Corrosion Inhibition of Mild Steel in *Sesamum indicum* -2M HCl/H$_2$SO$_4$ Interface

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The corrosion inhibition of mild steel in 2M HCl and H$_2$SO$_4$ solution with natural *Sesamum indicum* of varying concentrations have been studied using gravimetric and linear polarization techniques. The surface morphology of as-corroded samples was assessed with scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS). From the results obtained, the corrosion rate decreased with *Sesamum indicum* concentrations in both environments investigated. Inhibitor efficiency of 85.74, 84.99 and 71.61% were obtained at 50/50/100%v/v *Sesamum indicum* addition in 2M HCl solution for 12, 24 and 36 h exposure time respectively. While at 20%v/v *Sesame indicum* addition, 98.04, 97.60 and 97.46% inhibitor efficiency in 2M H$_2$SO$_4$ solution for 12, 36 and 24 h exposure time were obtained respectively using gravimetric method. Results from the linear polarization technique indicate higher potential value with an increase in the polarization resistance (R$_p$) and lower current density for the inhibited samples than the uninhibited mild steel as obtained from the Tafel plot corrosion rate analysis. Equally, the two methods used for the corrosion evaluation of mild steel/*Sesamum indicum* in HCl and H$_2$SO$_4$ were in agreement.

1. INTRODUCTION

The extensive use of mild steel in most industrial sector is fundamentally because of its low-cost and availability [1,2]. However, mild steel exhibit poor corrosion resistance in some service conditions. Therefore, efforts towards enhancing the corrosion resistance of the alloy become a continuous idea. As reported, HCl and H$_2$SO$_4$ are used extensively in pickling steels [3]. Generally, the corrosion of steel/mild steel in HCl [1,2,4-12] and in H$_2$SO$_4$ [13-17] environments has been widely reported. Over the years, the use of corrosion inhibitors has been subject of interest and promising technique to improve the corrosion characteristic of the alloy [2,7,9,13,18-20]. Although some

synthetic inhibitors when used for corrosion control, have been reported to indicate an excellent performance [21-24]. But majority of these inhibitors are not eco-friendly and are expensive [2,3,10]. As a result, the search for naturally occurring substances with low-cost and hazard-free inhibitors are gaining acceptance in corrosion control. In this direction, the use of oils has been demonstrated and reported to be one of the safe-inhibitor/eco-friendly for corrosion control [7,25-29]. In this work, an attempt was made to evaluate the corrosion inhibition of mild steel in *Sesamum indicum*/HCl and H_2SO_4 environments using gravimetric and electrochemical corrosion measurement.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and sample preparation

The material used was mild steel specimen (20 x 10 x 3 mm coupons) with chemical composition shown in Table 1. Initially, the coupons were mechanically polished with emery papers down to 600. In preparing the specimens for the experiment, the specimens were cut into dimension. These samples were degreased in ethanol, dried, weighed and stored in a desicator. The initial weight of each sample was taken and recorded. In each of hydrochloric (HCl) and tetraoxosulphate vi acid (H_2SO_4), 2 M concentration were prepared fresh as required for each experiment. The natural Sesame oil (*Sesamum indicum)* used was obtained from Technology Innovation Agency, Chemical Station, Ga-Rankuwa, TUT, Pretoria with molecular structure shown in Figure 1. All the corrosion measurements were conducted at room temperature ($25^{o}C$).

Table 1. Chemical composition of the mild steel

Element	C	Mn	Si	P	S	Al	Ni	Fe
% Composition	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance
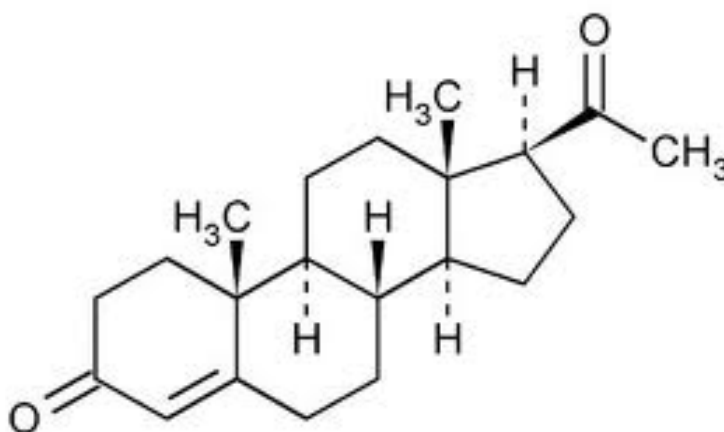
Figure 1. Molecular structure of Sesame oil (*Sesamum indicum*)

