



# INHIBITION OF MILD STEEL CORROSION BY 1-(8-HYDROXYQUINOLIN-2-YLMETHYL)UREA

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**Keywords:** Corrosion inhibitors, EIS, mild steel, organic inhibitors, 1-(8-hydroxyquinolin-2-ylmethyl)urea, SEM, EDAX and biocidal activities.

The corrosion behavior of mild steel in the presence of organic inhibitor namely 1-(8-hydroxyquinolin-2-ylmethyl)urea (HUF) has been investigated in aqueous solution containing 60 ppm of Cl<sup>-</sup>. Weight loss measurements and electrochemical impedance spectroscopy (EIS) were applied to analyze the effect of the organic compound on the corrosion inhibition of mild steel. The organic inhibitor that totally covered the mild steel surface was identified, exhibiting strong corrosion inhibition. Fluorescence spectral analysis was used to detect the presence of iron-inhibitor complex. The surface morphology has been analyzed by FTIR, UV-Visible spectroscopy, Scanning Electron Microscope (SEM) and EDAX. The inhibitor 1-(8-hydroxyquinolin-2-ylmethyl)urea has the ability to prevent the growth of certain microorganisms.

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## Experimental Techniques

Mild steel specimen; (0.0267% S, 0.061% P, 0.5 % Mn, 0.1 % C and the rest iron ) of dimensions 1.0 cm ×4.0×0.2 cm were polished to mirrors finish and degreased with acetone.

## Introduction

Corrosion is the gradual destruction of material, usually metal by chemical reaction with its environment. Mild steel under water containing chloride is eroded gradually by means of chemical reactions.<sup>1-3</sup> The corrosion is severe due to the presence of chloride ions and dissolved oxygen. Mild steel is widely used in infrastructure in marine environments.<sup>4</sup> Mild steel is widely used in industries. It comes in contact with chloride ions very frequently under numerous conditions and circumstances in industries. Various organic compounds have been reported as inhibitors for controlling corrosion of mild steel in water containing chloride ions. But the inhibitive efficiencies of organic compounds when used alone were found to be very less.<sup>5</sup> In various industries water being in great demand and the largest source of water is sea water which is at a peak in corrosiveness due to the presence of sodium chloride. Moreover mild steel the cheapest as well as highly applicable material in industries gets attacked by chloride ions. So it becomes a basic need to investigate various corrosion inhibitors for mild steel in sodium chloride solution. Most inhibitors are organic compounds containing polar groups strongly adsorbed on the metal surface.<sup>6,7</sup>

The aim of the present study is to evaluate corrosion inhibitive performance of 1-(8-hydroxy quinolin-2-yl-methyl) urea to mild steel immersed in aqueous solution containing 60 ppm Cl<sup>-</sup>. The corrosion inhibition efficiency was evaluated using weight loss method and electrochemical impedance spectroscopy. The protective film formed on the metal surface characterized with the help of surface analytical techniques such as fluorescence, FTIR and UV-Visible spectroscopy. The surface morphology has been analyzed by SEM and EDAX. The biocidal activity was measured against certain organisms.

## Weight loss method

Mild steel specimens triplicate were immersed in 100 ml of the solution containing 60ppm of Cl<sup>-</sup> in the presence and absence of 1-(8-hydroxy quinolin-2-yl-methyl) urea for one day. The weight of the specimens before and after immersion was determined using a shimadzu, model AY62. The corrosion products were cleaned with Clark's solution.<sup>8</sup> The inhibition efficiency (*IE*) was then calculated using the equation:

$$IE = 100[1-(w_2-w_1)]\% \quad (1)$$

where  $w_1$  is the weight loss value in the absence of inhibitor and  $w_2$  is the weight loss value in the presence of inhibitor.

## AC impedance spectra

Impedance studies were carried out in a CHI electrochemical workstation with impedance model 643, Austin, USA. A three electrode cell assembly was used. The working electrode was mild steel. The exposed surface area was 1 cm<sup>2</sup>. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The real part ( $Z'$ ) and the imaginary part ( $Z''$ ) of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initial  $E_{(v)} = 0$  V, high frequency limit was  $1 \times 10^5$  Hz, low frequency limit was 1 Hz, amplitude = 0.005 V and quiet time  $t_q = 2$  s. The values of charge transfer resistance  $R_t$  and the double layer capacitance  $C_{dl}$  were calculated.

$$C_{dl} = \frac{1}{2} \pi R_t f_{max}$$

where  $f_{max}$  is maximum frequency.

