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Corrosion Efficiency in Controlling Mild Steel in Sulphuric Acid Medium Using Formazan Derivative as Inhibitor

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Abstract

Formazan derivatives of p-dimethyl amino benzaldehyde (FD), and Formazan of benzaldehyde (FB) was studied to control the corrosion of Mild Steel (MS) material in one molar sulphuric acid. The results were analyzed by means of weight loss measurements, Tafel Polarization, AC impedance and surface morphological studies. The results showed that the compound FD and FB act as mixed-type inhibitors. Competence of the inhibitor mainly depends on the nature of the premeditated organic compounds and the construction of their protective film. FD shows high inhibition efficiency than FB.

Keywords: Mild steel, Corrosion, Inhibitors, Adsorption, Polarization.

1. Introduction

Mild steel materials are used in many industries like Oil refineries and Thermal power plants. The study of mild steel in various environments has been thought-out by various researchers [1-3]. A Number of researchers have dedicated their attention to develop more resourceful and non- hazardous inhibitors in order to trim down acid attack and fortification aspects of mild steel material. Towards the study of mild steel there is bounty of methods to evade the rust in the material. To make use of inhibitor is the best method in shielding mild steel

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from corrosion especially in acidic medium. [4-9]. In order to thwart mild steel materials, many organic based synthesized compounds were used. More consideration was paid on the choice of organic inhibitors, since the effect of electron donating or electron withdrawing groups are accountable for the corrosion inhibition all the way through adsorption mechanism. Furthermore the inhibition too depends on structure and nature of functional groups present in organic molecule [10-14]. Consequently, in this study, the corrosion inhibition of mild steel in 1M H_2SO_4 solution was studied in the existence and dearth of two organic inhibitors namely Formazan of p-dimethyl amino benzaldehyde FD), and Formazan of benzaldehyde (FB) for two hours at room temperature.

2. Experimental

2.1 Material preparation

The mild steel material of composition (in weight percentage) % C=0.015; Si=0.009; Mn=0.194; S =0.015; P=0.010; Ni =0.013; Mo =0.012; Cr=0.042 and Fe=99.689 were cut into pieces of 5 cm x 1 cm strips for the present weight loss measurement. They were refined according to the ASTM procedure [15] using SiC abrasive paper of different grits (from grits 120 to 1200) and degreased with Acetone and rinsed with distilled water. The specimens were also cut into 1x1x0.3 cm and embedded with an electrical connection using epoxy resin with exposed area of 1 cm^2 for electrochemical studies, which was used as a working electrode.

2.2 Preparation of Solutions

Preparation of Formazans: nitrite (0.2g) in water (2ml) at (0-5 ^oC). This solution was added to 0.01 M of Aniline (0.02 M) and diazotized in glacial acetic acid and HCl (0.5ml) with

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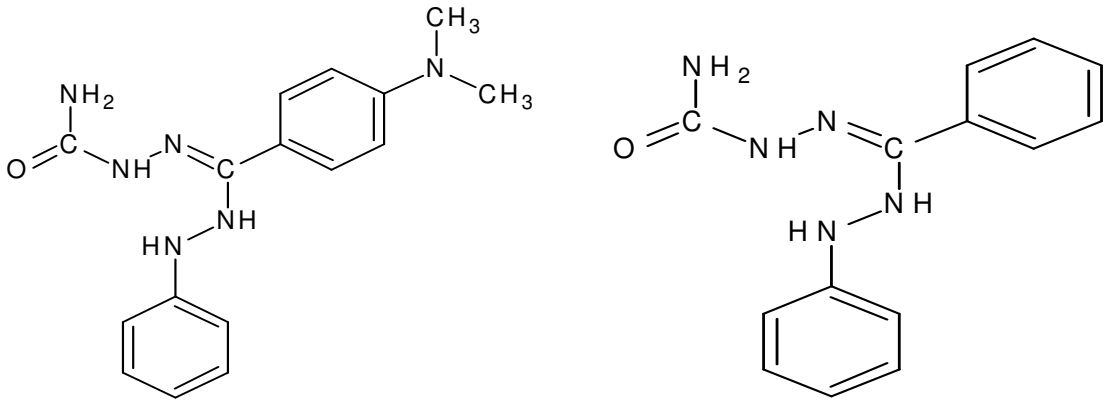
sodium semicarbazone in pyridine in the cold condition with constant stirring and left over night. The mixture was then poured into cold water after stirring. The colored solid estranged out which is then filtered, washed repeatedly with water, and recrystalised with ethanol. Inhibitor-(Formazan Derivatives) Formazan of benzaldehyde (FB) inhibitor solution was prepared by dissolving 0.1gm of Formazan of benzaldehyde (FB) in 100ml of test solution. Using these two inhibitors various milli molar concentrations of solutions were prepared for analysis. Formazan of p-dimethyl amino benzaldehyde (FD) solutions were prepared and its structure is shown in Figure 1(a) and Formazan of benzaldehyde (FB) were shown in Figure 1(b).



