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Reduction of copper corrosion in 5 M HCl solution by expired nontoxic Ofloxacin drug

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ABSTRACT

Several corrosion inhibitors have been used in industry to eliminate the corrosive influence of harsh hydrochloric acid solutions on the mechanical behavior of copper structures. Recently, expired drug products as corrosion inhibitor have been developed to replace the organic compounds (synthesized) which are expensive and toxic molecules. In this work, the expired nontoxic Ofloxacin drug is used to study the its effectiveness as a corrosion inhibitor for copper metal in 5 M HCl solution with the aid of weight loss, potentiodynamic polarization, AC impedance spectroscopy and scanning electron microscopy (SEM) studies. The weight loss results demonstrated that, 4 mg/L of expired Ofloxacin drug was the optimum concentration for inhibition of copper corrosion in acidic system. Tafel plot results revealed the mixed corrosion inhibition property of expired Ofloxacin drug. AC impedance spectroscopy and scanning electron microscope (SEM) results well supported the weight loss and potentiodynamic polarization results.

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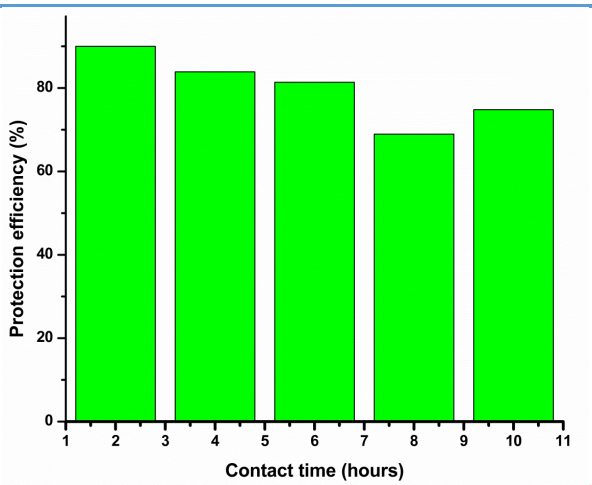
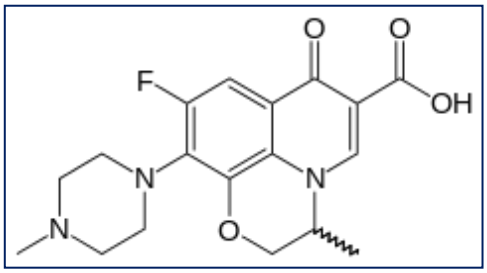
Graphical Abstract



Introduction

Copper metals are exposed to hydrochloric acid solutions which generally lead to serious copper metal degradation. Hydrochloric acid solutions are generally used in the chemical, pharmaceutical, and engineering units [1–3]. The introduction of the hydrochloric acid solution to the copper surface changes the chemical properties of copper metal. Several methods have been employed to protect the copper corrosion. The significant methodology applied for the prevention of copper corrosion in hydrochloric acid system is corrosion inhibitors. The corrosion inhibitors are the substances that reduce the corrosion of copper reaction via adsorption (physical or chemical) process [4-7]. Most of the organic corrosion inhibitors containing hetero atoms (N, O, P and S) in their atoms moieties are toxic corrosion inhibitors. Therefore, use of these compounds as corrosion inhibitors in industries is banned. Hence, nowadays research focus shifted towards the green corrosion inhibitors [8–10]. Many scientists reported the corrosion inhibition property of expired drug on different metals in various corrosive environments. Thus, in this investigation selected expired nontoxic Ofloxacin drug and studied their corrosion inhibition property on the surface of copper surface in 5 M HCl solution. The chemical structure of Ofloxacin drug is depicted in the Figure 1. The corrosion inhibition property of expired nontoxic Ofloxacin drug was confirmed by weight loss (gravimetric), Tafel plot, impedance spectroscopy and scanning electron microscopy (SEM) studies.



