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RESEARCH ARTICLE

CORROSION INHIBITION OF MILD STEEL BY CEFTRIAXONE IN 1M SULFURIC ACID MEDIUM

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ABSTRACT

Corrosion of mild steel and its inhibition by ceftriaxone in 1M sulfuric acid has been investigated by weight loss, open circuit potential (OCP), potential dynamic polarization and surface analysis by scanning electron microscopy SEM and electron x-ray diffraction (EDAX) techniques. Different concentration range of inhibitor solution from 10-500 ppm was used which revealed that 500 ppm solution shows excellent inhibition performance of nearly 94%. Ceftriaxone is mixed type of inhibitor but the cathodic Tafel polarization, β_c values continuously increases as the concentration of inhibitor increases; hence comparatively, the cathodic polarization is more pronounce than the anodic polarization. The SEM examination shows the formation of protective surface film of inhibitor molecules on the surface of mild steel. EDAX shows peaks of N and S on the mild steel. The adsorption of inhibitor obeys the Langmuir adsorption isotherm.

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INTRODUCTION

Corrosion of steel may cause physical damage, destruction, loss of life or drastic change in environment; therefore, it is today's need to study corrosion and its inhibition mechanism. The metal dissolution may occurs by the use of sulfuric acid during acid pickling, acid descaling and industrial cleaning etc. consequently, unwanted loss of metal takes place. The nascent hydrogen is formed during the process of acidic corrosion which gets dissolved in metal in atomic state, consequently the ductility of metal decreases (Dubey and Singh, 2012; Machu, 1970). Aside from acid corrosion, other factors like-temperature variation, tidal action of seawater, man-made pollutants, sufficient oxygen and ultraviolet rays causes severe corrosion damage (Bei Qian *et al.*, 2013). Corrosion of metal cannot be totally eliminated, but its intensity can be reduced by the selection of appropriate inhibitor material. There are various techniques like- ceramic oxide film formation, metal coating, sol-gel method and addition of inhibitor in aggressive corrosive medium for control of corrosion (Lidija *et al.*, 2013). Addition of inhibitor in corrosive medium is very good method since it is cost effective and least consumption of inhibitor which avoided wastage.

Many inorganic and organic compounds show good corrosion inhibition effect, but most of them are toxic, expensive and non-biodegradable. The cost, health issues and environmental regulation restrictions have made researchers focus on the development of heterocyclic aromatic organic compounds used as good corrosion inhibitors (Bentiss *et al.*, 2000; Chetouani *et al.*, 2003; Lagrenee *et al.*, 2001; Abd El-Rehim *et al.*, 2001; Tadros and Abd El-nabey, 1988; Arab and Noor, 1993; Bentiss *et al.*, 2002; Tebbji *et al.*, 2005; Bouklah *et al.*, 2005; Muralidharan *et al.*, 1995; Oguzie *et al.*, 2008; Saliyan and Adhikari, 2008). Most of the organic inhibitors are adsorbed on the metal surface and forming a compact barrier film (Muralidharan *et al.*, 1995). Organic compounds containing heteroatom such as nitrogen, sulfur, oxygen, phosphorous etc. and aromatic ring, double bond and triple bond serves as good corrosion inhibitors especially more effective in sulfuric acid medium (Oguzie *et al.*, 2008; Saliyan and Adhikari, 2008; Emregal and Atakol, 2003). The efficiency of inhibitor is depends on the number of heteroatom, lone pair of electrons and p-electrons present in alkenes, alkynes and aromatic rings of compounds (Kandemirli and Sagdin, 2007; Hackerman and Hurd, 1962).

The present work comprises the inhibition property of pharmaceutically active compound ceftriaxone towards corrosion of mild steel in 1M sulfuric acid. Corrosion

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mechanism of mild steel has been studied by electrochemical technique (OCP and potentiodynamic polarization) and surface analysis has been studied by SEM and EDAX.

Experimental

In the present investigation, mild steel was used as a corrosion testing substrate material since it has huge applicability in various industries. Mild steel refers to low carbon steel which have composition- C= 0.16%, Si= 0.10%, Mn= 0.40%, P= 0.013%, S= 0.02% and remainder iron. For gravimetric and electrochemical polarization analysis, the commercial grade mild steel sheets were sheared in to coupons of size, 3 cm x 1 cm x 0.3 cm. The aggressive solution was made of AR grade sulfuric acid obtained from Merck chemicals. 1M solution of sulfuric acid was prepared with double distilled water. The organic heterocyclic compound, ceftriaxone received from market was used as it is without further purification as a corrosion inhibitor. The experimental measurements were carried out at room temperature, $28^0C \pm 1^0C$ in non-stirred 1M sulfuric acid solution at concentration range of 10-500 ppm of the corrosion inhibitor.

