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Inhibitive effect of 8-hydroxy Quinoline on the corrosion of mild steel in 1M HCl

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ABSTRACT

The inhibitive action 8-Hydroxy quinoline on corrosion of mild steel in 1 M HCl was investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization technique. The results showed that the 8-hydroxy Quinoline inhibited mild steel corrosion and inhibition efficiency increased with increase in concentration of inhibitor. The adsorption is spontaneous and followed Langmuir's adsorption isotherm. Polarization study indicated that the inhibitor acted as mixed-type. The protective film formed on surface is confirmed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDX).Result obtained from weight loss technique are in good agreement with electrochemical and surface analytical results.

Key words: Mild Steel, Corrosion, HCl, SEM, EDX.

I. INTRODUCTION

Corrosion is the deterioration of a metal as a result of chemical reaction between it and the surrounding. Corrosion causes heavy economic losses. In India with GDP of amount 2 trillion, loses as much as 100 billion dollar every year on account of corrosion. Mild steel is widely used as construction material in most of major industries due to its excellent mechanical properties and low cost. The major problem of mild steel is its dissolution in acidic medium [1–6].Acids is widely used for acid pickling, descaling, oil well acidizing and other applications. Due to their high corrosive nature acid may cause damage to the system components. Thus it is necessary to develop some effective corrosion inhibitors .The use of organic inhibitor is the most effective and most economic method for protection of metal from corrosion. Generally, organic inhibitors inhibit metallic corrosion by adsorbing on the surface and thereby forming a protective barrier [7-14].The adsorption of an inhibitor is influenced by various factors such as electron density of donor site, presence of functional groups, electronic structure of inhibiting molecule, molecular area and molecular weight of inhibitor. Organic compounds containing heteroatoms including nitrogen, sulphur, and/or oxygen with polar functional groups and conjugated double bonds have been reported as effective corrosion inhibitor [14-20].

The aim of present work is to study the inhibition effect of 8-hydroxy Quinoline on mild steel in presence of 1 M HCl by using various techniques such as weight loss measurement, open circuit potential (OCP), and potentiodynamic polarization. Surface analytical techniques such as SEM AND EDX were also used to characterize corrosion product formed.

II. EXPERIMENTAL PROCEDURE

2.1. Material and sample preparation

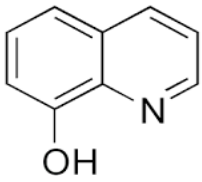
Mild steel of commercial grade in sheet form having composition as follows: C-0.16%, Si-0.10%, Mn –

0.40%, P - 0.012%, S - 0.02%, and Iron- balance, were used in the present investigation. For electrochemical polarization, samples of 1cm x 3cm were sheared from the commercial grade sheets. The surface of these samples was successively polished by using the Emery papers of grades 1 / 0, 2 / 0, 3 / 0, and 4 / 0 obtained from Signor, Switzerland to obtain a scratch free mirror finish surface. The polished samples were washed with detergent solution, rinsed with distilled water and finally degreased with acetone. The specimens were dried and stored in a desiccators containing silica gel as a dehydrating agent. The test solution of 1M HCl was prepared by diluting analytical grade HCl (MERCK, 37%) in double distilled water.

2.2. Synthesis of inhibitor

The 8-hydroxy quinoline used in present study was synthesized according to a previously described procedure [21].The completion of the reaction was verified by the disappearance of starting material on TLC plate. The IUPAC name, chemical structure and analytical data for synthesized compound given below.

Table 1. IUPAC name, molecular structure, melting point and analytical data of studied inhibitor.

Inhibitor	Molecular Structure	Analytical data
8-Hydroxy quinoline		**MP** – 74^{0}C - 76^{0}C. **FT-IR-υmax/cm^3.** 3500,1680,1400,1550, 1360,1150 1080.

2.3weight loss measurements

Weight loss measurements were carried out in a glass vessel with 100 ml of 1M HCl solution with and without concentration of inhibitor ranges from 100-500 ppm. The immersion time for weight loss was 24 h at 27 ^{0}C.After dilution the mild steel specimens were withdrawn, rinsed with double distilled water, washed with acetone, dried and weight. The experiments were carried out in duplicate and the average value of weight loss was noted.

