JCSE The Journal of Corrosion Science and Engineering

ISSN 1466-8858 Volume 15, Paper 18 submitted 2 October 2012

The inhibition action of Formazan Derivatives on the corrosion of mild steel in hydrochloric acid medium

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Abstract

The effect of Formazan derivative of *p*-dimethyl amino benzaldehyde (FD) on the corrosion of mild steel in acidic media (1M HCl and 2 M HCl) have been investigated using weight loss measurements, electrochemical impedance spectroscopy, potentiodynamic polarization and FT-IR spectroscopic techniques. Potentiodynamic polarization studies have shown that compound FD suppress both the anodic and cathodic process and they behave as mixed-type inhibitors. Changes in impedance parameters are indicative of the adsorption of these compounds on the metal surface and the inhibition efficiency was found to mainly depend on the nature of the investigated compounds. It was found from the experimental evidences that the adsorption on the mild steel surface follows the Langmuir isotherm model in all acidic media. These studies have also shown that Formazan of *p*-dimethyl amino benzaldehyde is a good inhibitor for mild steel in 1 M HCl and 2 M HCl acid solutions at room temperature in 2 hrs. In 1 M HCl the inhibition efficiency was high when compared to 2 M HCl acid solutions. The surface analysis ~~study~~ also confirms the corrosion inhibition of the mild steel by the inhibitor (FD).

Keywords: Mild steel, Corrosion Inhibitors, Weight loss method, AC impedance; potentiodynamic polarization.

1. Introduction

The utility of Mild steel in a vast area of applications has intensified the research in terms of corrosion resistance of it in various aggressive environments [1-3]. Several researchers have devoted their attention to develop more effective and non-toxic inhibitors to reduce both acid attack and protection aspects in Mild steel. Amongst the various methods available, the use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media [4-9].

The use of organic compounds based corrosion inhibitors against metal dissolution is often associated with chemical and/or physical adsorption, involving a variation in the charge of adsorbed substance and a transfer of charge from one phase to other [9-14]. Special attention was paid to the effect of electron donating on the atom, electron withdrawing or groups responsible for adsorption mainly depends on steric factors, aromaticity, the structural properties of the organic compounds studied such as the presence of π- electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface of mild steel [14-18]. Therefore, in this investigation, the corrosion inhibition of mild steel in 1 M HCl and 2 M HCl solution is studied in the absence and presence of Formazan of *p*-dimethyl amino benzaldehyde (FD) for two hours at room temperature.

2. Experimental

2.1 Material preparation

According to ASTM method as reported already [19], mild steel strips were cut into pieces of 5 cm × 1 cm having the following composition (in percentage) % C=0.017; Si=0.007; Mn=0.196; S=0.014; P=0.009; Ni=0.013; Mo=0.015; Cr=0.043 and Fe=99.686 was used. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with various grades of SiC abrasive papers (from grits 120 to 1200) and degreased using Acetone.

2.2 Preparation of Solutions:

All the solutions were prepared using NICE brand analar grade chemicals in double distilled water and bubbling purified by nitrogen gas for 30 minutes to carry out de-aeration of the electrolytes. 1 M HCl and 2 M HCl solutions were prepared by double distilled water while the inhibitor solution of 0.1% Formazan benzaldehyde was prepared by dissolving 0.1 gms of Formazan of *p*-dimethyl amino benzaldehyde (FD) in 100ml of test solution. Various milli molar (mM) concentration solutions of FD were also prepared. The structure of the inhibitor is shown in **Figure-1**.

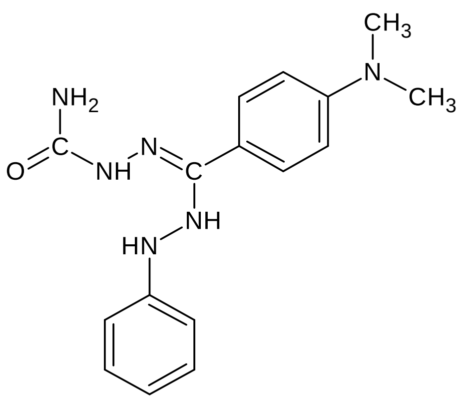


Figure 1- Formazan of p-dimethyl amino benzaldehyde (FD)

2.3 Weight loss measurement:

Mild steel specimens were immersed 1 M HCl and 2 M HCl for 2 h at room temperature (28 ± 2 ºC) for each inhibitor concentration. Then the specimens were removed, rinsed in double distilled water, acetone and the loss in weight of the specimen was determined. From this, the inhibiton efficiency (IE %) was calculated using the formula,

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

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

2.4 Electrochemical Studies:

All the electrochemical measurements were performed using the Electrochemical Workstation (Model No: CHI 600D, CH Instruments, USA) at a constant temperature of 28 ± 2 ºC maintained with 1 M HCl and 2 M HCl as an electrolyte. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively, while the working electrode comprised of mild steel specimen with 1cm^2 exposed area. The tip of the reference electrode was carefully positioned very close to the surface of the working electrode by the use of a fine Luggin capillary in order to minimize the ohmic potential drop. The remaining uncompensated resistance was also reduced by the electrochemical workstation. Potentiodynamic polarization studies were carried out at a scan rate of 0.01mV s^{-1} and at a potential range of -800 to -200 mV for optimum concentration of the inhibitors. The electrochemical impedance studies were carried out in the same setup as that of potentiodynamic polarization studies and the applied ac perturbation signal was about 10 mV within the frequency range 1Hz to 1 KHz. All the electrochemical impedance measurements were carried out at open circuit potential.