### Surface Characterization studies

The mild steel specimens were immersed in various test solution for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by various surface analysis techniques.

#### Surface analysis by UV-Visible spectroscopy

UV-Visible spectra were recorded in a Cary Eclipse Varian (Model U.3400) spectrophotometer.

#### Surface analysis by fluorescence spectroscopy

Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco-F-6300 spectra fluorometer.

#### Surface analysis by FTIR spectroscopy

The spectra were recorded in a Bruker (Model Tensor 27) spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets and the FTIR spectra were recorded.

#### SEM Analysis

SEM (Tescan, Vega 3, USA) provides a pictorial representation in the surface to understand the nature of the surface film in the absence and presence of inhibitors and extent of corrosion of mild steel. The SEM micrographs of the surface are examined.

#### Energy Dispersive Analysis of X-rays (EDAXs)

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, dried and observed in an Energy Dispersive Analysis of X-rays (EDAXs) to examine the elements present on the metal surface. The elements present on the metal surface were examined using Bruker computer controlled Energy Dispersive Analysis of X-rays (Bruker, Nano, GMBH, Germany).

#### Bacterial Enumeration

Bacterial cell are count based on their colony forming unit (CFU) by standard plate count. The protocols are as follows. Label the plate  $10^{-2}$ ,  $10^{-4}$ ,  $10^{-6}$  and  $10^{-8}$  at the bottom of plate and one plate as a blank or control. Using aseptic technique transfer 1 ml of four different cultures to 99 ml of sterile saline blank. A test tube labelled  $10^{-2}$  and the dilution is proceeded by taking 1 ml from  $10^{-2}$  test tube to the next 99 ml sterile saline blank labeled as to the next 99 ml sterile saline blank labeled as  $10^{-4}$  and proceed until  $10^{-8}$ . Shake all the test tubes for equal distribution of bacteria. Transfer 1ml of the sample into each of the labelled plates  $10^{-2}$  to  $10^{-8}$  correspondingly. Containing agar medium all the plates are immersed and incubate at  $37^{\circ}\text{C}$  for 24 hours. After the

incubation, select the plate containing 30 to 300 colonies and count the colonies. The number of CFU are calculated as  $\text{CFUs/dilution} \times \text{amount plated} = \text{No. of bacterial cell/ml}$ .

## Results and Discussion

### Weight loss method

The corrosion rates (CR) of mild steel immersed in aqueous solution containing 60 ppm  $\text{Cl}^-$  and also inhibition efficiencies (IE) in the absence and presence of inhibitor HUF obtained by weight loss method are given in table-1. It is observed that 250 ppm of HUF offer 75% of inhibition efficiencies.

**Table 1.** Corrosion rates (CR) of mild steel immersed in an aqueous solution containing 60 ppm  $\text{Cl}^-$  in the presence and absence of inhibitor systems at various concentration and the inhibition efficiency (IE %) obtained by weight loss method.

Cl <sup>-</sup> , ppm	HUF, ppm	CR, mdd	IE, %
60	0	34.55	-
60	50	14.51	58
60	100	12.43	64
60	150	10.36	70
60	200	9.67	72
60	250	8.63	75

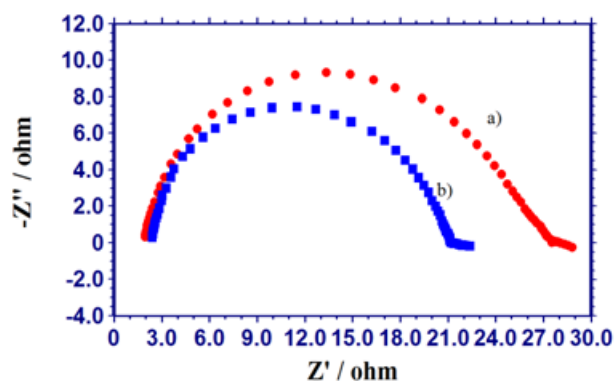
### AC impedance spectra

AC impedance spectra [electrochemical impedance spectra] have been used to confirm the formation of protective film on the metal surface.<sup>9-12</sup> The AC impedance spectra of mild steel immersed in aqueous solution containing 60 ppm of  $\text{Cl}^-$  in the absence and presence of inhibitors are shown in Fig. 1 (Nyquist plots) and Fig. 2 (Bode plots). The impedance parameters namely charge transfer resistance ( $R_t$ ) double layer capacitance ( $C_{dl}$ ) and impedance  $\text{lg}(z/\text{ohm})$  are given in Table 2. If a protective film is formed on the metal surface,  $R_t$  value increases and the  $C_{dl}$  value decreases.

