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Protective Effects of Expired Abarelix Drug as a Non-Toxic Corrosion Inhibitor for Mild Steel in 3M HCl Solution

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Abstract

The corrosion inhibition efficiency of expired Abarelix drug on the surface of the mild steel (MS) in 3 M HCl media was examined by weight loss, gasometric, atomic absorption spectroscopy, potentiodynamic polarization and AC impedance techniques. Gravimetric (weight loss) results showed that, protection efficiency is directly related to the expired Abarelix drug concentration and inversely proportional to the immersion time. Adsorption of expired Abarelix drug species on the mild steel in acid media was confirmed by gasometric, and atomic absorption spectroscopy techniques. Further, the decrease in corrosion current density value with an increase in the amount of expired Abarelix drug is an indication of corrosion inhibiting action of the expired Abarelix drug on the metal surface in acid system. Nyquist plots clearly indicate the inhibition role of expired Abarelix drug on the metal surface. Surface (scanning electron microscopy [SEM]) technique also showed that, morphology observed in protected MS system is different from the unprotected system.

Keywords: Expired Abarelix drug, Mild steel, Atomic absorption spectroscopy, Nyquist plot, Scanning electron microscopy

INTRODUCTION

Mild steel (MS) metals are emerging as central material in several industries because of their good metallurgical and physicochemical properties. MS undergo dissolution when they come in contact with the acid solution, which destroy the material property and affects the economics of the country. Hence, protection of mild steel from the corrosion is very much essential (Lebrini et al. 2005; Bahrami et al. 2010; Perumal et al. 2017; Raghavendra and Bhat, 2018; Khadom et al. 2018). Even though several methods are known for the prevention of MS corrosion, the inhibitors are the best choice for the prevention of dissolution rate of the MS in any media. Many synthetic species (inhibitors) containing the electron rich elements protect metals by the formation of a thin film over the MS surface (Sam John et al. 2017; Ankush Mishra et al. 2018). But, majority of synthetic molecules is expensive and noxious to the human beings. Hence, their application in actual branches should be banned. Expired drugs are in use in order to control the MS corrosion as they are unfit for the consumers and they are eco-friendly (Gunasekaran et al. 2004; Eddy et al. 2010; Priyanka Singh et al. 2017). Therefore, current study is aimed at exploring the MS protection property by expired Abarelix drug in the 3M HCl solution by employing the weight loss (mass loss), gasometric, atomic absorption spectroscopy, potentiodynamic polarization and AC impedance techniques. Topography studies were visualized by Scanning Electron Microscopy (SEM) method.

MATERIAL AND METHOD

Sample preparation

99 % of MS was employed for weight loss, gasometric, atomic absorption spectroscopy, potentiodynamic polarization, AC impedance and SEM techniques. MS are abraded by sand papers of different grades. The

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weight loss of MS sample was recorded by four digit analytical weighing balance. The MS metal completely submerged in 250 ml of 3 M HCl solution in a conical flask. Weight loss of MS was recorded without and with 1 mg/L, 2 mg/L, 3mg/L and 4 mg/L of expired Abarelix drug. The corrosion test was repeated to get concordant values.

Weight loss technique

Mass loss of MS was determined without and with inhibitor of different amounts at 60 ^{0}C with an immersion period of 3, 6, 9, 12, and 15 hours. The loss of MS weight was recorded in protected and unprotected systems (Tawancy et al. 2004). Finally, the protection efficiency can be calculated from the below relation:

$$\text{Corrosion protection efficiency} = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

Where, W_1= MS mass loss in plain corrosive solution and W_2= MS mass loss in corrosive solution plus inhibitor.

Atomic absorption spectroscopy (AAS) technique

The soluble of iron content of MS was noticed in the protected and unprotected systems by using the AAS (Mayakrishnan Prabakaran et al. 2018).

The protection efficiency can be calculated from the equation below;

$$\textbf{Corrosion protection efficiency} = \frac{B-A}{B} \times 100 \quad (2)$$

Where, B= Amount of dissolved iron content of MS in uninhibited system and A= Amount of dissolved iron content of MS in protected system.