2.2 Gravimetric measurement

The gravimetric corrosion test was carried out on the previously weighed samples with and without inhibitor at 25°C. The volume of the solution was 100 ml with and without the addition of *Sesamum indicum* inhibitor. The *Sesamum indicum* inhibitor concentration (C) was varied from 20, 50 and 100%v/v in 100 ml of 2M HCl and H_2SO_4 acidic solution. For each sample, using gravimetric method, the samples were washed, dried and weight taken at interval of 12, 24 and 36 h of exposure time. The corrosion rate and inhibitor efficiency were determined along with the degree of surface coverage.

2.3 Electrochemical measurement

Potentiodynamic polarization was used to characterize the corrosion rate of the mild steel in *Sesamum indicum*-acidic media. All the electrochemical measurements were obtained using Autolab frequency response analyser (FRA) coupled to potentiostat that was connected to a computer system. A glass corrosion cell kit with a platinum counter electrode, a saturated Ag/Ag reference electrode and mild steel sample as working electrode were used. The working electrodes were positioned at the glass corrosion cell kit, leaving 1 cm^2 surfaces in contact with the solution. Polarization test were carried out in two different solution consisting of 2M HCl and H_2SO_4 solution at room temperature using a potentiostat. The polarization curves were determined by stepping the potential at a scan rate of 0.003V/sec. The polarization curves were plotted using Autolab data acquisition system (Autolab model: AuT71791 and PGSTAT 30), and both the corrosion rate and potential were estimated by the Tafel extrapolation method using both the anodic and cathodic branches of the polarization curves.

2.4 Surface morphology

The as-corroded sample surface was examined with scanning electron microscopy equipped with energy dispersive spectroscopy to analyze the elements in the surface (model: Joel 6100).

3. RESULTS AND DISCUSSION

3.1 Results

Tables 2 and 3 showed gravimetric corrosion data for mild steel with inhibitor efficiency for 2M HCl and H_2SO_4/*Sesamum indicum* respectively. While Tables 4 and 5 are the electrochemical parameter for mild steel in HCl and H_2SO_4/*Sesamum indicum* condition respectively. The variations in corrosion rate with inhibitor concentration at various immersion times for the two environments are presented in Figures 2 and 3 respectively. Figures 4 and 5 illustrate the linear polarization curves for mild steel in the studied environments. The SEM-EDS of the surface morphology of as-received, as-corroded uninhibited and as-corroded mild steel-*Sesamum indicum*-HCl/ H_2SO_4 after 36 h immersion

time are shown in Figures 6-9. In Figures 10 and 11, the inhibitor efficiency (%IE) for 2M HCl and H₂SO₄/*Sesamum indicum* for different methods of corrosion evaluation are compared. Figure 12 shows the adsorption isotherm for the inhibitor in mild steel/H₂SO₄ condition.

3.2 Discussion

3.2.1 Gravimetric measurement

Table 2. Corrosion rate (CR), Inhibition efficiency and surface coverage (θ) for mild steel in 2M HCl without and with varying concentration of *Sesamum indicum* (%v/v) at 25°C

Time(hr)	C (%v/v)	Surface coverage (θ)	Inhibition Efficiency (%)	CR (mm/day)
12	0	-	-	0.9689
	20	0.7016	70.16	0.2889
	50	0.8574	85.74	0.1381
	100	0.7215	72.15	0.2691
	0	-	-	0.9684
24	20	0.6776	67.76	0.3122
	50	0.8499	84.99	0.1458
	100	0.7164	71.64	0.2745
36	0	-	-	0.9957
	20	0.6721	67.21	0.3264
	50	0.2612	26.12	0.2228
	100	0.7161	71.61	0.2826

Table 3. Corrosion rate (CR), Inhibition efficiency and surface coverage (θ) for mild steel in 2M H₂SO₄ without and with varying concentration of *Sesamum indicum* (%v/v) at 25°C