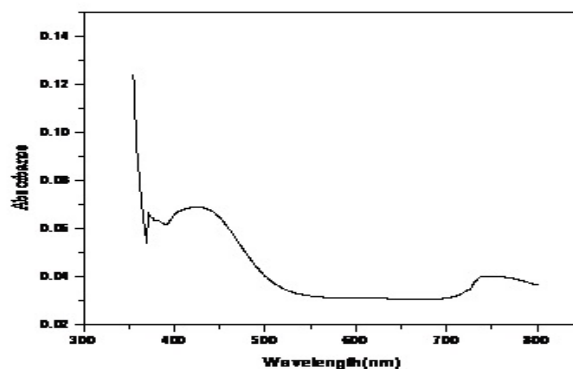
**Table 2.** The AC impedance spectra of mild steel immersed in aqueous solution containing 60 ppm of  $\text{Cl}^-$  in the absence and presence of inhibitor system

Systems	$R_t$ , $\Omega\text{cm}^2$	$C_{dl}$ , $\text{F cm}^{-2}$	$\log(Z \text{ ohm}^{-1})$
60ppm $\text{Cl}^-$	20.19	$5.235 \times 10^{-5}$	0.973
60ppm $\text{Cl}^-$ + 250ppm HUF	27.00	$3.901 \times 10^{-5}$	1.170

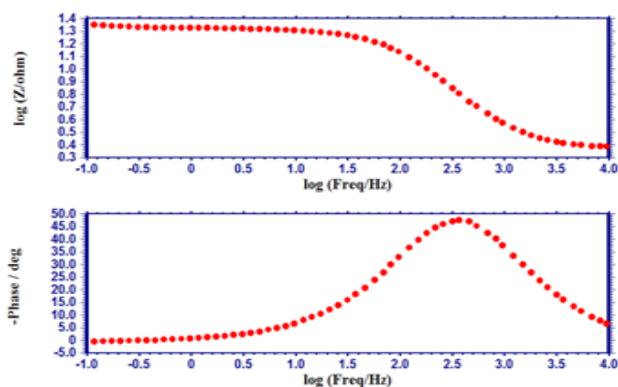
When mild steel is immersed in aqueous solution containing 60ppm of  $\text{Cl}^-$ ,  $R_t$  value is  $20.19 \Omega \text{ cm}^2$  and  $C_{dl}$  value is  $5.235 \times 10^{-5} \text{ F cm}^{-2}$ . When HUF is added to the aqueous solution containing 60ppm of  $\text{Cl}^-$   $R_t$  value increases from  $20.19 \Omega \text{ cm}^2$  to  $27.00 \Omega \text{ cm}^2$  and the  $C_{dl}$  value decreases from  $5.235 \times 10^{-5} \text{ F cm}^{-2}$  to  $3.901 \times 10^{-5} \text{ F cm}^{-2}$ . The impedance value increases from 0.973 to 1.170. This account for the high inhibition efficiency of HUF system and a protective film is formed on the metal surface. This is also supported by the fact that for the inhibitor system the phase angle increases from  $47$  to  $50.60^\circ$  (Fig. 2).



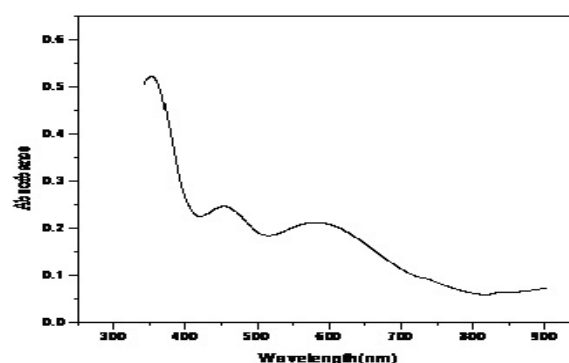
**Figure 1.** AC impedance spectra (Nyquist plots) of mild steel immersed in various test solutions: a) aqueous solution containing 60 ppm of  $\text{Cl}^-$ ; b) aqueous solution containing 60 ppm  $\text{Cl}^-$  + 250 ppm HUF.