2.4 electrochemical measurements

The variation of corrosion potential of mild steel in 1 M HCl was measured against saturated calomel electrode in absence and presence of various concentrations of inhibitors. The time dependence of OCP for different experiments was recorded for 1 hours exposure period .Then the sample was used for potentiodynamic polarization experiments .The potential was swept between -0.5V to 0.5 V at the scan rate 5mV/second. Electrochemical Measurement System, DC 105,containing software of DC corrosion techniques from M/S Gamry Instruments Inc., 734, Louis Drive, Warminster, PA-18974, USA has been used for performing corrosion potential and polarization experiments. For electrochemical polarization studies (corrosion potential, and potentiodynamic polarization) flag shaped specimens with sufficiently long tail were cut from the stainless steel sheet. These samples were polished as described earlier leaving a working area of 1cm^2 on both sides of the flag and a small portion at the tip for providing electrical contact. Rest of the surface was isolated from the corroding solution by coating with enamel lacquer including side edges. The test specimen was connected to the working electrode holder with the help of a screw. About 50ml of the corrosive medium was taken in a mini corrosion testing electrochemical cell. This volume was appropriate to permit desired immersion of electrodes. The electrochemical investigation was carried out using microprocessor based corrosion measurement system (CMS-105, Gamry Instruments Inc., USA.). The three-electrode system cell i.e.

working electrode, reference electrode (Saturated Calomel Electrode), and counter electrode (Graphite rod), was used throughout the electrochemical measurements. Open circuit potential measurements and potentiodynamic polarization experiments were carried out at the concentration of 100, 200,300,400 and 500 ppm of the inhibitor.

2.5 SEM AND EDX STUDIES

The composition and surface morphology of corrosion product on mild steel sample after immersion for 24 hours in 1 M HCl in the absence and presence of 500 ppm of 8-hydroxy Quinoline was studied using a scanning electron microscope and EDX examination using energy dispersive spectrometer. The accelerating voltage for SEM picture was 20.0 kv.

III. RESULTS AND DISCUSSION

3.1. Weight loss measurement

Weight loss data of mild steel in 1M HCl in the absence and presence of various concentrations of inhibitor were obtained and are given in Table 1. Inhibition efficiencies (%IE) were calculated according to [46]:

$$(\%\ IE) = \frac{(W_0 - W_{corr})}{W_0} \times 100 \quad \text{-----} (1)$$

Where, Wcorr and W_0 are the weight loss of mild steel in the presence and absence inhibitors, respectively.

The results show that the inhibition efficiencies increase with increasing inhibitor concentration. The results obtained from the weight loss measurements are in good agreement with those obtained from the electrochemical methods.

Table 2. The weight loss parameter obtained for mild steel in 1 M HCl containing different concentrations of 8-hydroxy quinoline.

Inhibitor	Concentration (ppm)	Weight loss (mg)	Surface coverage	Inhibition efficiency (%E)
Blank	-	**431**	-	-
8-Hydroxy quinoline	100	280	0.350	35.03
	200	185	0.570	57.07
	300	146	0.661	66.12
	400	99	0.770	77.03
	500	77	0.821	82.13

3.2 Adsorption isotherm

Fundamental information on the adsorption of inhibitor on metal surface can be provided by adsorption isotherm. The weight loss temperature results were used to calculate the adsorption isotherm parameters. The most frequently used isotherms are Langmuir, Frumkin, Temkin, Florry-Huggins and thermodynamic /kinetic model of El-Awady isotherm. It is found that the adsorption of studied inhibitor on mild surface obeys Langmuir adsorption isotherm. Langmuir adsorption isotherm is given by following equation:

$$C/\theta = 1/K_{ads} \quad \text{---------} (2)$$

Where θ is the degree of surface coverage, C is the molar inhibitor concentration in the bulk solution and K_{ads} is the equilibrium constant of the process of adsorption. Plot of C/θ versus C of 8- hydroxyl quinoline presented in fig.(4).The obtained plots are almost linear with correlation coefficient (R^2=0.999) for Langmuir adsorption isotherm .K_{ads} can be