Time(hr)	C (%v/v)	Surface coverage (θ)	Inhibition Efficiency (%)	CR (mm/day)
12	0	-	-	1.1800
	20	0.9804	98.04	0.0023
	50	0.9456	94.56	0.0064
	100	0.9728	97.28	0.0032
24	0	-	-	1.2100
	20	0.9760	97.60	0.0029
	50	0.9358	93.56	0.0074
	100	0.9631	96.31	0.0021
36	0	-	-	1.2800
	20	0.9746	97.46	0.00324
	50	0.9323	93.23	0.0086
	100	0.9252	92.52	0.0095
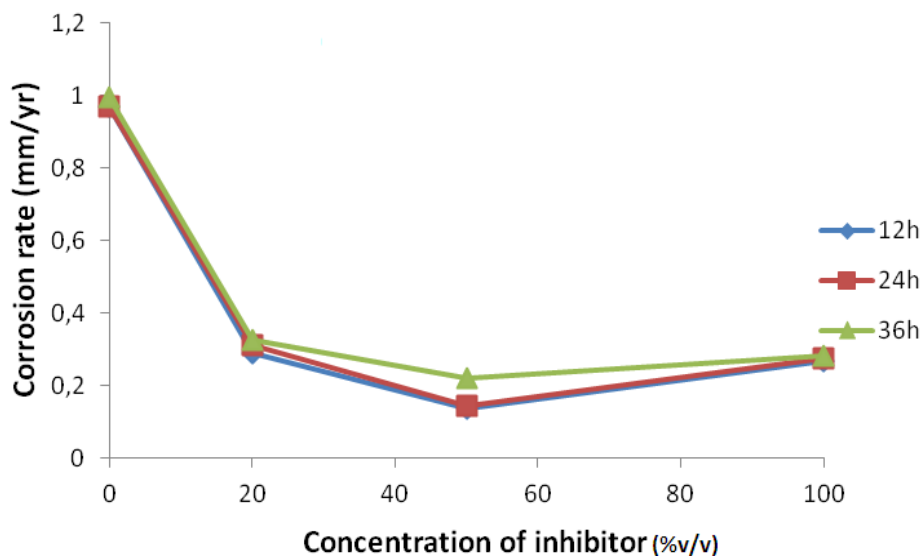
Figure 2. Variation of corrosion rate with concentration of inhibitor (*%v/v*) for mild steel in 2M HCl for different immersion time at 25°C
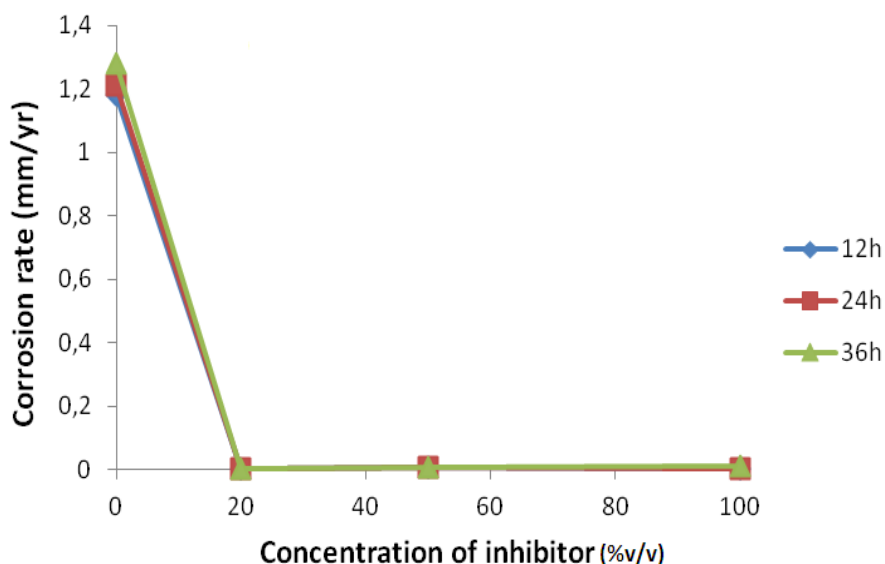
Figure 3. Variation of corrosion rate with concentration of inhibitor (*%v/v*) for mild steel in 2M H$_2$SO$_4$ for different immersion time at 25°C

Two different environments (2M HCl and H$_2$SO$_4$) were considered separately for the study of mild steel-*Sesamum indicum corrosion* behaviour at various inhibitor concentrations at 25°C. From the results, the corrosion rate (CR) of mild steel decreased with addition of *Sesamum indicum as* corrosion inhibitor for both environments and immersion time considered (Tables 2 and 3, Figures 2 and 3). For 2M HCl-*Sesamum indicum* interface, at 12 h immersion time for 50%v/v *Sesamum indicum,* corrosion rate decreased from 0.9689 to 0.138 mm/day indicating inhibitor efficiency (IE) of 85.74%. While at 100 and 20%v/v *Sesamum indicum* addition the IE were found to be 72.15 and 70.16 % respectively.