(a) **(b)**

Figure 1. (a) Formazan of p-dimethyl amino benzaldehyde (FD) and (b) Formazan of benzaldehyde (FB)

2.3 Weight loss measurement

The mild steel specimens were immersed in 1M H_2SO_4 for two hours at room temperature (28 ± 2 ºC) at various concentration of FD and FB inhibitor solution. The test specimens were removed after two hours and clean with acetone and distilled water solution. The

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weight in loss of the specimen was determined by weight loss method. From this, the inhibiton efficiency (IE %) was calculated using the following formula,

$$IE\ \% = \frac{W_o - W_i}{W_o} \times 100 \qquad (1)$$

Where, W_O and W_i (in g) are the values of the weight loss observed for mild steel in the absence and existence of inhibitor respectively.

2.4 Electrochemical Studies

This study was carried out using mild steel material as a working electrode, the platinum electrode and a saturated calomel electrode (SCE) are used as auxiliary and reference electrodes respectively. Using Luggin capillary tube the ohmic potential drop were minimized by keeping the reference electrode very closer to the surface of the working electrode. The Tafel polarization studies were conducted at an optimum concentration of FD and FB. The study was examined at a rate of 0.01mV s^{-1} and at a potential range of -800 to -200 mV. AC impedance studies were carried out at a frequency range of 1Hz to 1 KHz. Electrochemical Workstation (Model No: CHI 600D, CH Instruments, USA) was used for all the electrochemical studies.

Using the following formula the efficiency of the inhibitors (%) was calculated from the current density (I_{corr})

$$IE\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \qquad (2)$$

I_{corr} = Corrosion current density in the absence of inhibitor

$I_{corr(i)}$ = Corrosion current density in the presence of inhibitor.

2.5 Scanning Electron Microscope (SEM analysis)

The specimen were immersed into a blank and inhibitor solutions for two hours and then washed with double distilled water and kept on observation for surface analysis in Scanning Electron Microscope (SEM- HITACHI S3000H, Japan).

2.6 FT-IR Studies

FT-IR analysis was carried out using the scrapped corrosion product of mild steel. Using this spectral study the nature of adsorption of the inhibitor molecule over the metal surface were analyzed using FT-IR spectrophotometer (Perkin Elmer-1400).

3. Results and Discussion

3.1 Weight loss method

The comparison graph of corrosion behaviour and inhibitor efficiency of mild steel in 1M H_2SO_4 with Formazan of *p*-dimethyl amino benzaldehyde (FD) and Formazan of benzaldehyde (FB) is shown in **Figure 2 (a),** which was studied by weight loss method for two hours at room temperature. From the graph, it was experientially verified that the weight loss of mild steel in the acid decreases with increasing concentration of inhibitor, and the values were tabulated in **Table 1** from which it clearly states that the corrosion rate has decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. The efficiency of the FD was found as 78.43 % at 1M H_2SO_4 and FB was found as 52.19 % at 1M H_2SO_4 respectively at optimum concentration of the inhibitor solution for two hours at room temperature.

From the result obtained, it was also concluded that the inhibitor was very proficient for preventing mild steel corrosion in 1M H_2SO_4 with two inhibitors. The inhibitor efficiency was found maximum in 1M H_2SO_4 in FD than FB. **Figure 2(a)** revealed the comparison of corrosion rate (CR) with the two inhibitors FD and FB (in %) in 1M H_2SO_4 solution for two hours at room temperature. Comparison of inhibition efficiency (IE) with concentration of FD and FB (in %) in 1M H_2SO_4 solution for two hours at room temperature is shown in **Figure 2(b)**.

Table 1. Corrosion parameters in absence and presence of Formazan of *p*-dimethyl amino benzaldehyde (FD) Formazan of benzaldehyde (FB) and with 1M H_2SO_4.