Gasometric studies

The volume of hydrogen (H_2) gas evolution was examined by gasometric studies. The volume of hydrogen gas evolution in protected and unprotected system was recorded and protection efficiency can be calculated as per the following equation (3) (Fouda et al.2016).

$$\text{Inhibition efficiency} = \frac{V_a - V_p}{V_a} \times 100 \quad (3)$$

Where, V_a= H_2 gas liberated in plain system, and V_p= H_2 gas liberated in the protected system.

Tafel plot and impedance studies

Both Tafel and impedance curves were recorded by using CHI workstation. The OCP (open circuit station) used in this process is ± 250 mV at 0.1 v/S.

Surface studies

The SEM studies of MS surface without and with 4 mg of expired drug were screened at immersion period of one hour.

Results and Discussion

Weight loss studies

The results of weight loss studies are collected in table 1**.** It is clear that, protection rate enhanced by an increase in the expired Abarelix drug concentration and decrease with an increase in the contact time. A stable protective film created on the MS in 3 M HCl solution at 4 mg of expired Abarelix drug. The influence of solution contact time on the MS corrosion rate in the absence and presence of expired Abarelix drug was screened at different solution time by weight loss technique. Change in contact time has the greatest influence on the protection efficiency of the expired Abarelix drug. From the table, it is observed that, the examined corrosion inhibitor blocks the MS corrosion process at all the studied immersion period with inverse relationship. But, the inhibition property varies with different immersion time. Thus, the expired Abarelix drug acts as an MS corrosion inhibitor with time-dependent mode. At immersion period of 15 hours, the expired Abarelix drug shows minimum corrosion inhibition property which is due to unstable protective film formed on the MS surface at higher immersion period.

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Table 1 Weight loss results of Mill steel (MS) samples

Concentration (mg/L)	Immersion period in hours	Surface coverage (Θ)	Protection efficiency (in percentage)
Blank	3		
1		0.75	75.000 ± 0.011 %
2		0.80	80.000 ± 0.020 %
3		0.90	90.000 ± 0.022 %
4		0.95	95.000 ± 0.006 %
Blank	6		
1		0.77	77.142± 0.031 %
2		0.80	80.000± 0.025 %
3		0.85	85.714± 0.067 %
4		0.88	88.571± 0.010 %
Blank	9		
1		0.80	80.327±0.030 %
2		0.83	83.606±0.022 %
3		0.86	86.885±0.028 %
4		0.90	90.163±0.027 %
Blank	12		
1		0.76	76.666±0.023 %
2		0.78	78.888±0.019 %
3		0.81	81.111±0.021 %
4		0.83	83.333±0.015 %
Blank	24		
1		0.72	72.727±0.020 %
2		0.79	79.090±0.023 %
3		0.81	81.818±0.028 %
4		0.86	86.363±0.024 %

Gasometric studies

The amount of hydrogen gas evolved in protected and unprotected systems was tabulated in the Table 2. From the table, it is observed that, the amount of hydrogen gas evolved in inhibiting system is low as compared to the uninhibited system. The differences in the amount of hydrogen gas evolved in protected and unprotected system clearly show the corrosion inhibition property of expired Abarelix drug. The amount of hydrogen gas evolved enhances with contact time. The increase in the contact time of MS in 3 M HCl solution breaks the protective layer generated on the MS surface. Hence, free acid ions directly attack with MS surface and enhance the disintegration rate. As a result of these, minimum protection efficiency and slightly high MS corrosion rate observed at higher immersion period.

Atomic absorption spectroscopy technique

The amount of dissolved iron content in the 3 M HCl solution was examined without and with inhibitor by atomic absorption spectroscopy technique. The results of AAS are shown in the Table 3. The amount of dissolved iron content of MS in 3 M HCl solution is low compared to the unprotected system, which confirms the MS protection role of the corrosion inhibitor. The presence of expired Abarelix drug on the MS surface blocks the dissolution rate of MS surface. Hence, the amount of dissolved iron content decreases in the protected system.