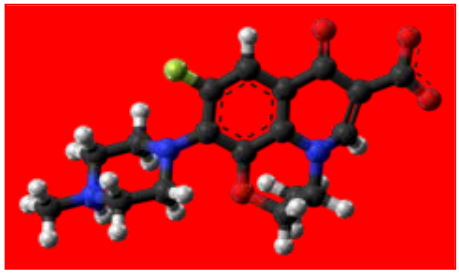


Figure 1. The chemical structure of Ofloxacin drug

Experimental

Materials and methods

The copper metal chemical composition used in this investigation is shown in the Table 1. The expired drug ofloxacin drug was collected from the local medical shop. The inhibitor concentration used in present investigation is 1 mg/L, 2 mg/L, 3 mg/L and 4 mg/L. The gravimetric (weight loss) was carried out according to American society for testing and materials (ASTM) standard. The weight loss experiment was performed with 100 mL of 5 M HCl solution with 2, 4, 6 and 8, and 10 h immersion period. The results of weight loss technique give a baseline to electrochemical studies. The protection efficiency can be obtained from the following equations;

$$\text{Corrosion protection (inhibition) efficiency (\%)} = \frac{(W_1 - W_2)}{W_1} \times 100$$

Where, W_1= Weight loss of copper without corrosion inhibitor and W_2= Weight loss of copper with inhibitor of different concentrations.

The electrochemical studies (both Tafel plot and AC impedance studies) were carried out to support the weight loss results. The copper electrode is submerged in the 100 mL of 5 M HCl solution for about 35-40 min in order to obtain the steady state open-circuit potential (OCP). Tafel plots are recorded with potential range of + 250 mV to -250 mV with a scan rate of 0.1 V/s. AC impedance spectroscopy was carried out in the frequency range of 10^5 - 1 Hz with an amplitude of 0.01 V.

The protection efficiency of the expired drug was obtained from the below relation:

$$\text{Corrosion protection (inhibition) efficiency} = \left[1 - \frac{i'_{corr}}{i_{corr}}\right] \times 100$$

$$\text{Corrosion protection (inhibition) efficiency} = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100,$$

Where, i'_{corr} = copper corrosion current density in protected system, i_{corr} = copper corrosion current density in unprotected system, R_{ct} = copper charge transfer resistance in unprotected system and $R_{ct\,(inh)}$ = copper metal charge transfer resistance in protected system. Surface studies were carried out by scanning electron microscopy (SEM) studies. The topography nature of copper metal in unprotected and protected system was examined by scanning electron microscopy (SEM) with an immersion period of 2 h.

Table 1. Chemical composition of copper

Element	Oxygen	Cu
Wt %	0.04	Remainder 99.09%

Results and Discussion

Weight loss technique

The corrosion of copper in the 5 M HCl solution containing four different amounts of expired Ofloxacin drug (1 mg/L, 2 mg/L, 3 mg/L and 4 mg/L) was studied by weight loss technique. The corrosion studies were performed with immersion period of 2, 4, 6, 8, and 10 h. The weight loss of copper metal in 5 M HCl solution without and with corrosion inhibitor is recorded and the obtained weight loss results are shown in the Table 2. From the Table 2, it is clear that, the increase in the amounts of expired Ofloxacin drug (from 1 mg/L to 4 mg/L) protects the copper metal from the acidic corrosion (which is observed from the rise in the protection efficiency values with increase in the concentration of expired drug). The rise in the concentration of expired Ofloxacin drug enhances the adsorption process. As a result of this, the strong protective film generated on the copper surface in 5 M HCl

solution. This protects the copper metal from the corrosion process. As seen in Table 2**,** the higher protection efficiency observed at immersion period of 2 h with 4 mg/L of expired Ofloxacin drug. With rise in the contact time from 2 to 10 h, the protection efficiency declines. The decrease in the protection of the corrosion inhibitor (expired Ofloxacin drug) with rise in the solution contact time signifies the desorption of protective layer (invisible) on the copper electrode surface in 5 M HCl solution. With rise in the immersion period (from 2 to 10 h), the protective film loses its stability because of aggressive nature of hydrochloric acid solution on the surface of copper. Hence, copper electrode directly exposed to 5 M HCl solution. As a result of this, protection efficiency decreases with rise in the contact time from 2 to 10 h.

Table 2. Gravimetric (weight loss) results

Concentration (mg/L)	Contact time (hours)	Protection efficiency in percentage
Bare	2	
1.0		80.00
2.0		82.50
3.0		85.00
4.0		90.00
Bare	4	
1.0		70.96
2.0		77.41
3.0		80.64
4.0		83.87
Bare	6	
1.0		65.11
2.0		68.60
3.0		76.74
4.0		81.39
Bare	8	
1.0		56.31
2.0		61.16
3.0		66.01
4.0		68.93
Bare	10	
1.0		52.75
2.0		60.62
3.0		68.50
4.0		74.80

Tafel plot evaluation

Figure 2 reveals the Tafel plot curves of copper in 5 M HCl solution without and with corrosion inhibitor (four different amounts of expired Ofloxacin drug). The results of Tafel plot analysis are shown in the Table 3. As can be seen in Table 3, the corrosion current density values decrease with a rise in the concentration of the expired Ofloxacin drug. The decrease in the corrosion current density values with rise in the concentration of the corrosion inhibitor is an indication of corrosion inhibition property of expired Ofloxacin drug on the copper electrode surface in the 3 M HCl solution. The obtained corrosion potential values significant variation

compared to bare system. However, there is no great variation in the cathodic and anodic Tafel slope values, which is an indication of mixed corrosion inhibition property of expired Ofloxacin drug on the surface of copper in 5 M HCl solution.