calculated from intercepts of the straight lines in figure 1

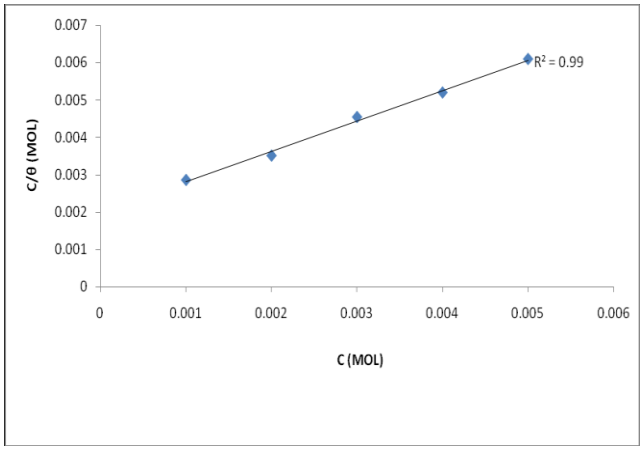


Figure 1. Langmuir adsorption isotherm for mild steel in 1 M HCl at various temperatures.

The standard free energy of adsorption (ΔG_{ads}) is calculated from equation [22].

$K_{ads} = (1/55.5) \exp(-\Delta G_{ads}/RT)$ ------- (3)

Where the constant 55.5 is the molar concentration of water in solution in mol L^{-1} .R is universal gas constant and T is absolute temperature. The negative values of ΔG_{ads} ensured the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface [23].Generally ,values of ΔG_{ads}, around -20 KJ mol^{-1}or lower are consistent with the electrostatic interaction between the charged molecules and charge metal, such as physisorption. When it is around -40 KJ mol^{-1} or higher values it involves charge sharing or charge transfer from organic molecules to the metal surface to form coordinate type of bond that is chemisorptions [24].In the present work the calculated value of ΔG_{ads} is 25.53kJ/mol, which indicate adsorption of inhibitor on mild steel surface involves both physical and chemical adsorption.

3.3. Open Circuit Potential Measurement (OCP)

Inherent reactivity of the metallic materials in a particular environment is determined from its open circuit potential (corrosion potential). The influence of the corrosive and inhibitive species present in the electrolyte may be predicted by analysing the nature of the OCP curve. The variation of open circuit potential of Mild Steel exposed to 1M HCl solution containing inhibitor i.e.8-hydroxy quinoline in the concentration range 100-500ppm is shown in Figure 2 .The steady state potential is obtained after 3600 seconds of the exposure period. In the presence of different concentration of inhibitors, OCP is shifted towards the positive potential direction in comparison to without inhibitor and get stabilized thus indicating the adsorption of the inhibitors on the metal surface. The magnitude of shift of polarization curve towards positive direction was found proportional to the concentration of the inhibitor.

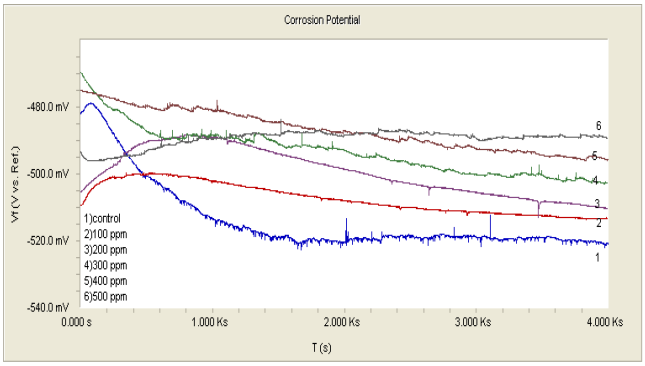


Figure 2. Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of 8-hydroxy quinoline.

3.4. Potentiodynamic polarization curves

Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of 8-hydroxy Quinoline are illustrated in fig.3.The presence of 8-hydroxy quinoline caused a clear decrease in both anodic and cathodic current densities with increase in inhibitor concentration, probably due to the adsorption of at the active sites of the electrode surface, retarding both metallic dissolution and hydrogen evolution reaction [25].The

electrochemical kinetic parameters,i.e.,corrosion current densities(i_{corr}),
corrosion potential (E_{corr}), cathodic Tafel slop (b_c) anodic Tafel slope (b_a) are presented in table (6).