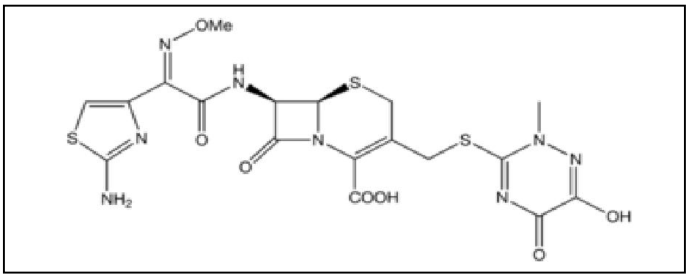

Figure 1. Structure of ceftriaxone molecule

Weight loss measurements

Weight loss measurements readings were carried out in triplicates in test tubes containing 10 ml. test solutions with and without inhibitor solution at the range from 10-500 ppm. The immersion time was 24 hrs at $28^0C \pm 1^0C$ after immersion time, the coupons were withdrawn from test tubes, rinsed with double distilled water, washed with acetone, dried and weighed. The average value of weight loss was noted.

Electrochemical Experiments

Electrochemical measurement system, DC 105, containing software of DC corrosion techniques from M/S Gamry Instruments Inc., (No. 23-25) 734, Louis Drive, Warminster, PA-18974, USA was used for corrosion potential and potentiodynamic polarization experiments. The experiments were performed in a three electrodes Pyrex glass vessel with mild steel coupon as a working electrode. The surface of mild steel coupons were abraded successively by different grades of silicon carbide emry papers of grades 1/0, 2/0, 3/0, 4/0 grade emery paper (John Okay), so as to get the surface free from scratches and other apparent defects. The polished mild steel working electrodes were washed with soap solution, rinsed with double distilled water, degreased with acetone, by leaving 1 cm^2 on one side and small portion at the tip for providing electrical contact, rest of the surface was coated with enamel lacquer including side edges and finally the coupon dried in desiccators. Other two electrodes are saturated calomel electrode as a reference electrode and graphite rod as a counter electrode. About 50 ml. of corrosive medium was taken in a mini corrosion testing electrochemical cell to permit desired immersion of electrodes. The above mentioned three electrodes were immersed in 1M sulfuric acid corrosive medium solution in a cell and connected to the electrochemical measurement system, DC 105, Gamry instrument through connecting wires. Potential was swept between -0.5 to +0.5 V at the scan rate of 5 mV/s. The open circuit potential was carried out for 2 hrs exposure time so that to obtained a steady horizontal curve and then potentiodynamic polarization was run. The variation in potential of mild steel in 1M sulfuric acid solution was measured against saturated calomel electrode in absence and presence of various concentrations, 10 ppm-500 ppm of inhibitor solutions. Different potentiodynamic polarization results obtained are reported in Table-2.

SEM and EDAX analysis

The surface morphology of mild steel have been studied after 24 hrs immersions in 1M sulfuric acid in absence and presence of ceftriaxone by SEM and EDAX Hitachi S-3400N. The accelerating voltage for SEM was 20.0 KV.

RESULTS AND DISCUSSION

Weight loss measurements

An average value of triplet readings of weight loss measurements of mild steel in 1M sulfuric acid after immersion time of 24 hrs at $28^0C \pm 1\ ^0C$ were taken with and without different concentrations of inhibitor. The data obtained is shown in Table-1. It is revealed that corrosion inhibition increases as the concentration of ceftriaxone increases. 500 ppm inhibitor solution exhibits its best performance of about 94 %. It may forms a uniform protective film on the surface of mild steel (Matjaz Finsgar, 2013; Mars G. Fontana, 2009). Corrosion inhibition efficiencies (IE) were calculated according to previous report (Ashassi-Sorkhabi *et al*., 2005).

$$IE\ \% = [W_o - W]/W_o \times 100$$

Where, W and W_o are the weight loss of mild steel in the presence and absence of inhibitor respectively.