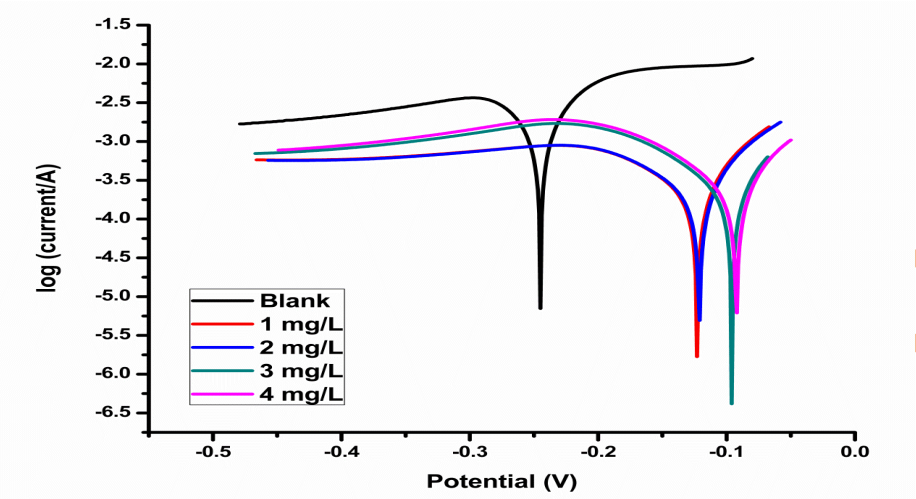


Figure 2. Tafel plots without and with four different amounts of expired drug

Table 3. Potentiodynamic polarization results

Concentration (mg/L)	Corrosion potential (mV)	Cathoidc Tafel slope (V/dec)	Anodic Tafel slope (V/dec)	Corrosion current (A)	Protection efficiency
Bare	-245	2.490	1.592	0.01258	
1.0	-123	2.142	1.073	0.000399	96.821
2.0	-121	2.316	1.059	0.0003619	97.123
3.0	-096	4.895	1.018	0.0003371	97.320
4.0	-092	5.217	1.073	0.0002774	97.794

AC impedance spectroscopy:

The results of impedance spectroscopy studies are demonstrated in the Figure 3 and Table 4. It was observed that, the area of depressed semicircle enhances with rise in the concentration of the expired Ofloxacin drug which is an indication of corrosion protection property of expired Ofloxacin drug on the copper in the 5 M HCl solution. The resulted table also shows that, the value of charge transfer resistance values enhances with rise in the concentration of the corrosion inhibitor. The results of impedance studies well support the Tafel plot and weight loss studies.

Table 4. Nyquist plot results

Concentration (mg/L)	Charge transfer resistance (Ω)	Protection efficiency (%)
Bare	49.91	
1.0	243.6	79.511
2.0	254.2	80.365
3.0	296.3	83.155
4.0	336.4	85.163