Here, the IE% is defined by following equation:

$$IE\% = = \frac{i_o - i_{corr}}{i_o} \quad \text{---------- (4)}$$

Where i_{corr} and i_{corr} are the corrosion current density values without and with inhibitor respectively. The corrosion current density decreased with increasing the concentration of the inhibitor, which indicates that the presence of 8-hydroxy quinoline retard the dissolution of mild steel in 1 M HCl solution and degree of inhibition depends on the concentration of inhibitor. It can also be observed that the corrosion

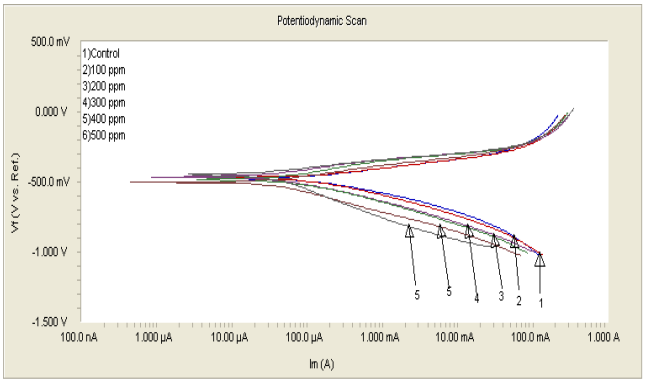


Figure 3. Potentiodynamic Polarization curves of mild steel in 1 m HCl in the absence and presence of different concentration of 8-hydroxy quinoline

Potential values remained almost constant in presence of inhibitor, suggesting that 8-hydroxy quinoline acted as mixed-type inhibitor. Furthermore ,it is observable that the shape of polarization curves are similar in the absence and presence of 8-hydroxy quinoline, suggesting that the inhibitor inhibits mild steel corrosion by simply adsorbing on mild steel surface without changing the mechanism of mild steel dissolution[26].

Table 3. Polarization data of mild steel in 1M HCl solution in absence and presence of different concentration of 8-hydroxy quinoline.

Acid Medium	Concentration (ppm)	$-E_{corr}$ (mv)	I_{corr} (µA/cm²)	β_a (v/dec)	β_c (v/dec)	IE %
1 M HCl	-	475.0	133.0	76.90 e^{-3}	134.4 e^{-3}	
	100	472.0	85.10	65.70 e^{-3}	127.0 e^{-3}	53.84
	200	481.0	54.10	90.40 e^{-3}	126.0 e^{-3}	68.15
	300	503.0	40.20	85.30 e^{-3}	140.1 e^{-3}	72.77
	400	508.0	35.20	86.90 e^{-3}	146.2 e^{-3}	79.65
	500	463.0	26.64	85.30 e^{-3}	125.20 e^{-3}	85.42

IV. SURFACE STUDIES

4.1.SEM studies

In order to evaluate the condition of metal surface in contact with acid solution in absence and presence of inhibitor, a surface analysis is carried out using scanning electron microscope and Energy dispersive X- ray spectrometer.

The surface morphology of the mild steel specimens immersed in1M HCl for 24 h without and with optimum concentration of the 8-hydroxy Quinoline is shown in following figure. A micrograph of the polished mild steel surface before immersion in 1M HCI is shown in figure 4(a).The micrograph shows the surface was smooth and without pits.Fig.4(b) represents SEM micrograph of mild steel surface immersed in 1M HCl without 8-hydroy Quinoline which appears to be highly corroded and damaged due to free acid attack.Fig.4(c) represents SEM micrograph of mild steel in the presence of optimum concentration of the 8-hydroxy Quinoline in acid solution causes significant improvement in the surface morphology. Thus it can be concluded that8- hydroxyl Quinoline forms protective surface film on the metal surface through adsorption which protect the metal from acid solution.