Inhibitor	Conc. of inhibitor (mM)	Corrosion Rate (mm/y)	Inhibitor Efficiency (%)
		1M H_2SO_4	1M H_2SO_4
FD	Blank	34.1038	---
	6.34	23.4045	31.37
	12.68	20.0610	41.17
	19.02	14.2656	58.16
	25.36	11.3679	66.66
	31.70	7.3557	78.43
FB	Blank	88.8259	---
	7.37	74.6717	15.93
	14.74	67.0931	24.46
	22.11	58.5114	34.12
	29.48	51.7129	41.78
	36.85	42.4625	52.19

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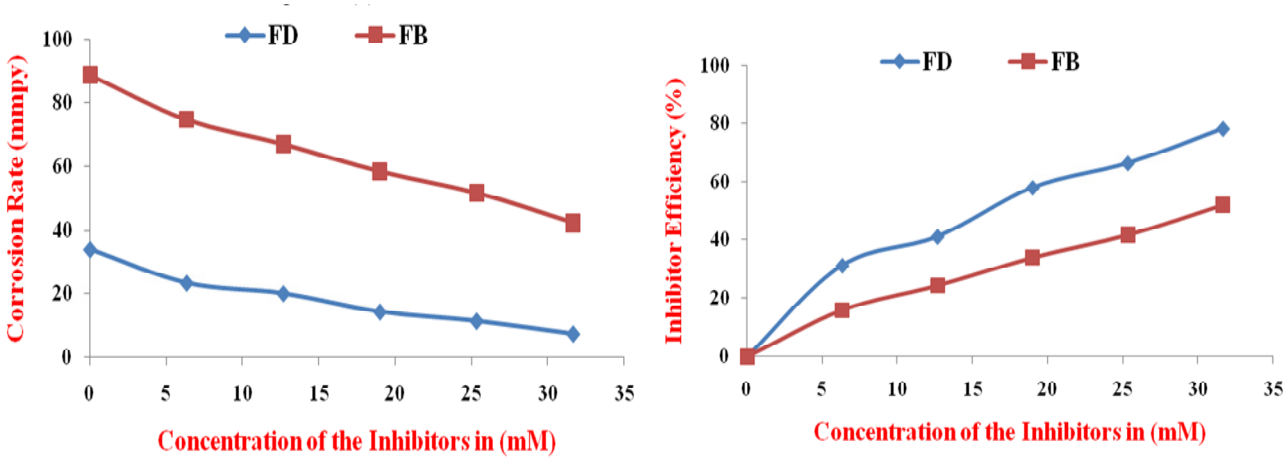

Figure 2. Comparision study of mild steel in 1M H_2SO_4 in FD and FB (a) Corrosion rate (b) Inhibiton effciency with respect to concentation of inhibitor.

3.2 Potentiodynamic polarization studies:

The results obtained from the potentiodynamic polarization shows the performance of FD and FB inhibitor over the mild steel in order to prevent corrosion in sulphuric acid. The Tafel curves obtained for optimum concentration of inhibitors were shown in **Figure 3**, and the various polarization parameters like anodic and cathodic Tafel slopes (-βa and -βc), corrosion current (I_{corr}) and corrosion potential (E_{corr}), were derived from potentiodynamic polarization studies on mild steel in acid media.

Due to the blocking of active sites on the metal surface, it is clear that inhibitors bring about considerable decrease in corrosion current density of inhibited curves and the E_{corr} values have also shifted slightly towards negative side in existence of inhibitors, it suggesting that the inhibitors restrain the corrosion of mild steel in acids solution by controlling cathodic reactions predominantly. It was, therefore revealed that the inhibitive action of FD and FB is shown to be a mixed type of inhibitor. The **Table 2** clearly represents the results obtained from

potentiodynamic polarization studies.

The I_{corr} values have decreased when comparing with two different inhibitors at their optimum concentration. The obtained values from corrosion current density and the inhibition efficiency were also compared with weight loss measurement which shows a result with complementary to each other. When comparing these two inhibitors FD shows the maximum inhibition efficiency of 81.25 % and FB shows 71.43 % in 1M H_2SO_4. This can be easily explained by the retardation of hydrogen evolution in the optimum concentration of inhibitors [16]. Moreover, due the presence of the nitrogen (N-H group) atom in the inhibitor molecule this also retards the corrosion by absorbing the inhibitor molecule on the surface of the mild steel metal through electrostatic attraction and hence FD acts as good inhibitor system.

Table 2. Polarization parameters of mild steel electrode immersed in the presence and absence of the optimum concentration of the inhibitors.

