitors for mild steel in hydrochloric acid media, with PO performing better than HS with inhibition efficiency up to 98.5% in 0.1 M HCl.

Potentiodynamic polarization method showed that PO effectively reduces corrosion current density more than HS.

Gravimetric result further confirmed that both inhibitors consistently reduced corrosion rate with time, which proved that the plant extracts were stable.

The experimental data of the two plants PO and HS provided good fit to the Langmuir adsorption isotherm model, with PO showing a better fit than HS, with effective adsorption at higher concentration.

Linear regression analysis of the standard free energy of adsorption (ΔG_{ads}) revealed spontaneous adsorption of both inhibitors on mild steel in acidic media and confirmed physiosorption mechanism of adsorption.

Recommendations

Given that PO exhibited higher inhibition efficiency (98.5%) than HS in 0.1 M HCl, Industries that make use of mild steel in acidic environments should selectively PO for corrosion protection, because it has proved to give better protection from the study.

Characterization of the plant extracts should be carried out to ascertain the components that were responsible for inhibition.

Studies should be done on the corrosion behaviour of HS and PO for mild steel in tetraoxosulphate (VI) acid or trioxonitrate (V) acid so as to adapt its usage to wider applications.

Similar work should be carried out using aluminium as the metal, in the place of mild steel.

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