Specifically, Figure 2 shows a decrease in corrosion rate with concentration of inhibitor for all the immersion time at 25°C. Equally for 2M H$_2$SO$_4$-*Sesamum indicum* interface, similar trends were observed with much higher corrosion resistance throughout the immersion time (Figure 3). For this condition, higher % IE was demonstrated by the natural oil as the immersion time increased. Specifically, at immersion time of 12 h, IE was calculated to be 98.04% at 20%v/v *Sesamum indicum* addition. While at the same inhibitor concentration for 24 and 36 h immersion time corrosion rate/IE were calculated to be 0.0029/97.60% and 0.00324/97.46% respectively. However, this behaviour has been attributed to the increase in the element that forms stable oxides as evidenced in the EDS (Figures 8 and 9). The thin layer of the oxides adhered to the metal surface resulting into a decrease in the corrosion rate. Similar results have been reported [10,18,30].

3.2.2 Potentiodynamic polarization

In the polarization measurement (see Tables 4 and 5), linear polarization resistance was used as criterion for the electrochemical corrosion evaluation for mild steel in 2M HCl and H$_2$SO$_4$/*Sesamum indicum*. In Figures 4 and 5, the anodic and cathodic polarization curve for the mild steel in acidic media-*Sesamum indicum* and uninhibited conditions were shown. Considering the corrosion condition of 2M HCl-*Sesamum indicum*-mild steel, it can be seen that the current density decreased with an increase in inhibitor concentration and corrosion potential (E$_{corr}$) increased for 20, 50 and 100%v/v *Sesamum indicum* additions respectively (Figure 4). From the linear polarization resistance value, it shows that addition of the inhibitor resulted into an increase in the R$_p$ of the mild steel from 8.489E-1 (uninhibited) to 5.581E+0 (inhibited) condition with an IE of 84.79%. The increase in R$_p$ generally suggested an improvement in the corrosion resistance of the metal in the presence of the inhibitor. This shows that the metal is protected within the immersion time considered. Considering the electrochemical corrosion for 2M H$_2$SO$_4$-*Sesamum indicum*-mild steel (Figure 5), similar trend in the corrosion resistance were observed with IE of 93.13% obtained at 100%v/v inhibitor addition. Since both the anodic and cathodic branches changes with the addition of inhibitor concentrations, the natural oil *Sesamum indicum* can be said to have acted as a mixed-type corrosion inhibitor within the studied environments. Equally, the inhibition action of this natural oil can be traced to its chemical structure that enabled the adsorption of molecules on the mild steel surface, thus serving as a barrier to corrosion attack.

**Table 4.** The electrochemical parameters of mild steel in 2 M HCl-Sesamum indicum environments at 25°C

S/N	C (%v/v)	Icorr (A/cm^2)	ba (v/dec)	LPR Rp (Ωcm^2)	-Ecorr (V)	CR (mm/yr)
1	0	1.003E-4	0.040	8.489E-1	0.633	5.482E-1
2	20	7.581E-7	0.004	3.040E+0	0.406	4.143E-3
3	50	6.442E-5	0.010	1.295E+0	0.430	3.521E-1
4	100	1.020E-6	0.007	5.581E+0	0.425	5.578E-3

Table 5. The electrochemical parameters of mild steel in 2M H_2SO_4-*Sesamum indicum* environments at 25°C