Inhibitors	β_c (V dec^{-1})	β_a (V dec^{-1})	E_{Corr} (V)	I_{Corr} x10^{-4} (A)	Corrosion Rate (mmpy)	Inhibition Effeciency (%)
Blank	5.593	16.573	-0.420	1.6270	7.819	---
FD	7.610	14.740	-0.599	0.3050	1.466	81.25
FB	7.509	16.397	-0.564	0.4648	2.234	71.43

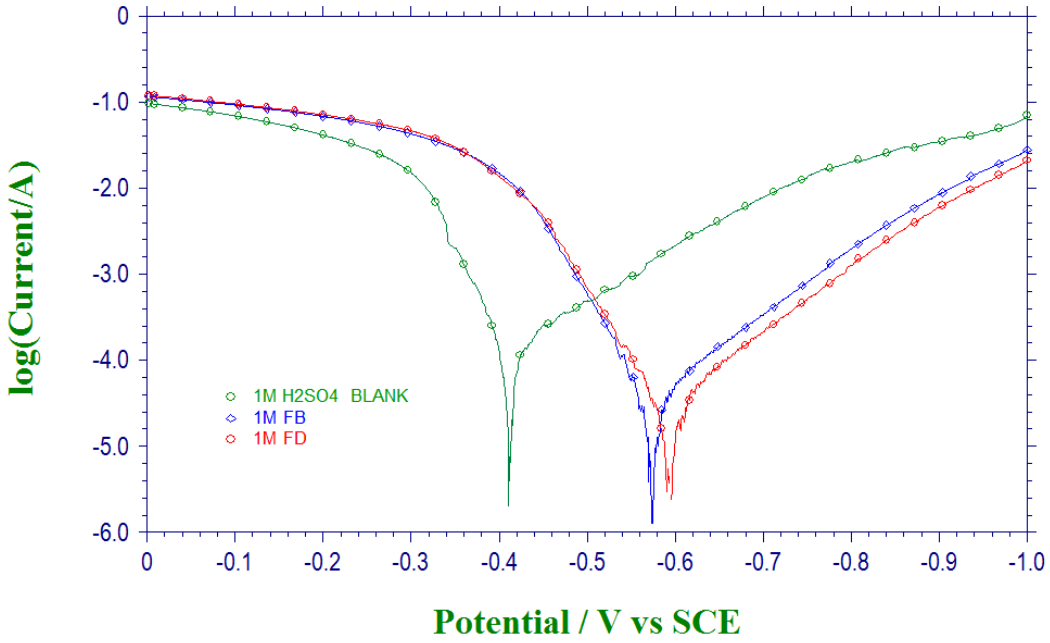

Figure 3. Potentiodynamic polarization curves of mild steel in 1M H_2SO_4 in the absence and presence of the inhibitors.

3.3 Electrochemical impedance spectroscopy (EIS)

EIS measurements was carried out at open circuit potential condition to examine the corrosion resistance of mild steel in 1M H_2SO_4 solution in the absence and presence of FD and FB. An equivalent circuit (Randle's circuit) with solution resistance (R_s), charge transfer resistance (R_{ct}) and a double layer capacitance (C_{dl}) were used for the present measurement. **Figure 4** shows the Nyquist plots obtained for mild steel electrode in 1M H_2SO_4 solution without and with optimum concentration of inhibitors. The obtained Nyquist plot shows only one capacitive loop and the diameter of the semicircle increases on the mounting of the electrostatic attraction of the inhibitor, which signifies that the formed inhibitive film was reinforced by the addition of such studied inhibitors. **Table 3** represent the main parameters obtained from the impedance technique and lower the double layer capacitance (C_{dl}) value for 1M H_2SO_4 medium indicates that the homogeneity of the surface of the mild steel coarse due to corrosion. Double

layer capacitance values have dropped off by the effective addition of inhibitors at the optimum concentration. The good inhibition efficiencies of the studied inhibitors have confirmed from the acquired Nyquist parameters and signify the decrease of charge accumulated on the double layer due to the formation of adsorbed inhibitor film on mild steel surface [17]. Augment in the thickness of the electrical double layer may put forward that the inhibitor molecule may act by adsorption at the metal/solution interface, and / or decrease in the (C_{dl}) which can result from a decrease in local dielectric constant [18]. From this result, it illustrates that, the capacitance of the electrical double layer (C_{dl}) decreases in the presence of the inhibitors. Due to the presence of electron density on the nitrogen of the N- H group present in FD gives outstanding inhibition efficiency than FB.

