

## Utilization of Expired Calcitriol as an Eco-friendly Corrosion Inhibitor on the Copper Metal in the Aerated Acidic Environment

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### Abstract

Corrosion inhibition mechanism of expired Calcitriol as a nontoxic corrosion inhibitor on the copper in the aerated 5 M HCl solution was thoroughly examined via weight loss (mass loss), Tafel plot (potentiodynamic polarization), AC impedance spectroscopy and surface topography techniques. Weight loss (mass loss) confirms the good corrosion protection efficiency of expired Calcitriol drug on the copper surface in 5 M HCl solution. Tafel plot study reveals the anodic type corrosion inhibition property of expired Calcitriol in the studied system. AC impedance spectroscopy and scanning electron microscopy (SEM) reveals the formation of an invisible compact layer on the copper electrode in 5 M HCl solution.

**Keywords:** Surface topography, expired Calcitriol, Weight loss, Tafel plot, AC impedance spectroscopy

### Introduction

Copper metal widely used in several industrial applications because of its noble characteristics. The copper metal comes in contact with hydrochloric acid solutions during several industrial operations, which leads to the corrosion of copper (disintegration of copper metal surface). The corrosion of copper can be prevented by the application of corrosion inhibitors (Ahamad et al., 2010; Pyun & Moon, 1999; Pyun & Lee, 2001). The use of corrosion inhibitors is the one of the efficient methods for the prevention of copper disintegration in the hydrochloric acid environment. The large number of synthetic organic compounds exhibits good corrosion inhibition property due to the presence of multiple heteroatom's that can generate large thick active invisible layer over the copper surface (Bourazmi et al., 2018; Jeetendra Bhawsar et al., 2018; Eddy et al., 2009; Bahrami et al., 2010). But, most of the organic compounds are toxic and expensive. Hence, currently there is an interest to utilize cheap and zero-toxicity corrosion inhibitors to overcome the gathering of carcinogenic materials. Medicinal compounds expected to show good corrosion inhibition property due to the presence of heteroatom's in their moieties (Lebrini et al., 2005; El-Etre 2003; Abiola & Otaigbe 2009; Gunasekaran & Chauhan 2004). Therefore, in this study chosen expired Calcitriol in order to examine their disintegration inhibition role on the copper surface in the 5 M HCl solution. The copper corrosion inhibition property of expired Calcitriol in the acidic environment was examined by mass loss, Tafel curves, AC impedance spectroscopy and scanning electron microscopy studies.

### Materials and methods

The copper metal of 99 % purity was used for the mass loss, electrochemical and surface studies.

The copper electrode washed with triple distilled water and dried by using the ethanol. The aggressive 5 M HCl solution was prepared by diluting the analytical grade of concentrated HCl solu-

tion with the double distilled water. The four different amounts, namely 0.25 mg/L, 0.5 mg/L, 0.75 mg/L and 1.0 mg/L of expired Calcitriol was prepared. The testing of corrosion inhibition action in the absence and presence of expired Calcitriol at four different amounts on the copper surface in the 5 M HCl solution was examined by weight loss technique.

The protection efficiency of expired Calcitriol was calculated from the mathematical equation represented below;

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

Where,  $W_1$  = Copper weight loss in unprotected system, and  $W_2$  = Copper weight loss in the protected system.

The electrochemical studies (both Tafel plots and AC impedance spectroscopy) were carried out by using the CHI660C workstation. The CHI660C workstation having three electrode system (copper metal = working electrode, platinum = counter electrode and calomel electrode = reference electrode).

The electrochemical studies were performed in the potential range + 250 mV to - 250 mV with a scan rate of 0.1 v/S. The Nyquist plot was recorded in the frequency range of  $10^5$  Hz to 1 Hz with 10 points per decade.