The percentage of the inhibition efficiency is calculated from the values of the current density (I_{corr}) with aid of the following formula,

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

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 mild steel specimens were immersed in the blank (1 M HCl and 2 M HCl) containing the inhibitor Formazan of *p*-dimethyl amino benzaldehyde (FD)for 2 h after which they were taken out, washed with distilled water and then the specimens was observed under Scanning Electron Microscope (SEM- HITACHI S3000H, Japan).

2.6 FT-IR Studies:

The corrosion products formed on the steel surface during weight loss measurement was removed by scrapping and was used for recording FT-IR spectra. This study reveals the possibility of the adsorption of the inhibitor on the metal surface. The Fourier transform infrared (FT-IR) spectra of the scraped films were recorded using a (Perkin Elmer-1400) FT-IR spectrophotometer.

3. Results and Discussion

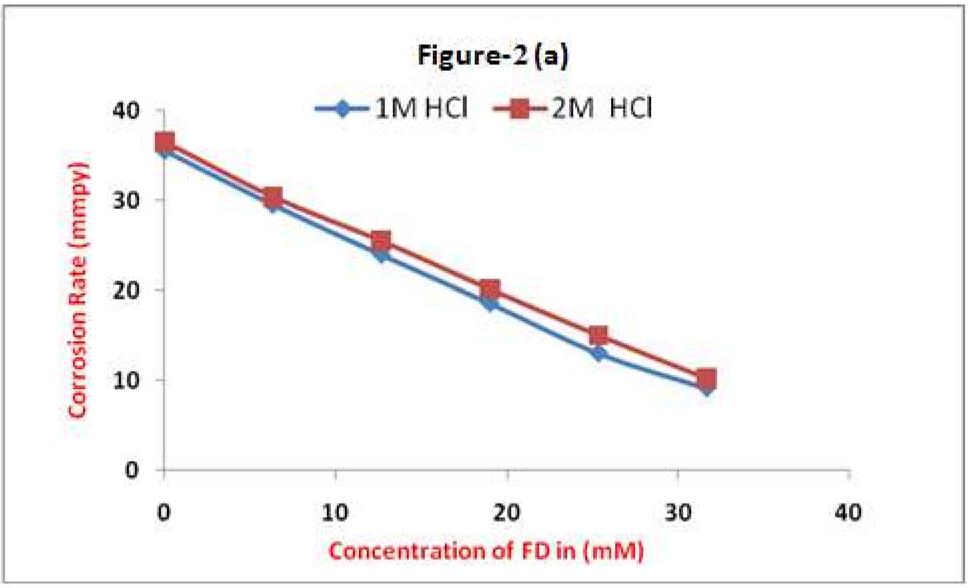
3.1 Weight loss method

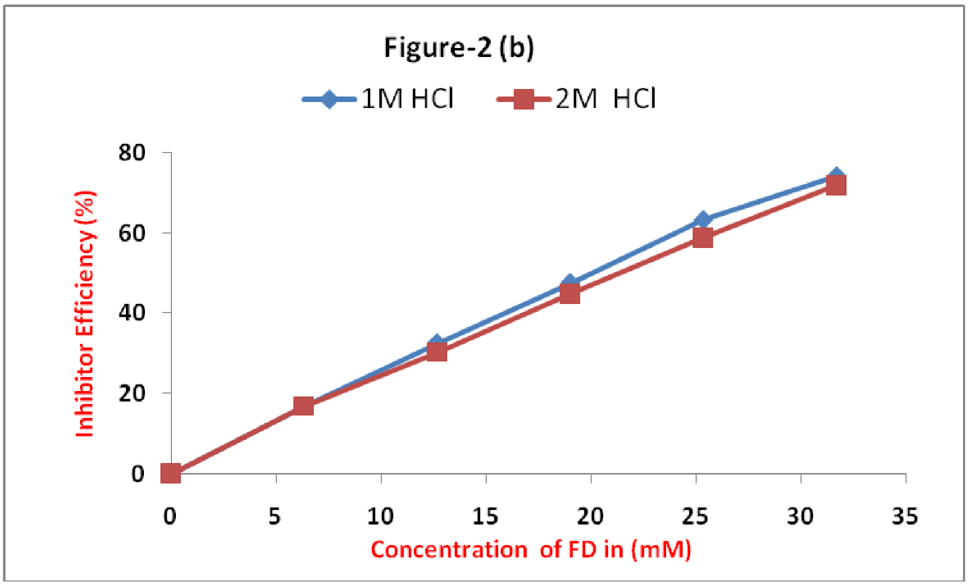
The comparison graph of corrosion behaviour and inhibitor efficiency of mild steel in 1M HCl and 2 M HCl with Formazan of *p*-dimethyl amino benzaldehyde (FD) which was studied by weight loss method at 2 h at room temperatures was given in **Figure 2 (a) & (b)**. From the graph, it was observed that the weight loss of mild steel in the acid decreases with increasing concentration of additives and the values were tabulated in **Table 1** from which it was clear that the corrosion rate has decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. In addition, the maximum corrosion inhibition efficiency of Formazan of *p*-dimethyl amino benzaldehyde (FD) was 74.29 % at 1M HCl and 71.95 % at 2M HCl respectively at 31.70 mM concentration of the inhibitor solution for two hours at room temperature.