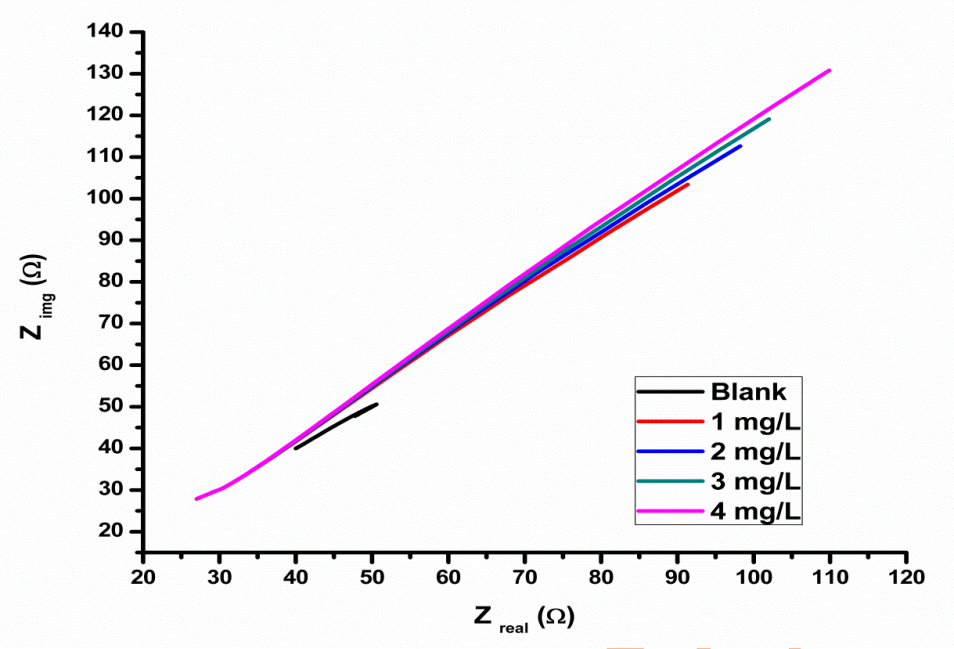
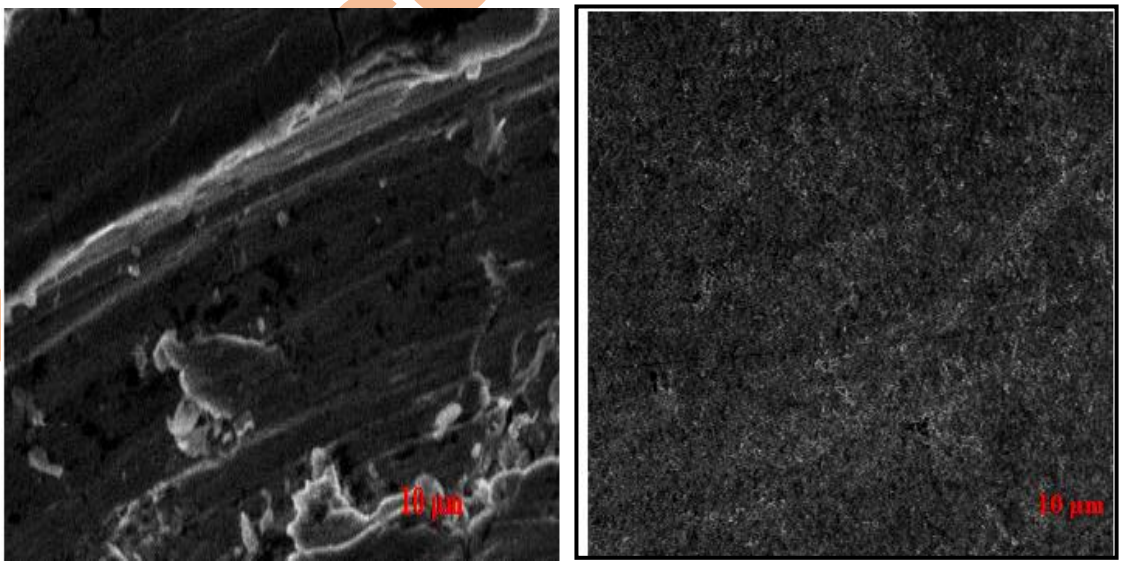


Figure 3. Nyquist plots

Scanning electron microscopy (sem) analysis

SEM photographs (Figure 4**a** and **b**) were considered to explicate the copper corrosion and the adsorption process. The Figure 4**a** show the copper photograph in unprotected system, the roughness of copper surface is due to the aggressive nature of hydrochloric acid solution. As a result of this, large number of cracks and voids observed on the surface of copper. In the presence of expired Ofloxacin drug of 4 mg/L, smooth layer of copper was observed, which is due to adsorption process by expired Ofloxacin drug.



a b

Figure 4. SEM images without and with corrosion inhibitor

Conclusions

The results obtained from the weight loss, Tafel plot, AC impedance and SEM techniques demonstrated the following conclusions; a) Expired Ofloxacin drug act as corrosion for copper in 5 M HCl solution with contact time dependent mode. b) The Tafel plot studies show the mixed corrosion property of expired Ofloxacin drug. c) Impedance studies confirms charge transfer process plays vital role in the inhibition of copper corrosion process. d) SEM studies fully support the weight loss, Tafel plot and AC impedance results.

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