The corrosion protection efficiency of nontoxic corrosion inhibitor was evaluated from the below mathematical equations:

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

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

Where,  $i'_{\text{corr}}$  = Protected copper metal corrosion current density,  $i_{\text{corr}}$  = Unprotected copper metal corrosion current density,  $R_{\text{ct}}$  = Unprotected copper metal charge transfer resistance,  $R_{\text{ct(inh)}}$  = Protected copper metal charge transfer resistance.

Scanning electron microscopy (SEM) technique was carried out to examine the copper electrode surface in the protected and unprotected systems.

## Results and discussion

### *Weight loss technique*

The weight loss of copper in the 5 M HCl solution without and with corrosion inhibitor was examined with different immersion time of 2, 4, 6, 8 and 10 hours. The weight loss results are shown in the **Table 1**. From the **Table 1**, it is clear that, the copper electrode weight loss in the protected system (in the presence of corrosion inhibitor) is low compared to the bare system (in the absence of corrosion inhibitor). The decrease in the weight loss of copper electrode in the protected system is an indication of corrosion inhibition property of expired Calcitriol on the copper surface in the studied acid system (5 M HCl solution). The electron rich elements in the expired Calcitriol drug participate in the adsorption process. As a result of this, protective layer is generated on the copper surface in the 5 M HCl solution. The formed protective film blocks the direct contact of hydrochloric acid with the copper electrode. Hence, protection rate enhances with a rise in the concentration of the expired Calcitriol drug. It is also observed that, the protection efficiency decreases with a rise in the contact time from 2 hours to 10 hours. This nature is due to the presence of an unstable protective layer at longer immersion period. The unstable protective later easily allows the hydrochloric acid solution towards active sites of copper electrode. Hence, weight loss of copper electrode enhances with a rise in the contact time from 2 hours to 10 hours. Therefore, protection efficiency slightly decreases with a rise in the contact time from the 2 hours to 10 hours.

**Table 1 Gravimetric results**

Concentration (mg/L)	Contact time (hours)	Protection efficiency in percentage
Bare	2	
0.25		83.750
0.50		86.250
0.75		88.750
1.00		91.250
Bare	4	
0.25		77.419
0.50		83.870
0.75		88.709
1.00		91.935
Bare	6	
0.25		65.116
0.50		72.093
0.75		77.906
1.00		80.232
Bare	8	
0.25		58.252
0.50		64.077
0.75		68.932
1.00		73.786
Bare	10	
0.25		60.629
0.50		66.141
0.75		70.866
1.00		78.740

**Table 2 Potentiodynamic polarization results**

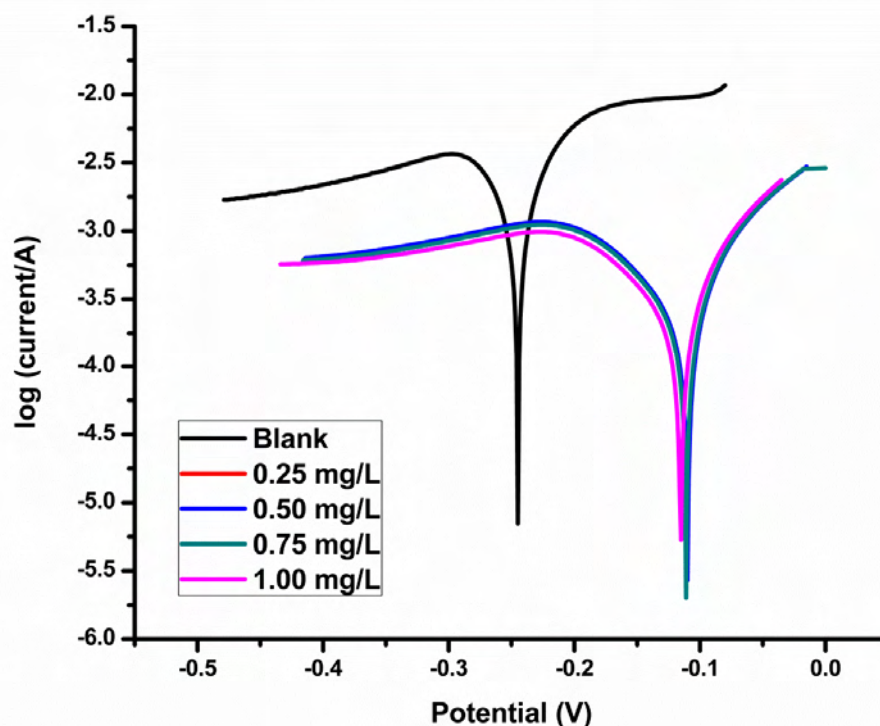
Concentration (mg/L)	Corrosion potential (mV)	Cathodic Tafel slope (V/dec)	Anodic Tafel slope (V/dec)	Corrosion current (A)	Protection efficiency
Bare	-245	2.490	1.592	0.01258	
0.25	-110	3.324	7.698	0.0007003	94.433
0.50	-110	3.322	7.715	0.0006953	94.472
0.75	-111	3.181	7.762	0.0006908	94.508
1.00	-115	2.819	1.002	0.0002922	97.677