Table 1- Corrosion parameters in absence and presence of Formazan of *p*-dimethyl amino benzaldehyde (FD) with 1M HCl and 2M HCl.

Inhibitor	Conc. of inhibitor (mM)	Corrosion Rate (mm/y)		Inhibitor Efficiency (%)	
		1M HCl	2M HCl	1M HCl	2M HCl
Formazan of *p*-dimethyl amino benzaldehyde (FD)	Blank	35.5526	36.5557	---	---
	6.34	29.5343	30.4259	16.92	16.76
	12.68	23.9618	25.5221	32.60	30.18
	19.02	18.6122	20.1725	47.64	44.81
	25.36	13.0396	15.0458	63.32	58.84
	31.70	9.1389	10.2534	74.29	71.95

It was also concluded that the inhibitor was very efficient for mild steel corrosion in 1M HCl and 2M HCl and when comparing with acids, the inhibitor efficiency was maximum in 1M HCl than 2M HCl. **Figure 2(a)** revealed the comparison of corrosion rate (CR) with concentration of Formazan of *p*-dimethyl amino benzaldehyde (FD) (in %) in 1M HCl and 2M HCl solution at two hour at room temperature. Comparison of inhibition efficiency (IE) with concentration of (FD) (in %) in 1M HCl and 2M HCl solution for two hours at room temperature is shown in **Figure 2(b)**.





3.2 Adsorption Isotherm:

Basic information on the interaction between the inhibitor and the mild steel surface can be proved by the adsorption isotherm and in general, inhibitors can function either by physical (electrostatic) adsorption or chemisorption with the metal. To obtain more information about the interaction between the inhibitor molecules and the metal surface, different adsorption isotherms were tested. The fractional surface coverage θ at different concentrations of inhibitors 1M HCl and 2M HCl solutions were determined from the weight loss measurements data [20] using the formula,

$$(\theta) = \frac{\mathrm{Wo} - \mathrm{Wi}}{\mathrm{Wo}} \qquad (3)$$

where, Wo and Wi are the values of weight loss of uninhibited and inhibited specimens, respectively.

$$Kc = \frac{\theta}{1-\theta} \text{ --------------} \qquad (4)$$

where, c is the concentration of the inhibitor, θ is the fractional surface coverage. The Langmuir isotherm, Eq. (4), which is based on the assumption that all adsorption sites are equivalent and that molecular binding, occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant K is related to the free energy of adsorption ΔG_{ads} as,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \text{ ----------------} \qquad (5)$$

Where, $C_{solvent}$ represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm^{-3}, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, Eq. (5), can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c \text{ -------------------------} \qquad (6)$$

so that a linear-relationship can be obtained on plotting c/θ as a function of c, with a slope of unity. The thermodynamic parameters K and ΔG_{ads} for the adsorption of the studied inhibitors on mild steel is obtained by Langmuir's adsorption isotherm are plotted in **Figure 3** and the obtained values are given in **Table 2.** It was found that the linear correlation coefficients clearly prove that the adsorption of the Formazan of *p*-dimethyl amino benzaldehyde (FD) from 1M HCl and 2M HCl solutions on the mild steel corrosion obeys the Langmuir adsorption isotherm. The negative values of ΔG^0_{ads} for the addition of inhibitors indicate that the process of adsorption of studied inhibitors is spontaneous in nature [21]. The free energy of adsorption of (ΔG_{ads}), in 1M HCl was found to be -17.612 $kJmol^{-1}$while for 2M HCl it was found to be -18.687 $kJmol^{-1}$ respectively.

It is well known that the values of ΔG_{ads} in the order of −20 kJ mol^{-1} or lower indicate a physisorption while those about −40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [22].

The calculated adsorption values for all the studied inhibitor show that the adsorption is of physical in nature, and there is no chemisorption between the inhibitor molecule and the metal surface. This indicates that the adsorption of FD at 2 h takes place through electrostatic interaction between the inhibitor molecule and the metal surface. Hence it indicates that the interaction between the inhibitor molecule and metal surface is physisorption.