S/N	C (% v/v)	Icorr (A/cm^2)	ba (v/dec)	LPR Rp (Ωcm^2)	-Ecorr (V)	CR (mm/yr)
1	0	4.231E-5	0.024	3.452E-1	0.478	6.421E-1
2	20	9.136E-6	0.007	1.047E+0	0.366	4.993E-2
3	50	1.339E-5	0.011	1.064E+0	0.428	7.317E-2
4	100	8.076E-6	0.017	2.218E+0	0.262	4.414E-2
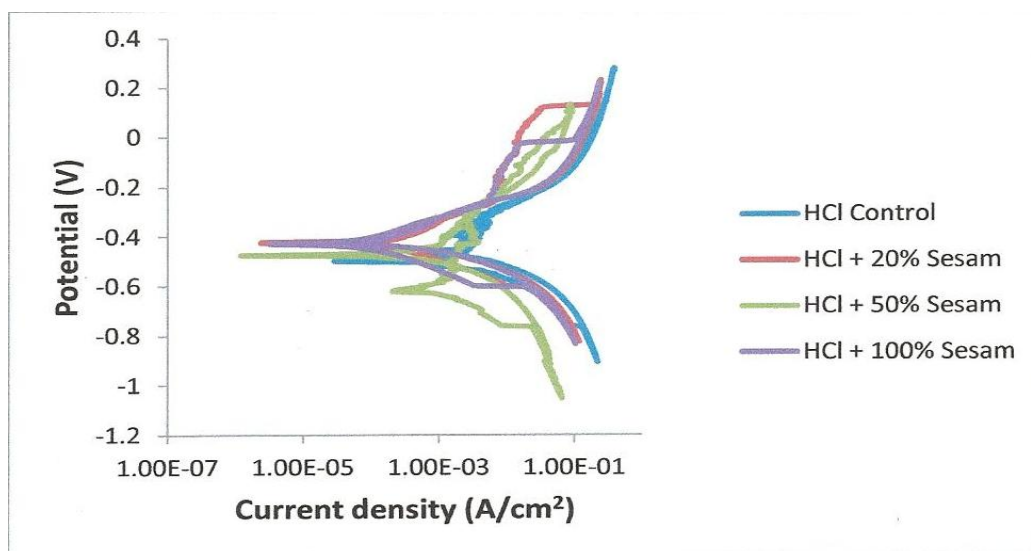
**Figure 4.** Linear polarization of mild steel in 2M HCl solution/*Sesamum indicum* environment at 25°C
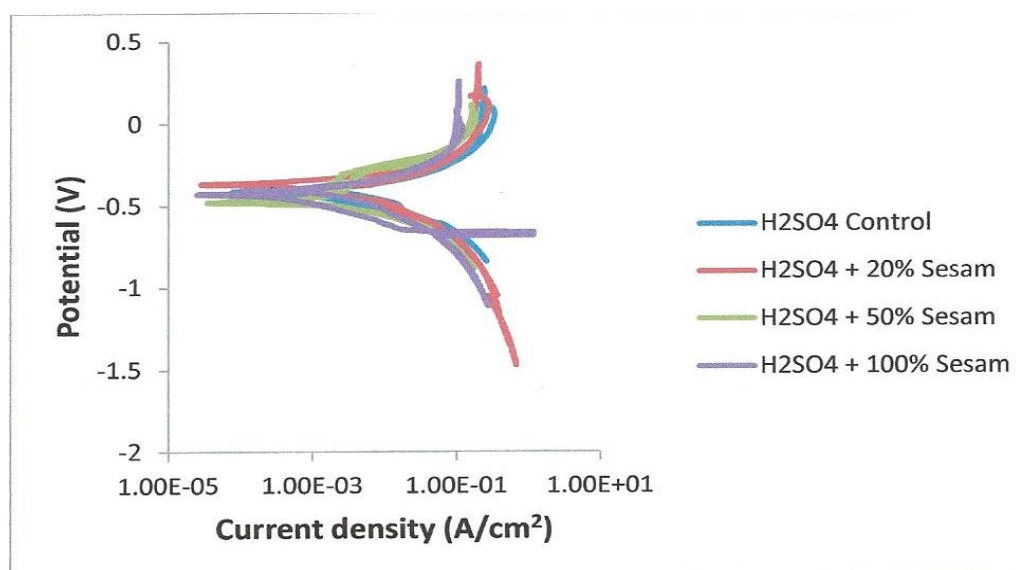
Figure 5. Linear polarization of mild steel in 2M H_2SO_4 solution/*Sesamum indicum* environment at 25°C