Table 1. Weight loss data for inhibition of corrosion of mild steel exposed to 1M sulfuric acid with different concentration of ceftriaxone

Inhibitor	Conc. (ppm)	Weight Loss (mg)	Surface coverage (θ)	Inhibition Efficiency (IE%)
Blank	-	283	-	-
Ceftriaxone	10	81	0.7137	71.37
	100	26	0.9081	90.81
	200	25	0.9116	91.16
	300	35	0.8760	87.60
	400	28	0.9010	90.10
	500	18	0.9363	93.63

Adsorption isotherm

Adsorption isotherms are often used to demonstrate the adsorbent performance on the substrate which describes the relation between surface coverage, θ and bulk concentration (Sastri, 1998). It is observed that the surface coverage values, θ (defined as θ = IE%/100) increases with increasing inhibitor concentrations as a result of more adsorption of inhibitor molecules on the surface of mild steel takes placed (Table-1). Adsorption behavior of ceftriaxone obeys the Langmuir's adsorption isotherm as it gives a straight line when graph of log θ/(1-θ) is plotted against log C as shown in Figure 2. The protective layer of inhibitor on the mild steel is the combination of both, physisorption and chemisorptions (Gao *et al.*, 1971).

Table 2. Adsorption parameters of ceftriaxone

C	Log C	Θ	(1-θ)	θ/(1-θ)	Log θ/(1-θ)
0.000010	-5.0000	0.7137	0.2863	2.4928	0.3966
0.000100	-4.0000	0.9081	0.0919	9.8813	0.9948
0.000200	-3.6989	0.9116	0.0884	10.3122	1.0133
0.000300	-3.5228	0.8760	0.1240	7.0645	0.8490
0.000400	-3.3979	0.9010	0.0990	9.1010	0.9590
0.000500	-3.3010	0.9363	0.0637	14.6985	1.1672

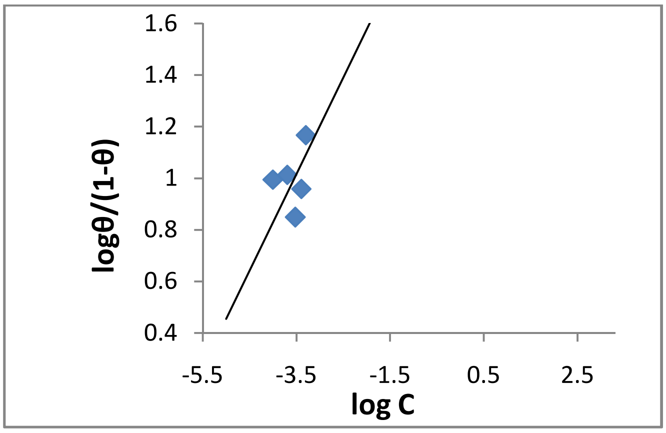

Figure 2. Adsorption isotherm of ceftriaxone

Open circuit potential measurement

Corrosion behavior of mild steel in 1M sulfuric acid and with different concentration of inhibitor in 1M sulfuric acid solution was studied by monitoring the changes in corrosion potential (E_{corr}) with time, 2 hrs of each experiment to obtained steady curve. It is observed that as the working electrode (mild steel) immersed in to the studied solution, the potential immediately increases for few seconds and then decreases and again increases. Then gradually attain steady state up to the end of the experiment as shown in Figure 3.

This sudden increase in potential may be due to the oxygen present on the surface of mild steel which in few seconds comes out in the form of baubles and then the exposed surface of the substrate start corroding (Riggs, 1973) consequently the potential decreases which shows corrosion of mild steel. After few seconds as the molecules of inhibitor start adsorption on the surface of mild steel, potential will again start increasing and within 30 min. it achieved equilibrium and obtained a steady curve of corrosion potential. Figure 3 show that OCP in absence of inhibitor has more negative (lower potential) value than in presence of inhibitor. It is seen that curves goes towards the positive direction as the concentration of inhibitor increases. This indicated the decrease in the rate of corrosion of mild steel in presence of inhibitor due to the formation of protective film on the surface of mild steel.