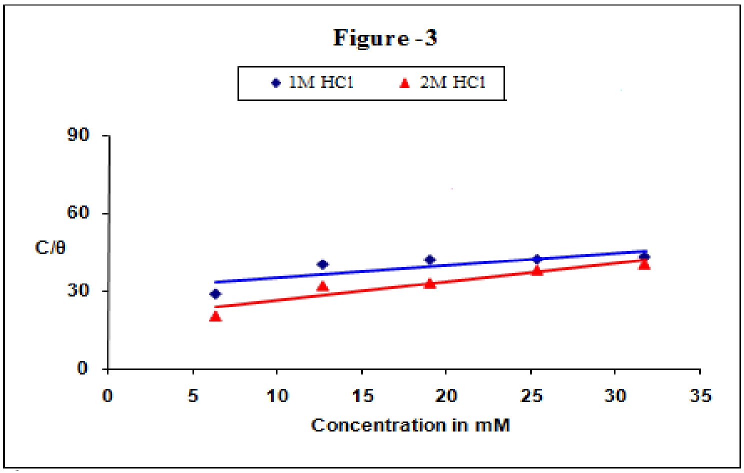


Figure 3 - Langmuir isotherm for adsorption of FD on mild steel surface studied at (1M HCl and 2M HCl).

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ISSN 1466-8858 Volume 15, Paper 18 submitted 2 October 2012

Name of the Acid	Concentration in (mM)	Surface coverage (θ)	ΔGads KJ / mol^{-1}	K x (10^{-2} M^{-1})
1M HCl	31.70	0.7429	-17.612	1.79
2M HCl	31.70	0.7195	-18.687	1.79

Table 2- Thermodynamic parameters for the adsorption of FD in (1M HCl and 2M HCl) on the mild steel.

3.3 Potentiodynamic polarization studies:

Potentiodynamic polarization results obtained for the inhibitory effect of Formazan of *p*-dimethyl amino benzaldehyde (FD) on mild steel corrosion in 1M HCl and 2M HCl are depicted clearly in **Figure 4(a) & (b)**. The various polarization parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (-ba and -bc) were derived from potentiodynamic polarization studies on mild steel in both acid media.

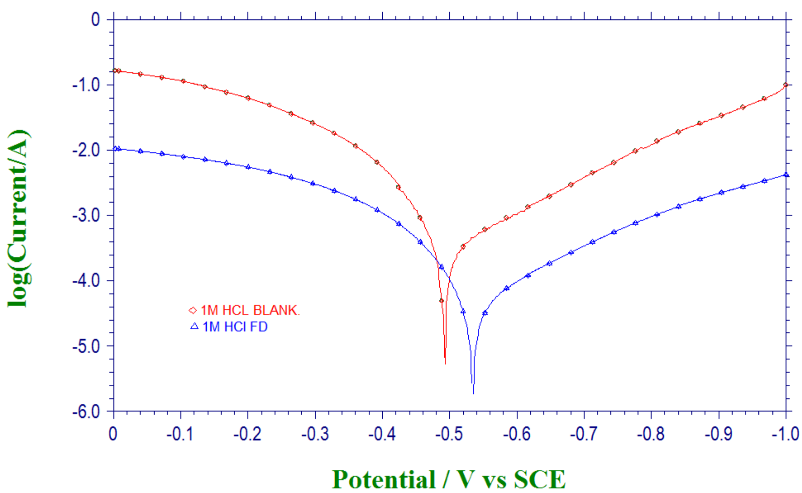

Figure 4 (a) Potentiodynamic polarization curves of mild steel in 1M HCl in the absence and presence of the inhibitor.

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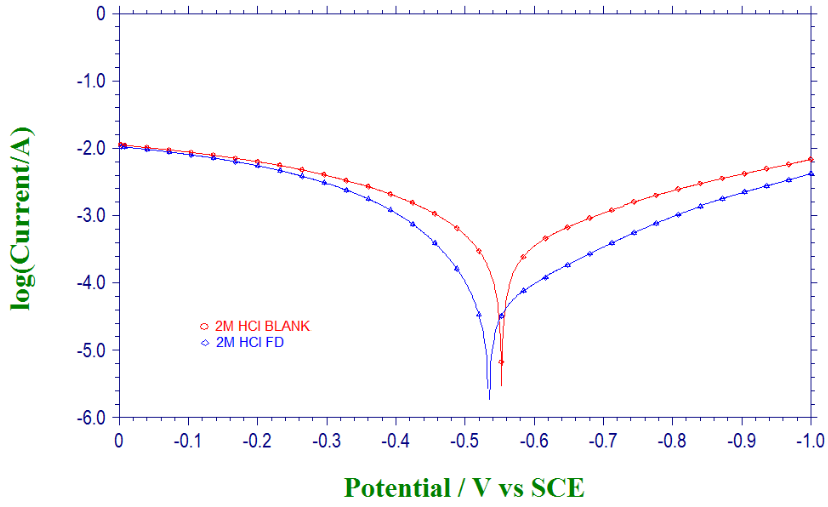

Figure 4 (b) Potentiodynamic polarization curves of mild steel in 2M HCl in the absence and presence of the inhibitor.