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Table 2. Gasometric results of mill steel samples in 3M HCl

Concentration (mg/L)	Immersion period in hours	Volume of hydrogen gas evolved in (ml)	Protection efficiency (in percentage)
Blank	3	28.3	
1		8	71.731 ± 0.013%
2		7	75.265 ± 0.014%
3		5	82.332 ± 0.012 %
4		3	89.399 ± 0.014%
Blank	6	39	
1		7.1	81.794 ± 0.032 %
2		6	84.615± 0.018 %
3		4.8	87.692± 0.013 %
4		3.1	92.051± 0.014 %
Blank	9	58	
1		11.1	80.862 ± 0.023 %
2		10.3	82.241 ± 0.024 %
3		8.1	86.034 ± 0.021 %
4		6.3	89.137 ± 0.022 %
Blank	12	87.5	
1		15.1	82.742 ± 0.023 %
2		11.3	87.085 ± 0.025%
3		10.1	88.457 ± 0.026 %
4		8.1	90.742 ± 0.027 %
Blank	24	100	
1		20	80.000 ± 0.024 %
2		15.8	84.200 ± 0.025%
3		15	85.000 ± 0.026 %
4		13.4	86.600 ± 0.025 %

Table 3. AAS results at 3 hours immersion period of mild steel

Concentration (mg/L)	Amount of mild steel dissolved in 3 M HCl solution (g)	Protection efficiency (%)
Blank	0.051	
1	0.009	82.352± 0.023 %
2	0.007	86.274± 0.027 %
3	0.006	88.235± 0.021 %
4	0.005	90.196 ± 0.024 %

Tafel plot studies

Tafel plot of MS surface in 3 M HCl environment without and with 1 mg, 2 mg, 3 mg and 4 mg of expired Abarelix drug as shown in the Figure 1. The results of Tafel plots are presented in the Table 4. From the table 4, it is clear that, the value of MS corrosion current density decreases with a rise in the expired Abarelix drug amounts. The decrease in the corrosion current density value with increase in

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the inhibitor concentration is a clear hint of corrosion inhibition property of expired Abarelix drug on the MS in the 3 M HCl solution. The protective layer generated on the MS surface reduces the corrosion current density value and corrosion rate. There is no significant change in the corrosion potential (E_{corr}) cathodic (βc) and s anodic Tafel slope (βa) values. Hence, expired Abarelix drug classified as a mixed type corrosion inhibitor, which indicates the both cathodic and anodic corrosion inhibition behavior of expired Abarelix drug. In this study, the E_{corr} is less than 85 mV. Hence, it is classified as a mixed corrosion inhibitor.