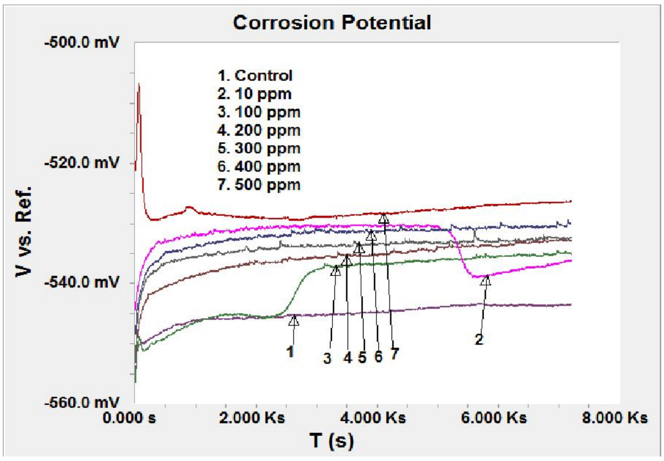

Figure 3. Open circuit potential of mild steel in 1M sulfuric acid without and with different concentration of ceftriaxone

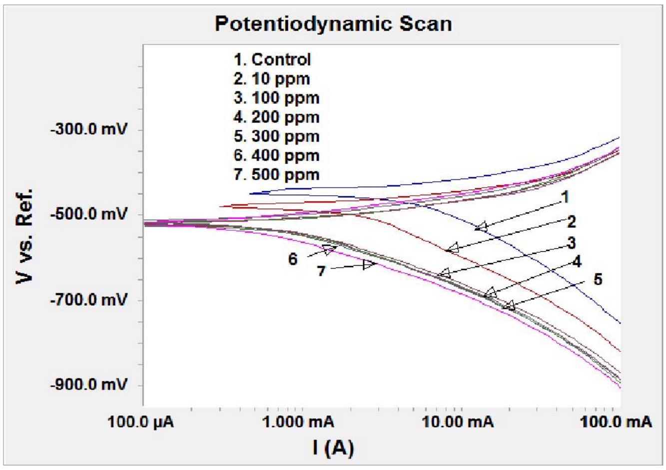

Figure 4. Potentiodynamic polarization of mild steel in 1M sulfuric acid with and without different concentration of ceftriaxone

Table 3. Electrochemical parameters of mild steel in 1M sulfuric acid with and without different concentration of inhibitor

Conc. (ppm)	βa (V/dec.) e-3	βc (V/dec.) e-3	Icorr (µA. cm⁻²)	Ecorr (mv)	Corr. Rate (mpy)	% IE
Control	163.4	316.5	13200	-435	6.043e3	
Ceftriaxone						
10	117.3	246.8	4040	-387	1.848e3	69.39
100	85.70	191.9	1530	-364	699.2	88.40
200	110.6	190.6	1470	-363	671.4	88.86
300	105.7	199.0	1870	-368	853.1	85.83
400	94.00	182.8	1210	-360	551.1	90.83
500	77.50	166.5	775	-358	354.2	94.12

Potentiodynamic polarization measurement

Potentiodynamic polarization curves of mild steel in different concentrations of ceftriaxone are depicted in figure 4. It is seen that cathodic curves are comparatively more polarized than anodic curves. Corrosion potential, E_{corr} values increases from -435 mV to -358 mV without and with inhibitor concentration from 0 ppm to 500 ppm respectively (Table 3). The classification of compounds evidenced that when the change in E_{corr} value is more than 85 mV, the compound is an anodic or a cathodic type of inhibitor (Yan *et al*., 2005; Tang *et al*., 2006). But, the displacement obtained about 77 mV. Therefore, ceftriaxone should be a mixed type of inhibitor. Table-1 shows that the cathodic Tafel slope, β_c increased more as compared to β_a. This is evidenced that ceftriaxone is less anodic and more cathodic-mixed type of inhibitor. Corrosion efficiency was calculated by using the following equation:

Inhibition Efficiency, (IE %) = $100(i_0 - i) / i_0$

Where, i_0 and I are the corrosion current densities in the absence and presence of inhibitor respectively. From the Table 3, it is also revealed that corrosion current decreases as the concentration of inhibitor increases. Ceftriaxone shows its best inhibition performance of about 94% at 500 ppm of inhibitor solution.

SEM and EDAX analysis

SEM micrographs of mild steel in 1M sulfuric acid for 24 hrs in absence and presence of 500 ppm of ceftriaxone are shown in Figure 5. It is seen that the substrate in absence of inhibitor is rough and strongly damaged; whereas the substrate in 500 ppm comparatively is smooth (shown in Figure 5-B and C). It revealed that inhibitor adsorbed with formation of protective film on the surface of mild steel which is responsible for the inhibition of corrosion of mild steel. EDAX spectra shown in Figure 6, shows the peaks for N and S. This confirmed the adsorption of ceftriaxone molecules on the surface of mild steel through N and S atoms.