It could be observed from the Table that the E_{corr} values have shifted slightly towards negative side in presence of inhibitors suggesting that the inhibitors inhibit the corrosion of mild steel in acids solution by controlling cathodic reactions due to the blocking of active sites on the metal surface. It is evident that inhibitors bring about considerable polarization of the cathode. It was, therefore inferred that the inhibitive action of FD is of mixed type. The corresponding results of potentiodynamic polarization parameters are represented in **Table 3**.

Table 3 - Polarization parameters of mild steel electrode immersed in the absence and presence of the optimum concentration of the inhibitors.

Name of the Acid	Inhibitors	β_c (V dec^{-1})	β_a (V dec^{-1})	E_{Corr} (V)	I_{Corr} x10^{-4} (A)	Corrosion Rate (mmpy)	Inhibition Effeciency (%)
1M HCL	Blank	5.026	10.632	-0.493	3.913	18.810	---
	FD	5.905	9.103	-0.514	0.9472	4.552	75.79
2M HCL	Blank	4.809	6.088	-0.553	3.332	16.010	---
	FD	5.905	9.103	-0.514	0.9472	4.552	71.57

The non-constancy of Tafel slopes for different inhibitor at optimum concentration reveals that the inhibitor action due to the interference in the mechanism of the corrosion processes at cathode. The I_{corr} values have decreased when comparing with different inhibitors at optimum concentration. The inhibition efficiencies ~~were~~ determined from the values of corrosion current density and the inhibition efficiency ~~values~~ were found to show good agreement with those obtained from weight loss measurements. FD shows the maximum inhibition efficiency of 75.79 % in 1M HCl and 71.57 % in 2M HCl. This result suggests that the addition of inhibitors retards the hydrogen evolution reaction [23]. Hence the FD acts as good inhibitor system due to the higher electrostatic attraction of FD and metal surface by the high electron density of the nitrogen (N-H group) atom in the inhibitor molecule.

3.4 Electrochemical impedance spectroscopy (EIS)

The corrosion of mild steel in 1M HCl and 2M HCl solution in the absence and presence of Formazan of *p*-dimethyl amino benzaldehyde (FD) was investigated by EIS measurements at open circuit potential condition. Nyquist plots for mild steel obtained at the interface of electrode and electrolyte in the absence and presence of optimum concentration of inhibitors is given in Figure 5(a) & (b). The Nyquist diagram obtained with 1M HCl and 2M HCl shows only one capacitive loop and the diameter of the semicircle increases on the increasing the electrostatic attraction of the inhibitor suggesting that the formed inhibitive film was strengthened by the addition of such inhibitors. All the obtained plots show only one semicircle and they were fitted using one time constant equivalent model (Randle's model) with capacitance(C) and charge transfer resistance (R_{ct}). The main parameters deduced from the impedance technique are given **Table 4**.

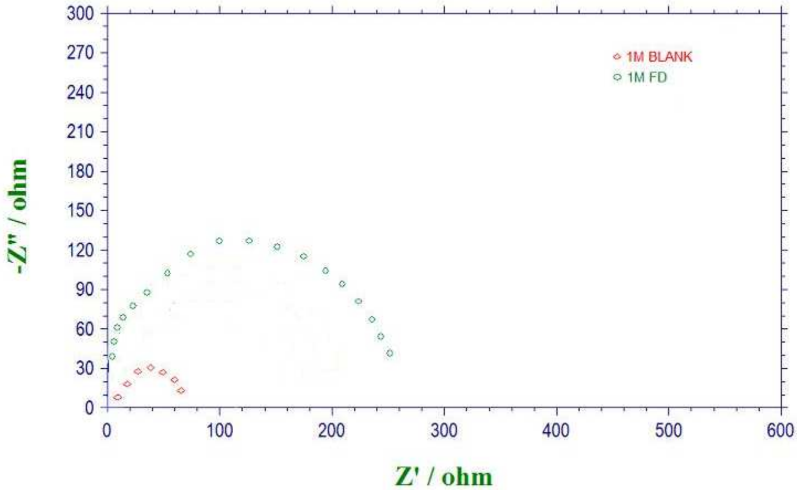

Figure 5 (a) -A.C. Impedance curves of mild steel electrode immersed in 1M HCl in the absence and presence of the inhibitors.