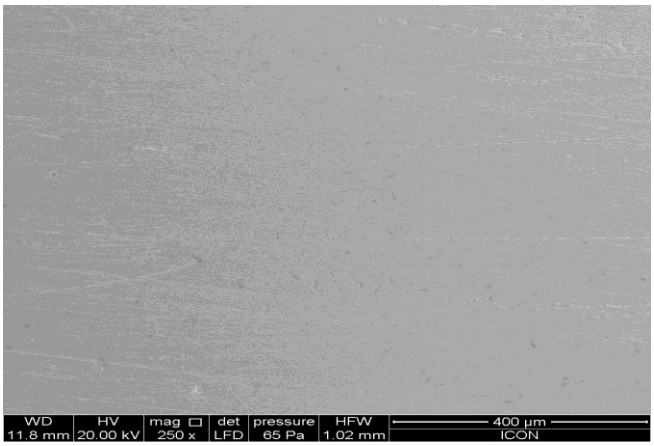


Figure 4.(a). SEM micro graphs of mild surface before immersion in 1 M HCl

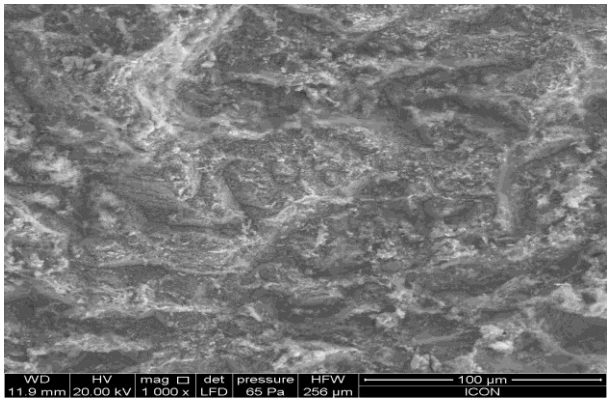


Figure 4.(b). SEM micro graphs of mild surface after one day immersion in 1 M HCl and

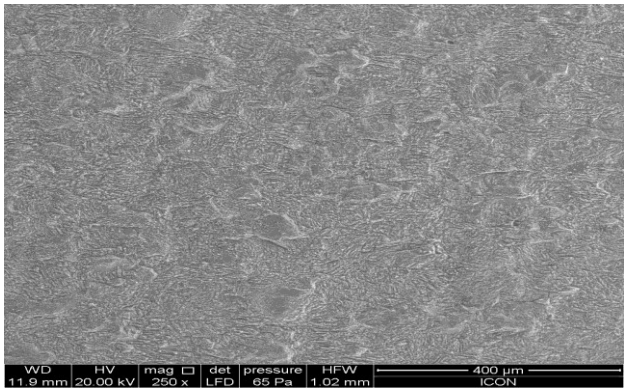


Figure 4(c). SEM micro graphs of mild surface after one day of immersion in 1 M HCl+500 ppm of 8-nitro quinoline.

4.2 EDX studies

Figure 5 (a) shows spectra of mild steel specimen before immersion in 1 M HCl which shows a signal for Fe and oxygen. Figure 5(b) shows EDX spectra of mild steel specimen immersed in 1 M HCl in the absence of 8-hydroxy Quinoline which is characterized by signal corresponding only for Fe. However, Figure 5(c) shows EDX spectrum in the presence of 8-hydroxy Quinoline with additional signal for nitrogen (N) which attributed due to adsorption of 8-hydroxy Quinoline on mild steel surface.