**Table 3 Nyquist plot results**

Concentration (mg/L)	Charge transfer resistance ( $\Omega$ )	Protection efficiency (%)
Bare	49.91	
0.25	178.9	72.101
0.50	251.1	80.123
0.75	477.6	89.549
1.00	511.9	90.250

### *Tafel plot studies*

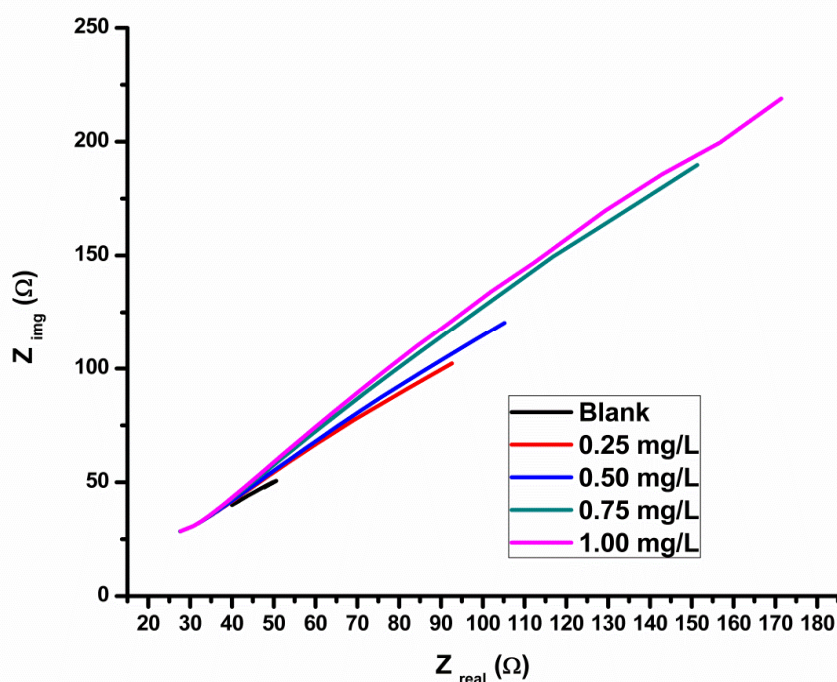
The results of potentiodynamic polarization of copper in the 5 M HCl solution without and with four different amounts of expired Calcitriol drug was shown in the **Figure 2**. The results of Tafel plots are shown in the **Table 2**. The results are presented in the **table 2** shows that, the copper corrosion density values decreases with rise in the concentration of the corrosion inhibitor, which is due to the presence of protective layer on the surface of the copper metal in the 5 M HCl solution. The presence of protective layer on the copper surface in the 5 M HCl solution decreases the direct contact between the copper electrode and 5 M HCl solution. Hence, corrosion current density values decreases with rise in the concentration of the expired Calcitriol drug. Further, there is a change in the anodic Tafel slope values compare to blank one. Hence, expired Calcitriol drug can be classified into anodic type corrosion inhibitor in the 5 M HCl solution.