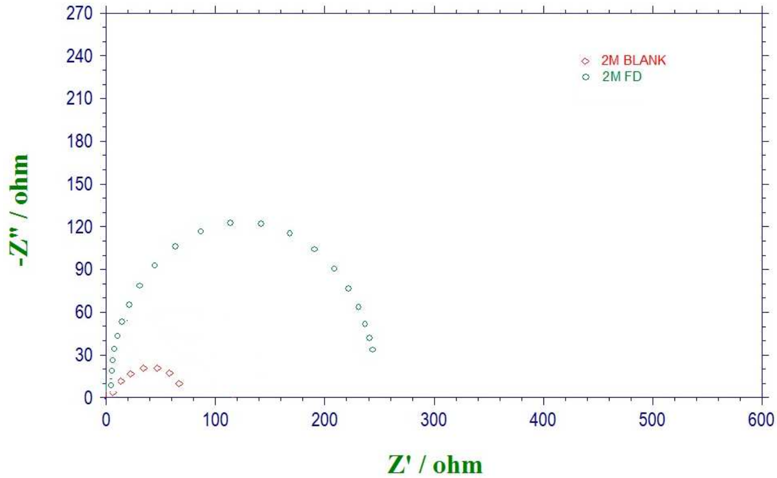

Figure 5 (b) - A.C. Impedance curves of mild steel electrode immersed in 2M HCl in the absence and presence of the inhibitors.

Table 4 - A.C. Impedance parameters of mild steel electrode immersed in 1M HCl in the absence and presence of the inhibitors.

Name of the Acid	Inhibitors	Parameters		
		R_{ct} (ohm cm^2)	C_{dl} ($\mu F\ X10^{-5}$)	Inhibition Efficiency (%)
1M HCl	Blank	72.72	4.118	-
	FD	274.80	1.592	73.53
2M HCl	Blank	70.12	4.618	-
	FD	242.00	1.534	71.02

The lower double layer capacitance (C_{dl}) value for 1M HCl and 2M HCl mediums indicates that the homogeneity of the surface of the mild steel roughened due to corrosion. The double layer capacitance C_{dl} values have decreased on the effective addition of different inhibitors at the optimum concentration. The studied system indicates that the reduction of charge accumulated in the double layer due to formation of adsorbed inhibitor layer [24]. The inhibiting efficiencies show that the inhibitory actions may be due to the adsorption of the inhibitors on mild steel surface [25].

The compound investigated FD has been found to give an excellent inhibition due to the electron density on the nitrogen of the N-H group. This leads to the strong electrostatic attraction of FD on the metal surface thereby resulting in the high inhibition efficiency. Generally on the metal side, electrons control the charge distribution whereas on the solution side is controlled by ions. Since ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer [26]. It can be obtained from **Table 4** that, the capacitance of the electrical double layer (C_{dl}) decreases in the presence of the inhibitors. Decrease in the (C_{dl}) which can result from a decrease in local dielectric constant and / or an increase in the

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ISSN 1466-8858 Volume 15, Paper 18 submitted 2 October 2012

thickness of the electrical double layer, suggests that the inhibitor molecule may act by adsorption at the metal/solution interface [27].

3.5 FT-IR spectral studies:

FT-IR analyses of metal surface can be useful for predicting whether organic inhibitors are adsorbed or not adsorbed on the metal surface [28]. FTIR spectra were used to support the fact that corrosion inhibition of mild steel in acid medium is due to the adsorption of inhibitor molecules on the mild steel surface as well as providing new bonding information on the steel surface after immersion in inhibited HCl solution at optimum concentration. **Figure 6(a)** shows the IR spectrum of the Formazan of p-amino benzaldehyde (FD). In this spectrum the peak appeared at 3367cm^{-1} corresponds to amide N-H stretching, 1510 cm^{-1} corresponds to C=0 group, 1417 cm^{-1} corresponds to C-C stretching and from 1230 cm^{-1} to 1000 cm^{-1} the wavenumber indicates the presence of C-O bonding nature.

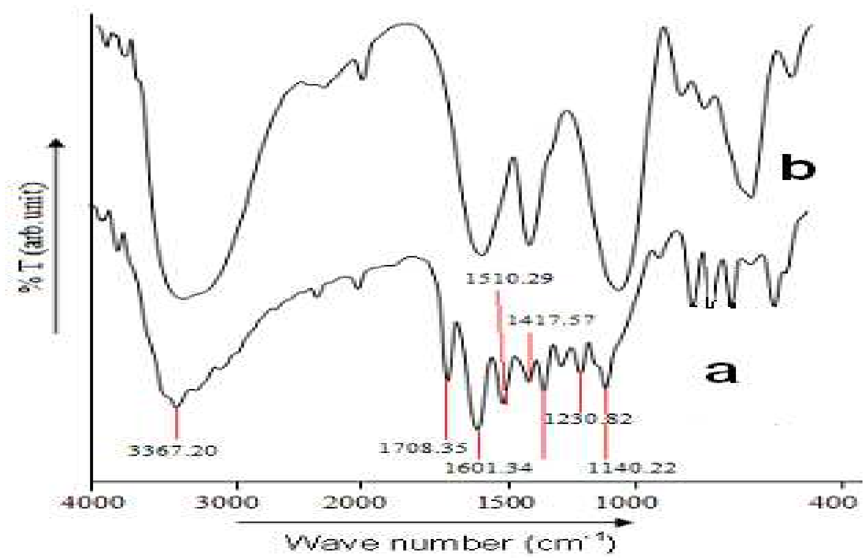

Figure 6 - IR spectrum of the corrosion product showing adsorption in the presence of aqueous extract of Formazan of p-amino benzaldehyde (FD).