Mechanism

Mild steel in 1M sulfuric acid is highly corrosive. Ceftriaxone being an acid gives protons in aqueous solution which is reduced at the cathodic region and negative charged acetate group of inhibitor thus electrostatically weakly adsorbed on the positive charged iron surface (physisorption) (Reshetnikov, 1986). Table 3 shows the cathodic Tafel slope, β_c is increased more as compared to β_a ceftriaxone is a heterocyclic aromatic compound containing N, O and S electrons donor atoms which donates lone pair electrons to the d-orbitals of iron forming strong coordinate-covalent bonds.

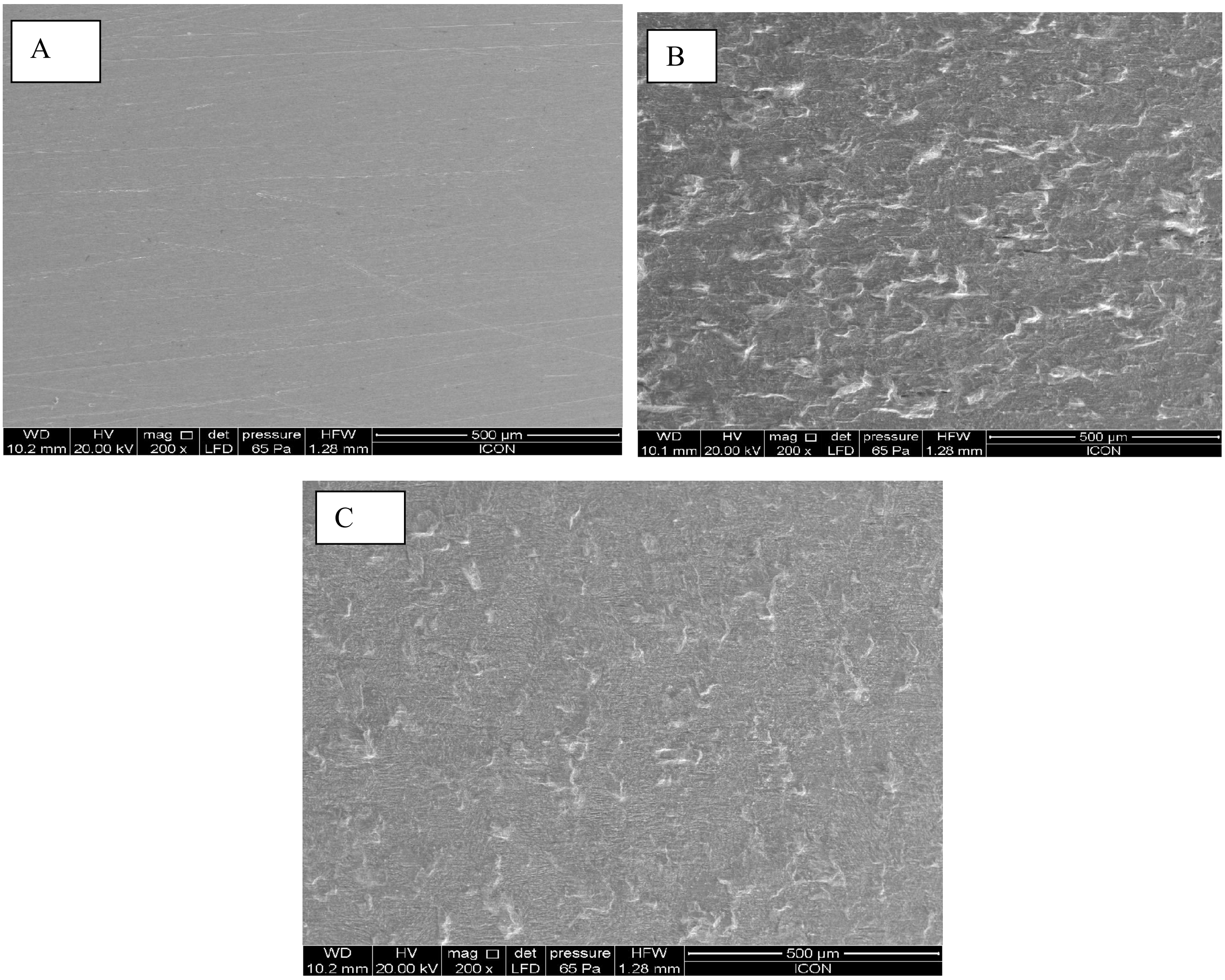

Figure 5. SEM of mild steel: a) Polished and without inhibitor. b) After immersion 1M sulfuric acid without inhibitor. c) After immersion in 1M sulfuric acid with 500 ppm of inhibitor