3.2.3 Scanning electron microscope-Energy dispersive spectroscopy (SEM-EDS)

The SEM micrographs of mild steel surfaces are shown in Figures 6-9. The uninhibited mild steel sample in 2M HCl solution (Figure 7) indicates a severe surface degradation and pit formation as compared with as-received mild steel (Figure 6). Figures 8 and 9 showed that the *Sesamum indicum* natural oil was able to exhibit some degrees of inhibition which retarded the corrosion rate of the mild steel in both HCl and H_2SO_4 solution. In addition, the inhibited samples can be observed to be covered with thin layer of the corrosion inhibitor resulting to the protection of the mild steel against corrosion. From the EDS in Figures 8 and 9, the higher level of O is as a result of ferrous hydroxide formation and the combination of C and O is due to the constituents contained in the *Sesamum indicum* structure (Figure 1). This acts as active inhibitor that retards the corrosivity of the mild steel in the acidic media. Equally, the surface morphology of the sample observed with SEM-EDS helps to explain the corrosion behaviour of the sample further.
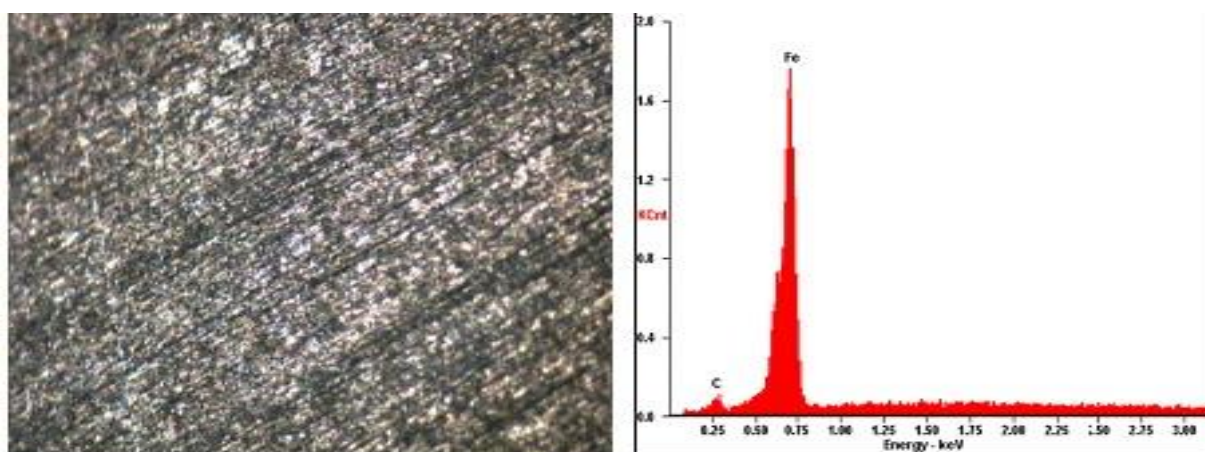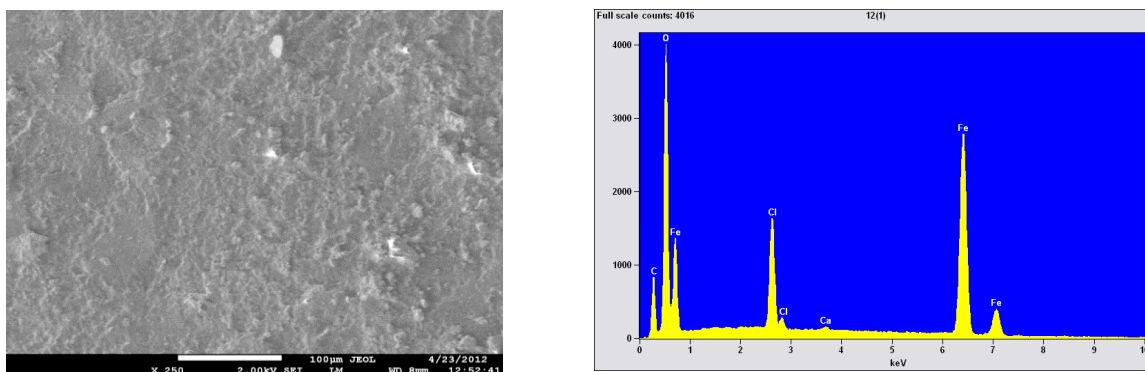

Figure 6. SEM micrograph of the as-received mild steel sample with the EDS
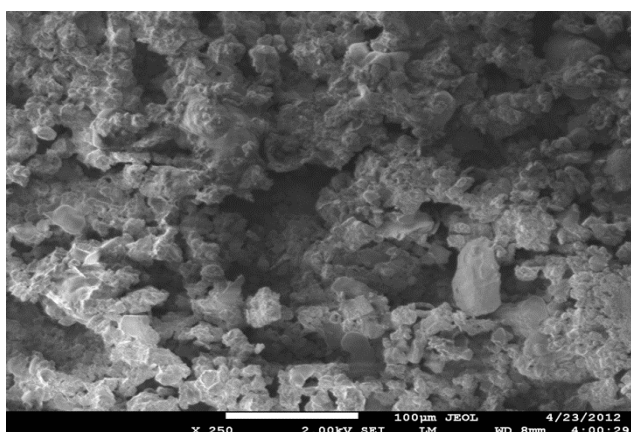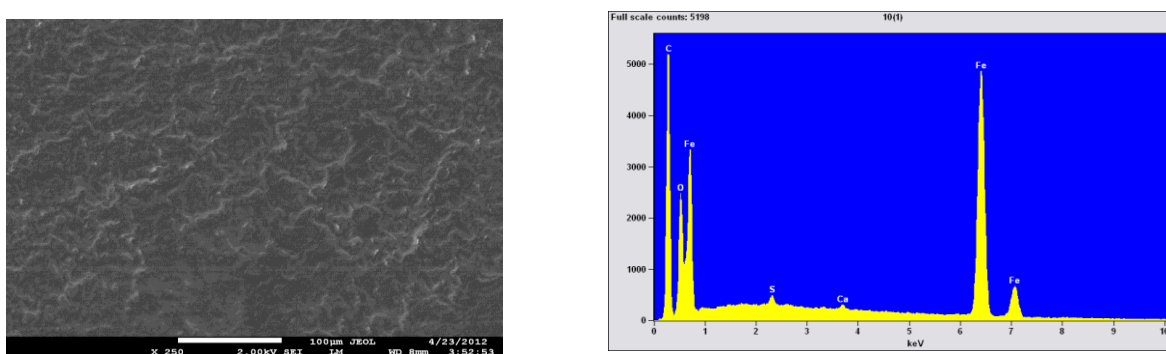