Figure 6 (b) is similar to **Figure 6 (a)** which indicates the corrosion products contains Formazan of p-amino benzaldehyde. Therefore from the spectra it is revealed that the inhibition is due to the physical adsorption of corresponding organic molecule. Moreover the spectrum shows there is no any coordinate type of metal inhibitor bond.

3.6 SEM Analysis:

The polished mild steel specimens were immersed in the acid solution (1M HCl and 2M HCl) and in the acids containing inhibitor Formazan of p-amino benzaldehyde (FD) for 2 h, and then the specimens were taken out, dried and observed under Scanning Electron Microscope (SEM). The micrograph are shown in the **Figure 7 & 8** depicts that the polished specimen which was kept in the blank solution of 1M HCl and 2M HCl, associated with polishing scratches. **Figure 9 & 10** shows specimen which was kept in the 31.70 mM concentration of inhibitor solution with 1M HCl and 2M HCl depends upon the concentration of the inhibitor solution suggesting that the presence of adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably. This is attributed to the involvement of the compounds in the interaction with the active sites of metal surface. This results in enhanced surface coverage of the metal so that there is a decrease in the contact between metal and the aggressive medium [29].

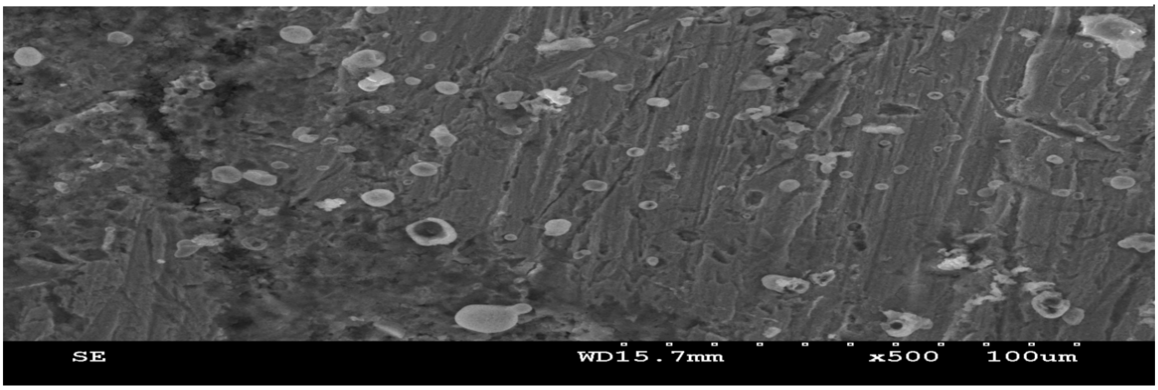

Figure 7- SEM images obtained for the mild steel surfaces immersed for 2 h in 1M HCl (blank acid solution)

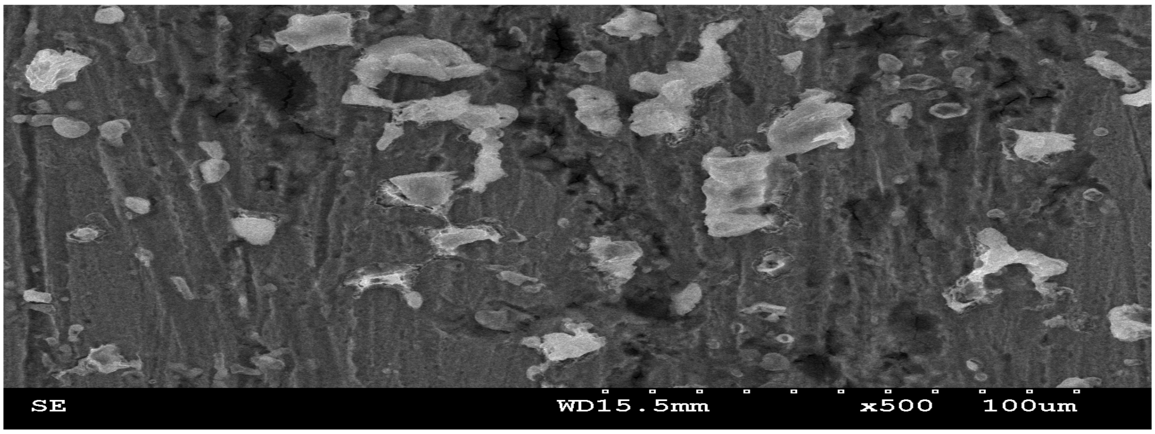

Figure 8 - SEM images obtained for the mild steel surfaces immersed for 2 h in 2M HCl (blank acid solution)