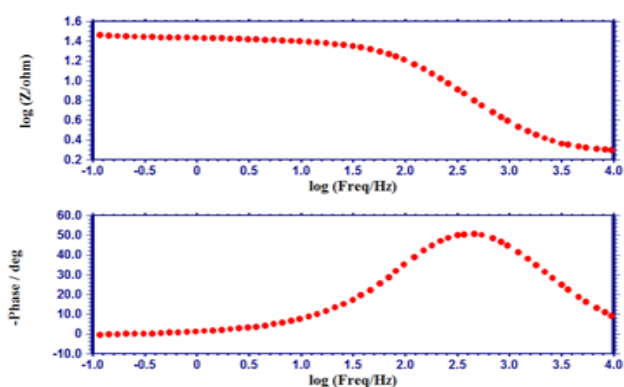
**Figure 3a.** UV-absorption spectrum of solution containing HUF



**Figure 2a.** AC impedance spectra (Bode Plot) of mild steel immersed in aqueous solution containing 60 ppm of  $\text{Cl}^-$



**Figure 3b.** UV-absorption spectra of solution containing HUF- $\text{Fe}^{2+}$



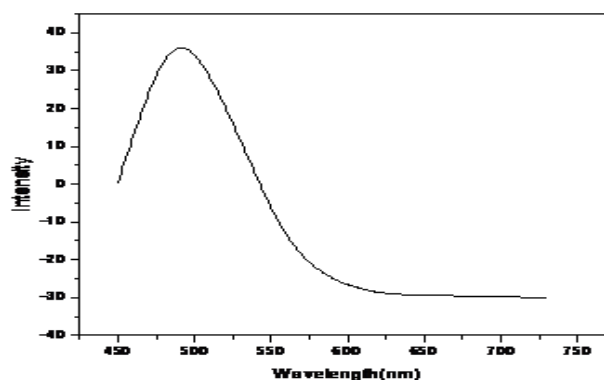
**Figure 2b.** AC impedance spectra (Bode Plot) of mild steel immersed in solution containing 60 ppm of  $\text{Cl}^-$  + 250 ppm of HUF

### Analysis of the UV-Visible spectra

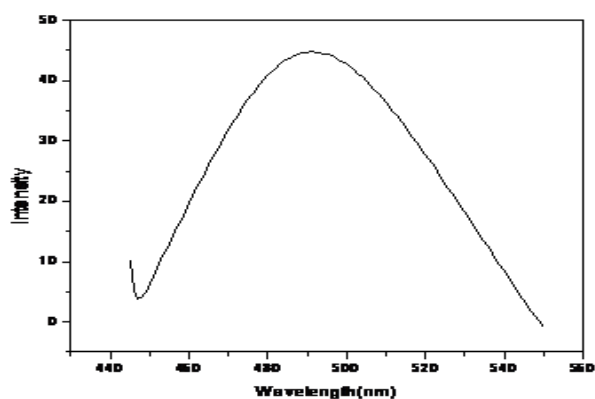
The UV-Visible absorption spectrum of an aqueous solution containing HUF is shown in Figure 3a. Peaks appear at 380 nm and 440 nm. When  $\text{Fe}^{2+}$  solution is added to the solution new peaks appear at 580 nm. There is increase intensity of peaks also. This confirm the formation of  $\text{Fe}^{2+}$ -HUF complex in solution.<sup>13, 14</sup>

### Fluorescence spectra

The emission spectrum ( $\lambda_{\text{ex}}$ :480 nm) of solution containing HUF- $\text{Fe}^{2+}$  solution is shown in Figure 4a. The emission spectrum of the film formed on the metal surface after immersion in solution containing 250 ppm of HUF is shown in Figure 4b. Peaks appear at 490 nm. Hence it is concluded that the protective film consists of HUF- $\text{Fe}^{2+}$  complex. The number peak obtained is only one. Hence it is confirmed that the complex of somewhat highly symmetric in solution.<sup>15</sup>