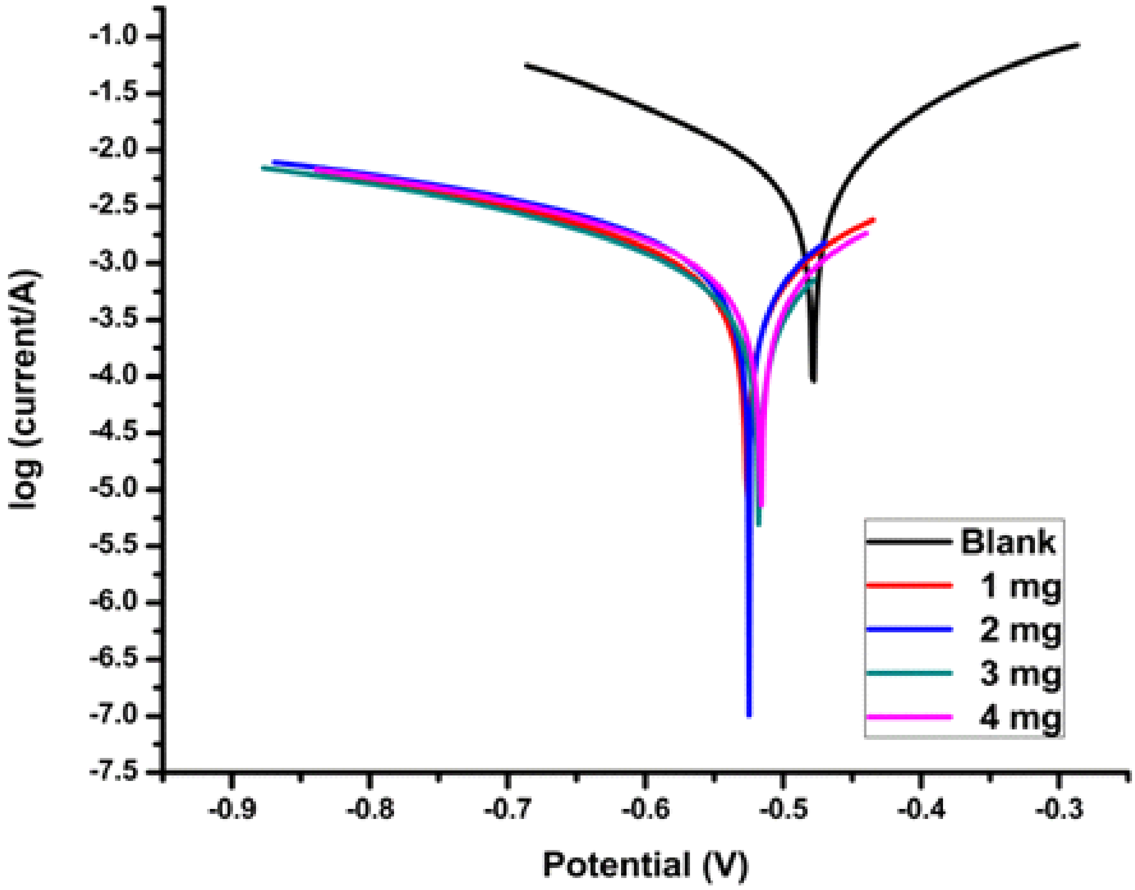

Fig. 1. Tafel plots without and with expired Abarelix drug

Table 4 Tafel results of mild steel surface in 3M HCL

Concentration (mg/L)	Corrosion potential (mV)	Cathoidc Tafel slope (V/dec)	Anodic Tafel slope V/dec)	Corrosion current (A)	Protection efficiency (%)
Blank	478	5.792	7.183	0.006398	
1	526	4.582	6.669	0.0008230	87.136
2	525	4.501	1.317	0.0004317	93.252
3	518	4.993	1.401	0.0003013	95.290
4	516	4.644	1.663	0.0002838	95.564

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Impedance spectroscopy

Nyquist plots without and with corrosion inhibitor as shown in the Figure 2. The results of impedance plots are shown in the Table 5. The charge transfer resistance values obtained by using the circuit is shown in the Figure 3. The charge transfer resistance values are directly proportional to expired Abarelix drug concentration. Higher the value of charge transfer resistance values higher will be the protection efficiency. The high charge transfer resistance value observed at 4 mg of expired Abarelix drug, which indicates that, high protection of MS surface achieved at 4 mg of expired Abarelix drug.