**Figure 2** Tafel plots without and with corrosion inhibitor

### *AC impedance spectroscopy*

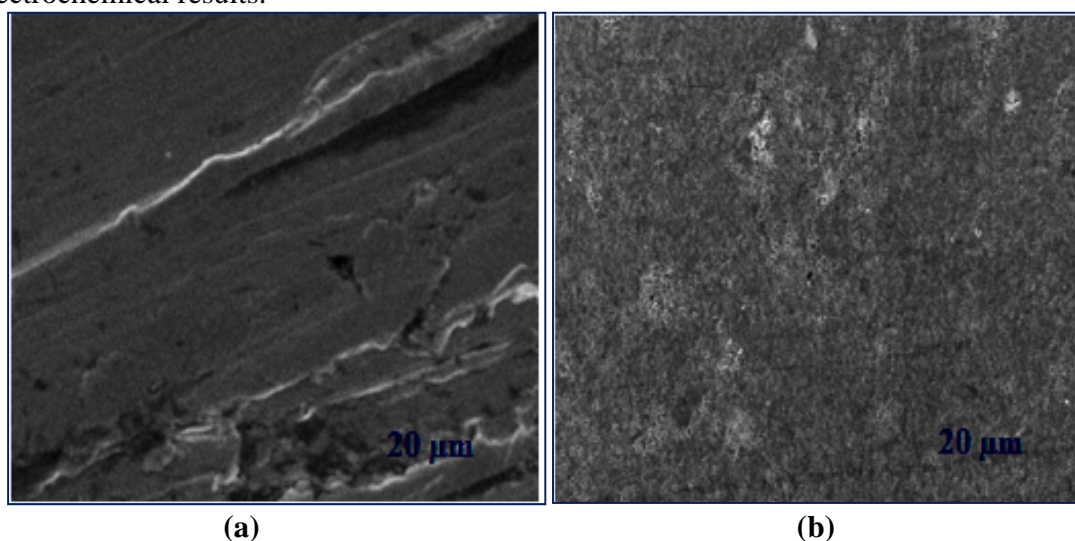
AC impedance spectroscopy is another electrochemical technique used to examine the effectiveness of expired Calcitriol drug that is used to protect the copper surface in the 5 M HCl solution. The Nyquist plot results are shown in the **Figure 3** and **Table 3**. The charge transfer resistance values enhances with a rise in the concentration of the expired Calcitriol drug is an indication of the copper corrosion inhibition property of the expired Calcitriol drug in the 5 M HCl solution. The corrosion inhibition property of expired Calcitriol drug is due to the charge transfer process. The maximum corrosion inhibition property obtained from the AC impedance spectroscopy technique is 90.250 %.



**Figure 3 Nyquist plots without and with inhibitor**

#### Scanning electron microscopy

The SEM images were obtained from the copper surface submerged in the 5 M HCl solution without and with expired Calcitriol drug. The resulted images are shown in the **Figure 3 a, b**. In unprotected system, the copper electrode is highly damaged which is due to the direct attack of corrosive ions. In the protected system, smooth surface observed which is due to the formation of protective film on the copper surface in the 5 M HCl solution. The SEM images fully support the chemical and electrochemical results.



**Figure 3 (a, b) SEM images without and with corrosion inhibitor**

### Conclusions

The present research article describes the experimental investigation of the corrosion inhibition property of the expired Calcitriol drug on the copper surface in the 5 M HCl solution with the aid of weight loss, Tafel plot and AC impedance spectroscopy techniques. Weight loss studies show that, the protection efficiency rises with increase in the concentration of the expired Calcitriol drug. The Tafel plot studies show the anodic corrosion inhibition property of expired Calcitriol drug on the copper surface in the 5 M HCl solution. AC impedance spectroscopy and SEM studies fully supports the results of weight loss and Tafel plot studies.

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