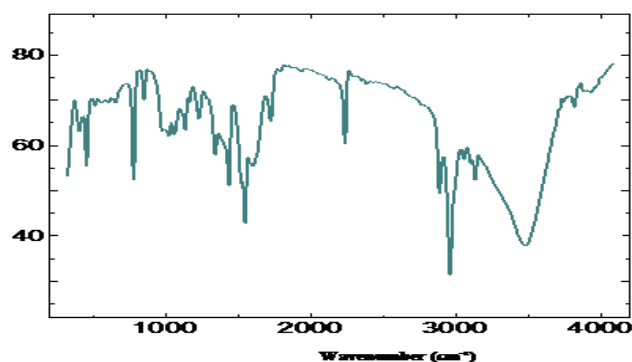
**Figure 4. a)** Fluorescence spectrum of HUF solution



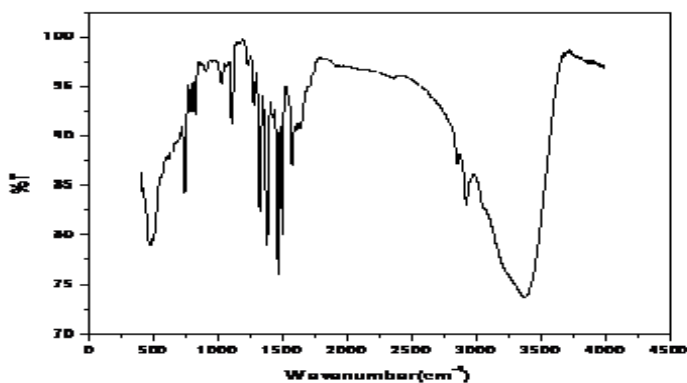
**Figure 4. b)** Fluorescence spectra of film formed on metal surface after immersion in solution containing 60 ppm  $\text{Cl}^-$  + 250 ppm of HUF

### FTIR Spectra tests

The FTIR spectra have been used to analyze the film formed on the metal surface.<sup>16</sup> The FTIR spectrum (KBr) of pure 1-(8-hydroxyquinolin-2-ylmethyl)urea (HUF) is shown in Figure 5a. The OH stretching frequency appears at  $3490.94 \text{ cm}^{-1}$ . The C=O stretching frequency appears at  $1610.59 \text{ cm}^{-1}$ . The aliphatic CH stretching frequency appears at  $2986.03 \text{ cm}^{-1}$ . The peak due to secondary nitrogen (NH) appears at  $3150 \text{ cm}^{-1}$ . The peak due to pyridine nitrogen (C=N) appears at  $1512.33 \text{ cm}^{-1}$ . The peak due to aromatic C=C appears at  $1540.98 \text{ cm}^{-1}$ . The peak due to primary nitrogen is absent in the region  $3400 \text{ cm}^{-1}$ , this is due to the tautomeric nature of urea moiety.



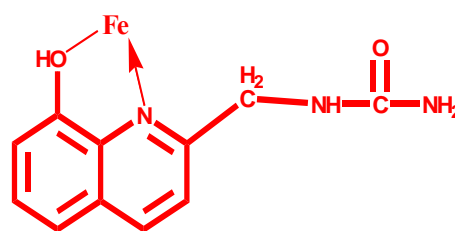
**Figure 5a.** FTIR spectra of pure HUF



**Figure 5b.** FTIR spectra of film formed on metal surface after immersion in HUF

The FTIR spectrum (KBr) of the film formed on the metal surface after immersion in the aqueous solution containing 60 ppm of  $\text{Cl}^-$  + 250 ppm of HUF for a period of one day is shown in Figure 5b. The phenolic OH stretching frequency has shifted from  $3490.94 \text{ cm}^{-1}$  to  $3400 \text{ cm}^{-1}$ . The pyridine nitrogen (C=N) stretching has shifted from  $1512.33 \text{ cm}^{-1}$  to  $1570 \text{ cm}^{-1}$ . The C=O stretching frequency has shifted from  $1610.59 \text{ cm}^{-1}$  to  $1690 \text{ cm}^{-1}$ . The aliphatic CH stretching frequency appears at  $2926.03 \text{ cm}^{-1}$ . That it is concluded that oxygen atom of phenolic group and nitrogen atom of pyridine ring have coordinated with  $\text{Fe}^{2+}$  formed on the metal surface.

The structure of the resulting HUF- $\text{Fe}^{2+}$  complex is shown in Figure 6.