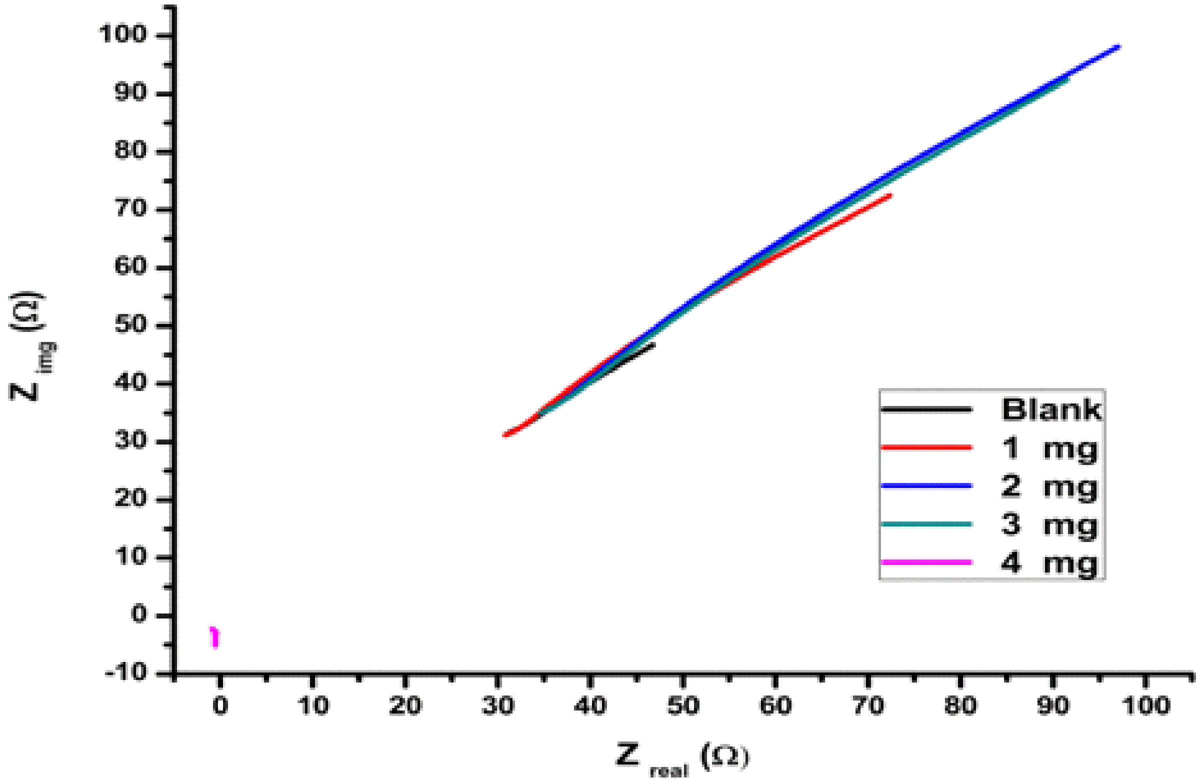

Fig 2. Nyquist plots

Table 5 Charge transfer resistance values obtained in impedance studies

Concentration (mg/L)	Charge transfer resistance (Ω)	Protection efficiency (%)
Blank	37.80	
1	41.79	9.540
2	88.75	57.400
3	93.26	59.460
4	113.6	66.725

Scanning electron microscopy technique

MS surface topography is shown in the Figure 4. MS surface. MS surface in unprotected system is very rough and smooth in protected system. This difference clearly confirms the corrosion inhibition property of expired Abarelix drug.

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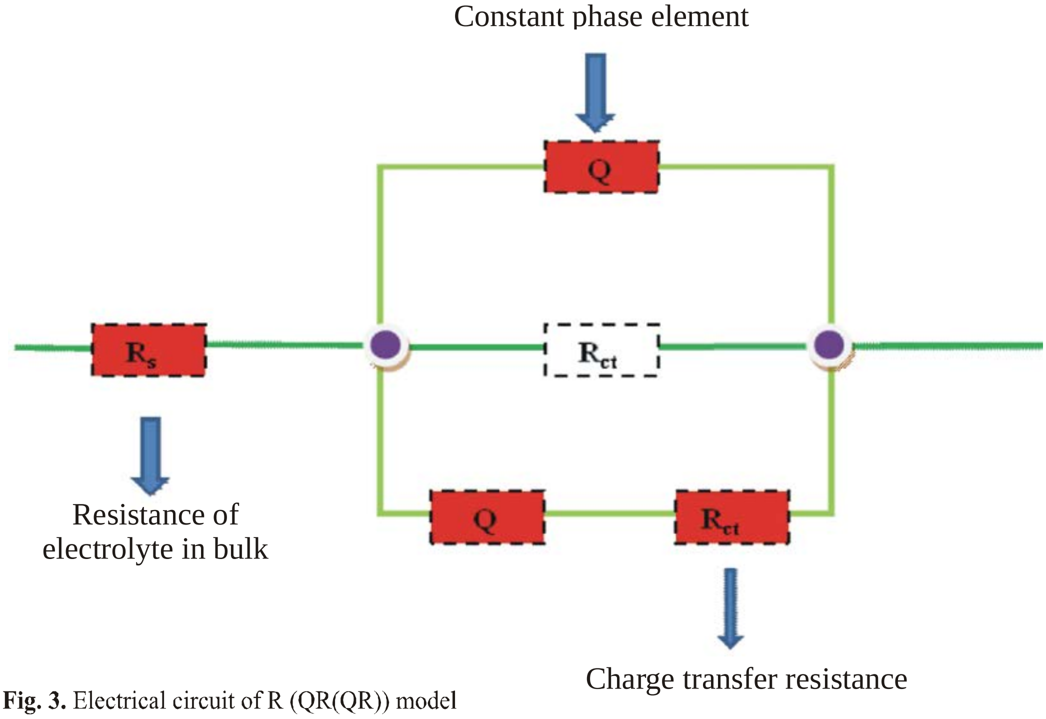