Figure 7. SEM micrograph of as-corroded uninhibited mild steel in 2M HCl solution after 36 h of immersion time
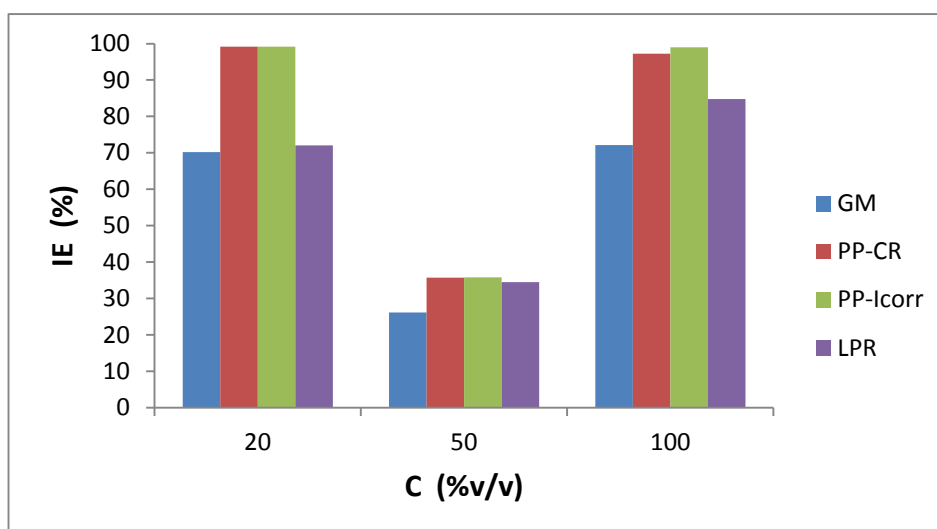
Figure 8. SEM micrograph of as-corroded mild steel in 50%v/v *Sesamum indicum* -2M HCl sample after 36 h of immersion time with the EDS


Figure 9. SEM micrograph of as-corroded mild steel in 50%v/v *Sesamum indicum* -2M H$_2$SO$_4$ sample after 36 h of immersion time with the EDS
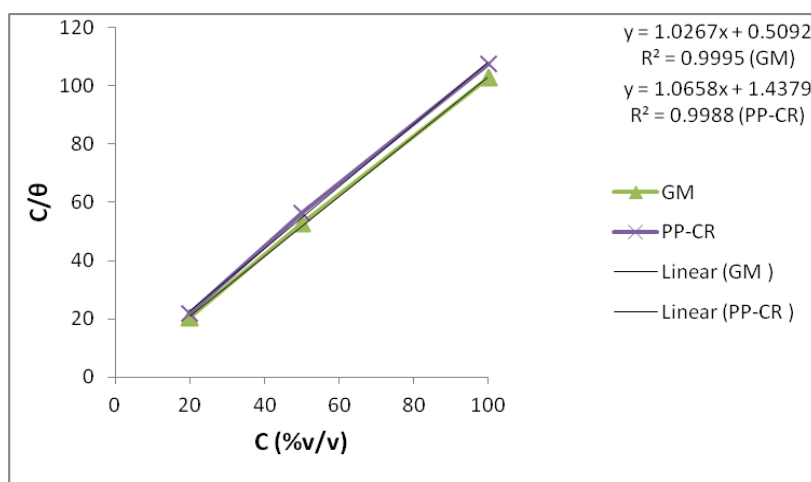
3.2.4 Inhibitor efficiency and adsorption behaviour