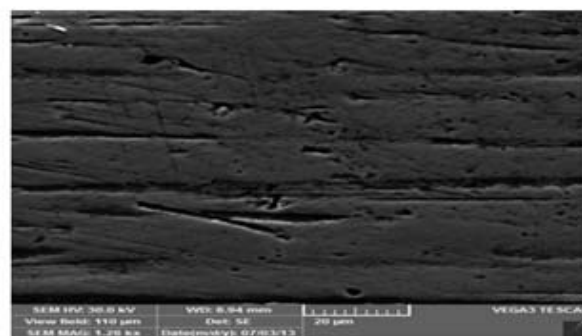


**Figure 6.** Structure of  $\text{Fe}^{2+}$  complex

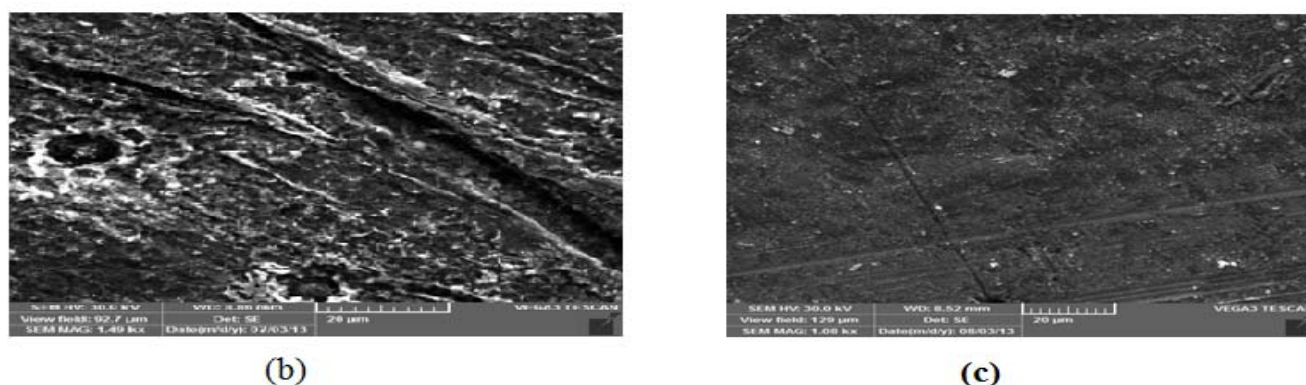
This view is in agreement with the structure proposed by M. Albrecht *et al.* for zinc complex.<sup>17</sup>

### SEM Analysis of Metal Surface

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of mild steel, the SEM micrographs of the surface are examined.<sup>18-20</sup> The SEM images of different magnification ( $\times 20$ ) of mild steel specimen immersed in aqueous containing 60 ppm  $\text{Cl}^-$  for one day in the absence and presence of inhibitor system are shown in Figures 7a, 7b and 7c respectively. The SEM micrographs of polished mild steel surface (control) in Figure 7a show the smooth surface of the metal. This shows the absence of any corrosion products (or) inhibitor complex formed on the metal surface.



(a)



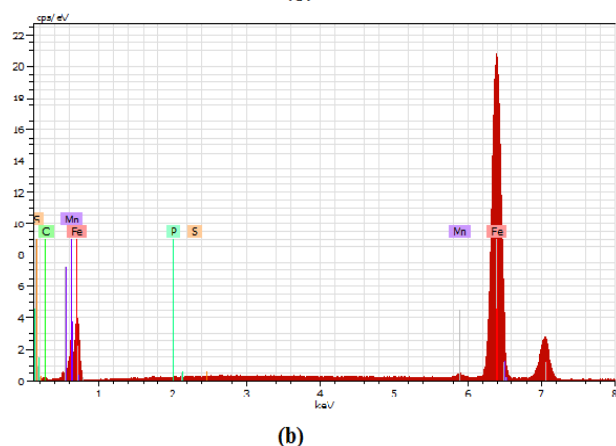
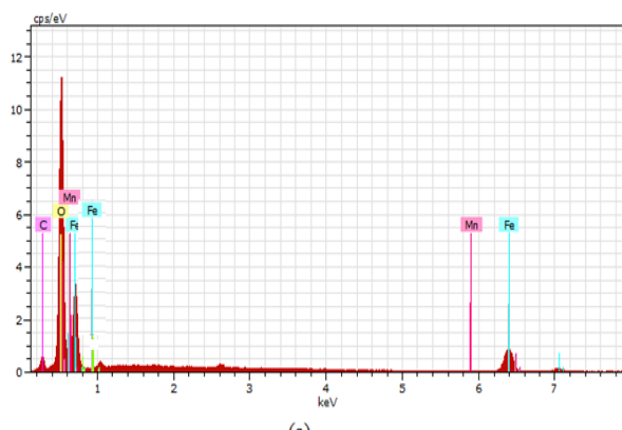
**Figure 7.** SEM analysis of mild steel; magnification  $\times 20$  (control). (b) Mild steel immersed in aqueous solution containing 60 ppm of  $\text{Cl}^-$ , magnification  $\times 20$  (blank). (c) Mild steel immersed in aqueous solution containing 60 ppm of  $\text{Cl}^-$  + 250 ppm of HUF magnification  $\times 20$