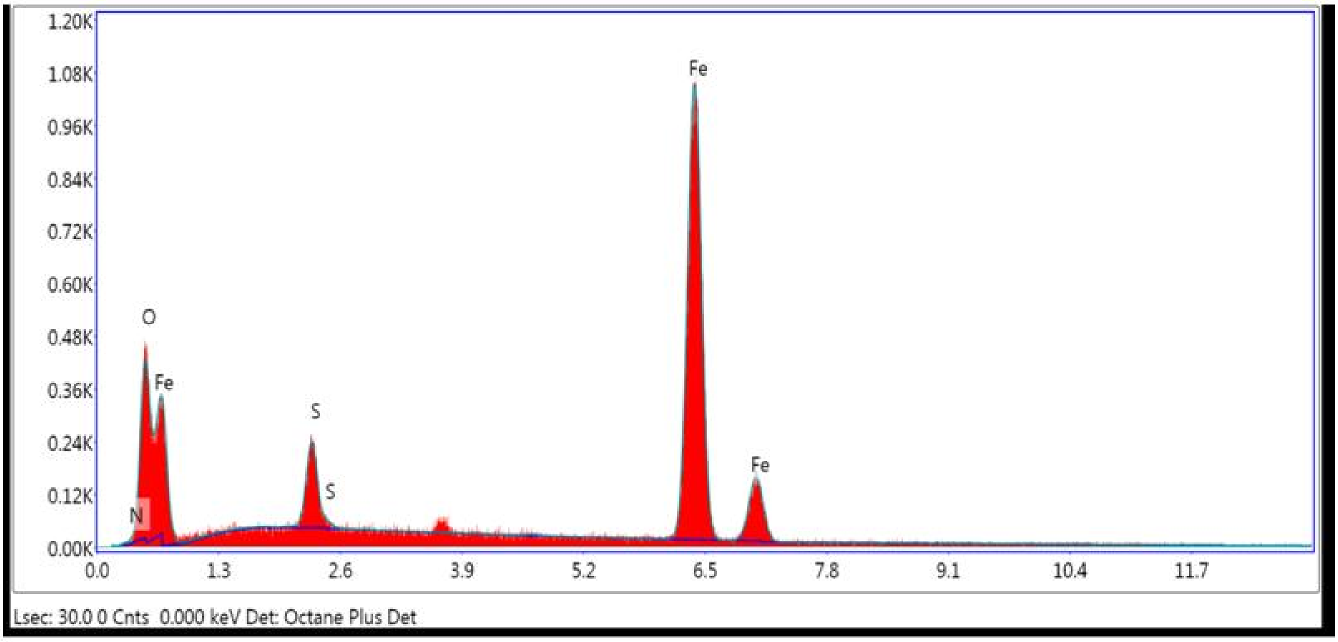

Figure 6. EDAX measurement of ceftriaxone on the mild steel surface

The delocalized π-electrons of aromatic rings also covalently bonded with the partially filled d-orbitals of iron (Rozenfeld, 1977; Popova *et al*., 2004). Corrosion inhibition efficiency is depends on the number of aromatic rings in the compound (Yongming Tang *et al*., 2013). Ceftriaxone has three aromatic rings thus it acts as a very good corrosion inhibitor and exhibits its best performance of about 94 %.

Conclusion

The result obtained by gravimetric analysis, hold in good agreement with the result obtained by electrochemical studies. This revealed that ceftriaxone is acting as a very good corrosion inhibitor of mild steel in 1M sulfuric acid solution. The inhibition efficiency increases with increase in inhibitor concentration. Thus, it is concluded that 500 ppm solution of ceftriaxone gives its maximum inhibition efficiency of about 94 %. Ceftriaxone is a mixed type of inhibitor but more cathodic, since the cathodic polarization is more.

The SEM examination with 500 ppm inhibitor solution shows smooth and uniform mild steel surface as compared to absence of inhibitor in 1M sulfuric acid solution.

This smooth mild steel surface may be due to the formation of uniform and protective surface film of inhibitor molecules on the mild steel. The adsorption of inhibitor obeys the Langmuir adsorption isotherm. Thus mild steel is protected from dissolution in sulfuric acid medium.

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