Table 3. A.C. Impedance parameters of mild steel electrode immersed in 1M H_2SO_4 in the absence and presence of the inhibitors.

Inhibitors	Parameters		
	R_{ct} (ohm cm^2)	C_{dl} (μF $X10^{-5}$)	Inhibition Efficiency (%)
Blank	63.34	4.831	-
FB	218.10	1.697	70.49
FD	382.52	1.275	83.17

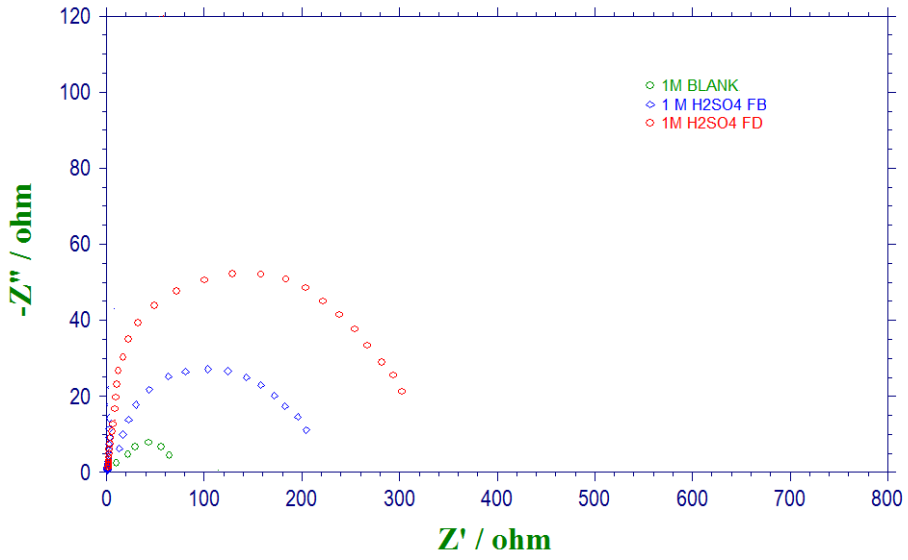

Figure 4. A.C. Impedance curves of mild steel electrode immersed in 1M H_2SO_4 in the absence and presence of the inhibitors.

3.4 FT-IR spectral studies:

FT-IR spectral studies give valuable information on predicting the type of adsorption as well as bonding formation in the mild steel surface which occurs at optimum concentration of inhibitors used. FT-IR spectrum of the inhibitor FD was represented in **Figure 5 (a)**. In this spectrum the peak appeared at 3367cm^{-1} corresponds to amide N-H stretching, 1510 cm^{-1} corresponds to C=O group, 1417 cm^{-1} corresponds to C-C stretching and from 1230 cm^{-1} to 1000 cm^{-1} are due to the presence of C-O bonding nature. After the weight loss measurement, the corrosion product formed on the mild steel surface were scraped and used for FT-IR spectral characterization. The obtained spectra are given in **Figure 5 (b and c)** which is similar to **Figure 5 (a)** which indicate that the corrosion products include FD and FB. Consequently from the spectral data it is concluded that physisorption takes place between metal surface and the inhibitor molecule.

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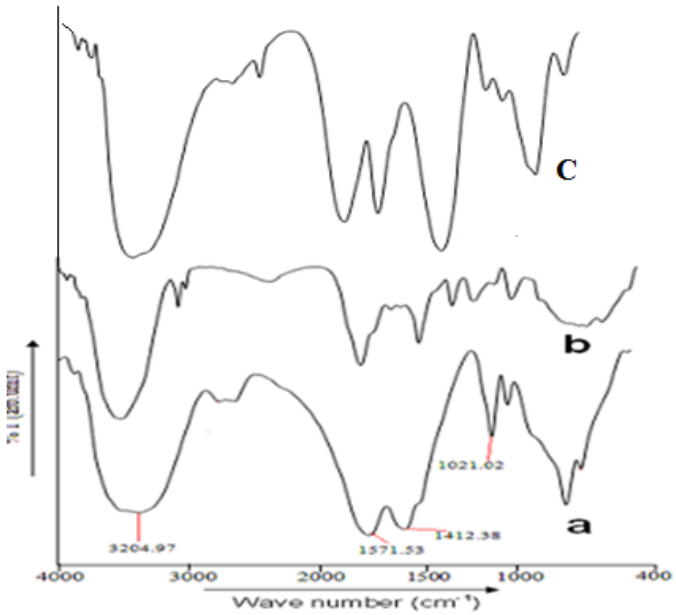

Figure 5. FT-IR spectrum of the corrosion product obtained after electrochemical test in the absence (a), presence of FD (b) and FB (c).