The SEM micrographs of mild steel immersed in aqueous containing 60 ppm  $\text{Cl}^-$  (Figure 7b) show the roughness of the metal surface which indicates the highly corroded area of mild steel. However, Figure 7c indicates that in the presence of inhibitor (60 ppm  $\text{Cl}^-$  + 250 ppm HUF) the rate of corrosion is suppressed, as can be seen from the decrease of corroded areas. The metal surface is almost free from corrosion due to the formation of insoluble complex on the surface of the metal.

### Energy Dispersive Analysis of X-Rays (EDAXs)

The EDAXs survey spectra were used to determine the elements present on the metal surface before and after exposure to the inhibitor solution. The objective of this section was to confirm the results obtained from chemical and electrochemical measurements that a protective surface film of inhibitor is formed on the metal surface. To achieve this, EDAX examinations of the metal surface were performed in the absence and presence of inhibitors system.<sup>19-22</sup>

EDAX spectrum of mild steel immersed in aqueous solution containing 60 ppm  $\text{Cl}^-$  is shown in Figure 8 (a). They show the characteristics peaks of some of the elements constituting the mild steel sample. The EDAX spectrum of mild steel immersed in aqueous solution containing 60 ppm  $\text{Cl}^-$  + 250 ppm HUF is shown in Figure 8 (b). In addition, the intensity of O signals is reduced and the intensity of Fe signal is increased. The appearance of Fe signal and this enhancement of O signal are due to the presence of inhibitor. These data show that metal surface covered the Fe, S, C, P and Mn atoms.



(a) Mild steel sample immersed in aqueous solution containing 60 ppm of  $\text{Cl}^-$ . (b) Mild steel sample after immersion in aqueous solution containing 60 ppm of  $\text{Cl}^-$  + 250 ppm of HUF.

### Bacterial Enumeration count

The results of bacterial enumeration count<sup>23-25</sup> of the aqueous solution containing 60 ppm of  $\text{Cl}^-$  and 60 ppm of  $\text{Cl}^-$  with HUF inhibitor are presented in Table 3. The aqueous solution containing 60 ppm of  $\text{Cl}^-$  without inhibitor shows more bacterial count against the growth of pathogenic bacteria strains such as E. Coli, Streptococcus, Pseudomonas and Entrobacter. The aqueous solution containing 60 ppm of  $\text{Cl}^-$  with inhibitor HUF shows less bacterial count against the growth of pathogenic bacteria strains such as E. Coli, Streptococcus, Pseudomonas and Entrobacter. A good result was obtained when addition of HUF inhibitor to the corrosive media.

**Table 3.** Colonies forming unit (CFU) of mild steel in aqueous solution containing 60 ppm of Cl<sup>-</sup> in the absence and presence of HUF inhibitor obtained by bacterial enumeration count method.

Systems	Colonies Forming Unit (per ml)			
	E.Coli	Streptococcus	Pseudomonas	Enterobacter
60ppm Cl <sup>-</sup>	140×10 <sup>6</sup>	146×10 <sup>6</sup>	130×10 <sup>6</sup>	127×10 <sup>6</sup>
60 ppm Cl <sup>-</sup> + 250 ppm HUF	84×10 <sup>6</sup>	75×10 <sup>6</sup>	78×10 <sup>6</sup>	76×10 <sup>6</sup>

## Conclusion

The present study leads to the following conclusions. The formulation consisting of 60 ppm of Cl<sup>-</sup> and 250 ppm of HUF offers 75 % inhibition efficiency in controlling corrosion of mild steel. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR, fluorescence and UV-Visible spectra reveals that the protective film consists of HUF-Fe<sup>2+</sup> complex formed on metal surface. SEM and EDAX confirm the presence of a protective film on the metal surface. The bacterial enumeration has been reduced by the addition of HUF inhibitor to the corrosive media.

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