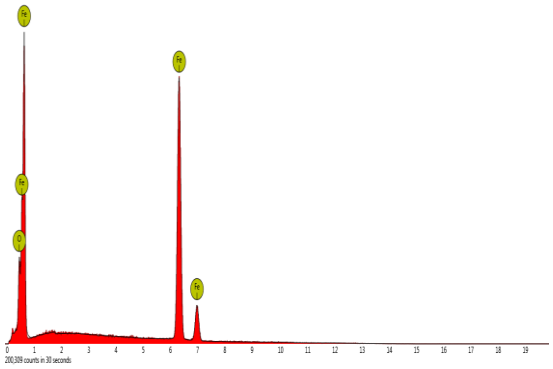


Figure 5(a). EDX spectra of polished mild steel surface

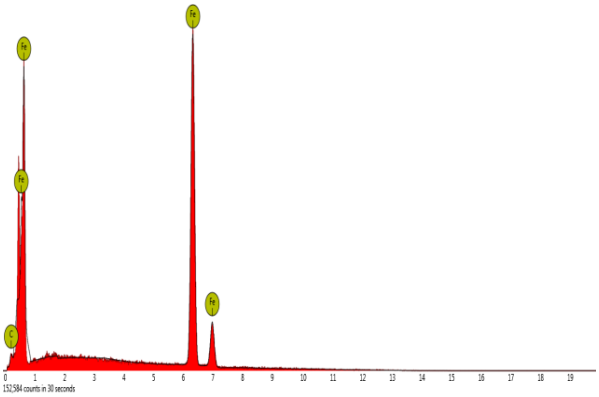


Figure 5 (b). EDX spectra of mild steel after one day immersion in 1 M HCl

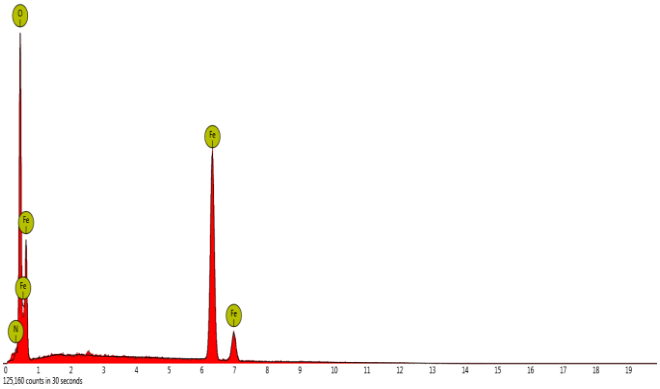


Figure 5(c). EDX spectra of mild steel after one day of immersion in 1 M HCl +500 ppm of 8-hydoxy Quinoline.

V. MECHANISM OF INHIBITION

Corrosion inhibition of mild steel in acid solution can be described on the basis of adsorption phenomenon.8-hydroxy Quinoline contains various functional groups such as –OH,C=C and C=N through which it can adsorb on metal surface. The adsorption can be chemisorption or physisorption and some time both processes can take place. 8-hydroxy Quinoline can absorb onto metal surface by three different ways.

1. Sharing of electrons of nitrogen and oxygen with iron surface.
2. Interaction between pi electrons of benzene ring of 8-hydroxy Quinoline with the metal surface.
3. It is also possible that the N atom of 8-hydroxy Quinoline can be easily protonated in acid medium. This protonated N atom can show electrostatic interaction with negatively charged metal surface.

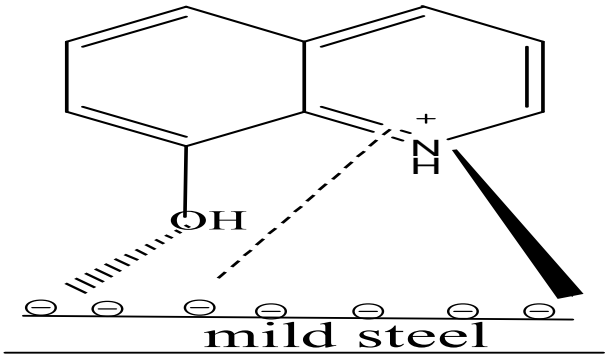


Figure 6. Pictorial representation of adsorption behaviour of the 8-hydroxy quinolone on mild steel in 1M HCl

VI. CONCLUSION

On the basis of the above results the following concision can be drawn.

1. 8-hydroxy Quinoline acted as an effective corrosion inhibitor for mild steel in 1M HCl solution.
2. The corrosion process was inhibited by adsorption of inhibitor molecule on the mild steel surface.
3. The inhibition efficiency increased with increase in the concentration of the inhibitor.

4. Adsorption study showed that the inhibition mechanism obeyed Langmuir adsorption isotherm.
5. The negative value of free enegy of adsorption indicated strong and spontaneous adsorption of inhibitor on mild steel surface.
6. Potentiodynamic polarization studies shown that inhibitor retards both the anodic and cathodic partial reactions. Thus 8-hydroxy Quinoline acted as mixed type inhibitor.
7. SEM/EDX studies revealed that corrosion inhibition is due to the adsorption of 8-hydroxy Quinoline at mild steel/acid solution interface.

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