3.5 SEM Analysis:

Surface morphological analyses were carried out for the mild steel specimen obtained after the electrochemical studies carried out in absence and presence of optimum concentration of inhibitors. The micrograph shown in the **Fig. 6a, b & c** represents the specimen immersed in the blank (1M H_2SO_4), acids containing inhibitor FD and FB respectively. From the micrograph, it clearly illustrates that the specimen immersed in blank was highly corroded while the specimens immersed in FD and FB were unvarying and it signify the corrosion inhibited surface. This outcome confirms the surface coverage of the mild steel, which clearly indicates that there is a decrease in the contact between metal and the aggressive medium [19].

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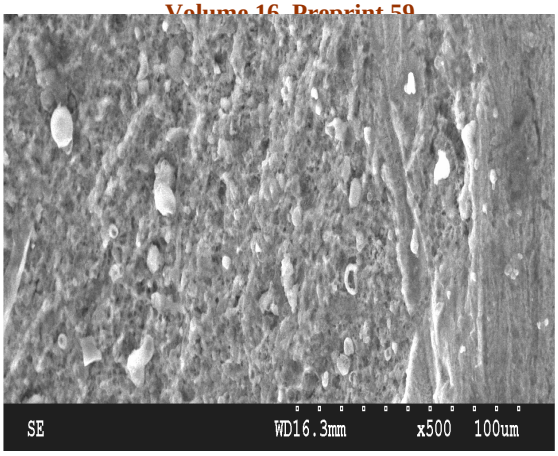
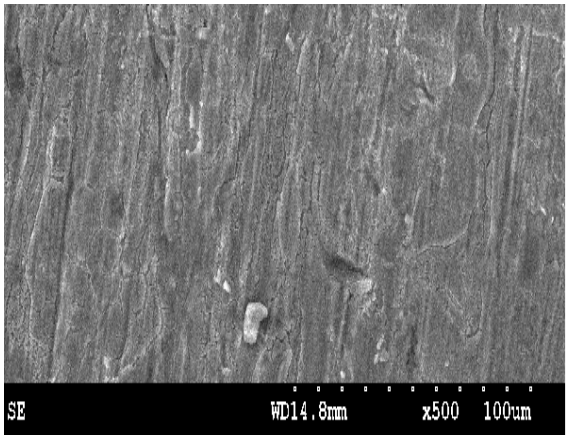
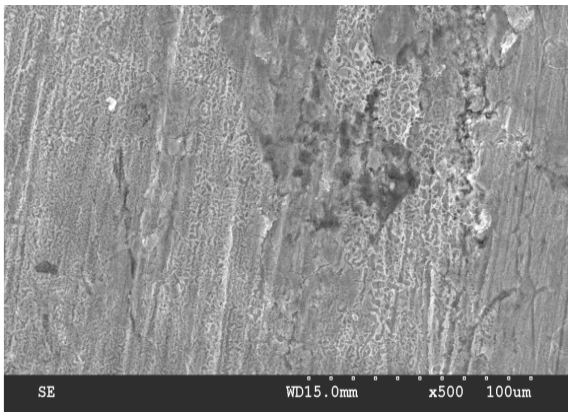


(a)



(b)



(c)

Figure 6. SEM images obtained for the mild steel surfaces immersed for 2 h in 1M H_2SO_4 in the absence (a), presence of inhibitor FD (b) and FB (c).

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Conclusion:

From the above research work it is concluded that the

1. Formazan of p-amino benzaldehyde (FD) and Formazan of Benzaldehyde (FB) shows good inhibition efficiency. When compare the result of the inhibitors, FD show better inhibition than FB.
2. The maximum inhibition efficiency of FD was found to be 78.43 % in 1M H_2SO_4, whereas FB shows 52.19 % at optimum concentration of inhibitors.
3. Polarization measurements show that the compound under investigation FD and FB retard the both type of reaction (anodic and cathodic). Therefore the inhibitors act as mixed type inhibitor.
4. FT-IR analysis support that the inhibition efficiency due to the formation of physisorped inhibitor film.
5. The morphological investigation also confirms the effective protection of mild steel, through the less damaged and minimum depths found in the inhibited surface.

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