Figure 10. Comparative chart of inhibitor efficiency (IE) for 2M HCl solution/*Sesamum indicum* concentration obtained by gravimetric (GM), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion current (PP-Icorr) and linear polarization resistance (LPR)
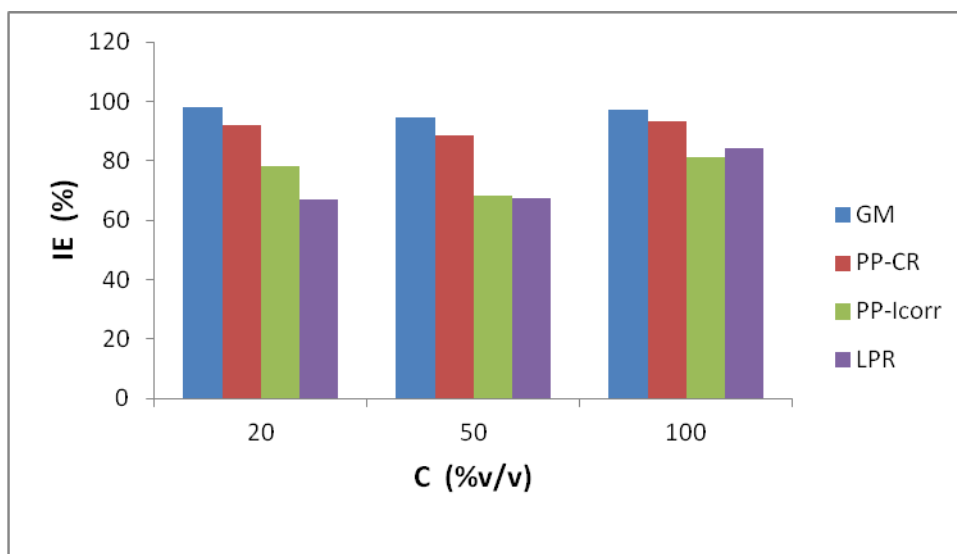
Figure 11. Comparative chart of inhibitor efficiency (IE) for 2M H$_2$SO$_4$ solution/*Sesamum indicum* concentration obtained by gravimetric (GM), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion current (PP-Icorr) and linear polarization resistance (LPR)

Figure 12. Langmuir isotherm for the adsorption of *Sesamum indicum* compounds on the mild steel surface in 2M H$_2$SO$_4$ solution at 25$^{\text{o}}$C obtained by gravimetric and potentiodynamic polarization method

The percentage inhibitor efficiency (% IE) of the mild steel-*Sesamum indicum* in both HCl and H$_2$SO$_4$ solution were computed using the equation reported [31]. The computed data for the IE using gravimetric (GM), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion density (PP-I$_{\text{corr}}$), and linear polarization resistance (LPR) are presented in Figures 10 and 11 for 2M HCl and H$_2$SO$_4$/*Sesamum indicum*. From the results, it shows that % IE of the *Sesamum indicum* oil increases with an increase in the inhibitor concentrations. The reason been

that, as the inhibitor concentration increases, the surface area covered by this inhibitor increased hence higher IE was obtained. *Sesamum indicum* oil can be said to exhibit a mixed-type corrosion inhibition because of the simultaneous change in the anodic and cathodic region during the electrochemical measurement. This is in agreement with previous studies [5,11,32]. The adsorption mechanism showed that the relationship between C/θ and C is linear at 25^oC for both the environments (Figure 12). Since the linear regression coefficient/or correction factors (R^2) are almost unity; GM (0.9995), PP (0.9988) the adsorption behaviour is believed to have obeyed Langmuir adsorption isotherms.

4. CONCLUSIONS

1. *Sesamum indicum* natural oil has been found to be a good corrosion inhibitor for mild steel in HCl and H_2SO_4 solution at 25^oC.

2. The percentage IE and corrosion resistance of the mild steel increased with inhibitor concentrations in both the environments for all the methods considered.

3. The adsorption behavior of the *Sesamum indicum* in acidic media for mild steel can be said to obey Langmuir adsorption isotherms.

4. The potentiodynamic polarization curves demonstrated that the *Sesamum indicum* natural oil acts as a mixed-type inhibitor.

5. SEM-EDS examination showed that there was improvement in the surface morphology of the as-corroded inhibited mild steel compared to uninhibited samples.

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