Fig. 3. Electrical circuit of R (QR(QR)) model

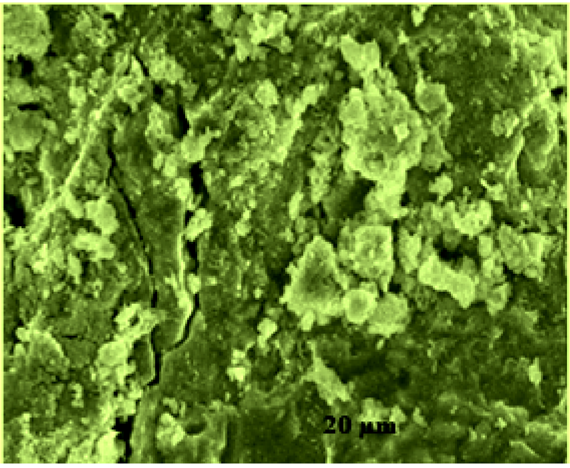

Figure 4 SEM images **A)** without expired Abarelix drug

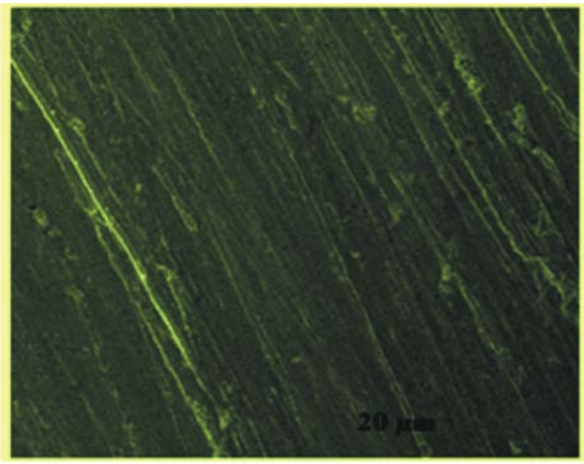

Figure 4 SEM images **B)** with expired Abarelix drug

In our previous investigation (Raghavendra, 2018), we studied the corrosion inhibition property of expired perindopril drug on the mild steel surface in the 3 M HCl solution.

The expired perindopril drug shows the 95 % corrosion inhibition property (via weight loss technique) at 4 mg/L of expired drug product with an immersion period of three hours. In our current investigation, expired Abarelix drug also shows the 95 % corrosion inhibition property 4 mg/L of expired product on the mild steel surface in the 3 M HCl solution. The electron rich elements present in the expired perindopril drug plays a vital role in the inhibition of mild steel corrosion process in the acidic environment. The protection efficiency obtained from the chemical technique is different from the electrochemical technique. The different experimental condition and time is the main reason for the observed deviation in the protection efficiency values.

CONCLUSION

The corrosion inhibition property of expired Abarelix drug was confirmed by weight loss, gasometric, AAS, Tafel plot and impedance spectroscopy techniques. Weight loss technique shows the corrosion inhibition property of

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expired Abarelix drug mainly depends on the contact time of MS in 3 M HCl solution. Mixed corrosion inhibition property was confirmed by Tafel plot studies. Surface study by SEM confirms the inhibiting property of expired Abarelix drug.

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