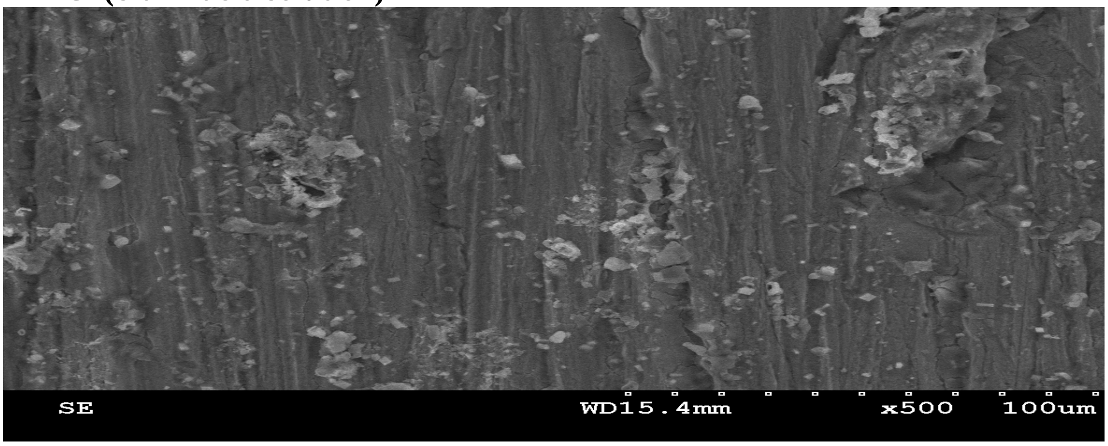

Figure 9 - SEM images obtained for the mild steel surfaces immersed for 2 h in 1M HCl with 31.70 mM inhibitor solution.

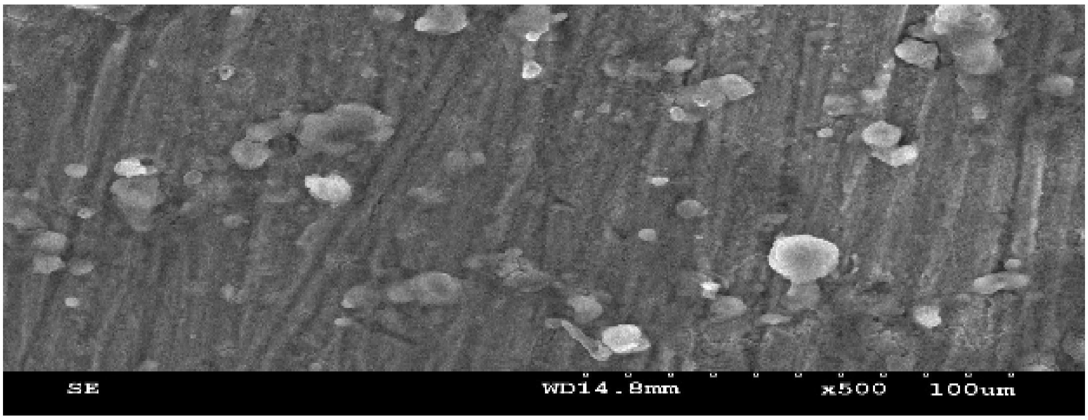

Figure 10 - SEM images obtained for the mild steel surfaces immersed for 2 h in 2M HCl with 31.70 mM inhibitor solution.

Conclusions:

The present study leads to the following conclusions in controlling the corrosion of mild steel by Formazan of p-amino benzaldehyde (FD) in 1M HCl and 2M HCl.

1. Formazan of p-amino benzaldehyde (FD) was found to be an effective inhibitor in the acidic medium giving inhibition efficiency upto 74.29 % in 1M HCl and 71.95 % in 2M HCl respectively.
2. The adsorption of the compound investigated follows the Langmuir isotherm and the adsorption is physical in nature.
3. Polarization measurements demonstrate that the compound under investigation (FD) inhibit both anodic and cathodic reaction and hence it act as mixed type inhibitor.
4. Impendance measurements indicate that, the presence of electron donating group on the inhibitor increase the charge transfer resistance and decreasing the double layer capacitance. The type of the substitutents group and the type of the functional atoms of the inhibitor molecule are found to play an important role in the inhibition process.
5. Results obtained from weight loss measurements and electrochemical measurements are in good agreement.
6. FT-IR analysis confirm that the inhibiton efficiency of the inhibitor in mild steel through electrostatic attraction of inhibitor molecule and the metal surface.
7. The morphological investigation also confirms the effective protection of mild steel, through the less damaged and minimum pits found in the inhibited surface.

Acknowledgement: Helpful discussions with Professor V.Collins Arun Prakash and Professor K.M.Govindaraju from Mahendra Engineering College are gratefully acknowledged and also we thankful to AMET University and Mahendra Engineering College for providing Lab Facilities to bring out this work.

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