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Expired Amitriptyline Drug as a New Nontoxic Inhibitor Protecting Mild Steel Corrosion in HCl Solution

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Abstract

The corrosion inhibition behavior of expired amitriptyline drug on the mild steel in 3M HCl solution was investigated through potentiodynamic polarization, alternating current impedance spectroscopy and atomic absorption spectroscopy techniques. Furthermore, the surface morphology of mild steel in 3M HCl solution was screened by scanning electron microscopy technique. The electrochemical results showed that increasing the expired amitriptyline drug concentration enhanced the protection efficiency of the corrosion inhibitor, depicting that the inhibition property is dependent on the expired amitriptyline drug amounts. Potentiodynamic polarization plots clearly hint the mixed corrosion inhibition property on the mild steel in 3 M HCl solution. The charge transfer resistance values in the presence of the expired amitriptyline drug were higher compared to the bare system. Further, atomic absorption spectroscopy and scanning electron microscopy results fully supports the corrosion inhibition property of expired amitriptyline drug on the mild steel surface in acidic system.

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Introduction

Mild steel metal is exposed to the hydrochloric acid solution in industrial pickling and descaling processes. Mild steel corrosion usually describes the deterioration or destruction of a mild steel due to the reaction with the acidic environment (usually HCl) [1-3]. Among the many approaches for the mitigation of mild steel corrosion, use of corrosion inhibitors is the prominent one. Many organic compounds show the corrosion inhibition property over the mild steel surface in the 3 M HCl solution. Most of the synthetic organic compounds are hazardous and contaminate the surrounding atmosphere. The corrosion resistance and cost of the organic species are the main concern and must be considered for the industrial level applications [4-8]. Hence, nowadays cheap and nontoxic corrosion inhibitors are considered.

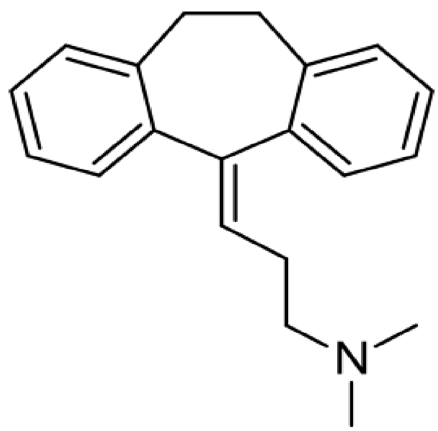

Fig. 1 Chemical structure of amitriptyline drug.

The corrosion inhibitors are introduced into the hydrochloric acid solution to decrease or prevent the mild steel weight loss and consumption of acid rate. The cheap, nontoxic and eco-friendly corrosion inhibitors are widely ranged from the expired drugs, animal extracted forms and plant extract species [9, 10]. Although many expired dugs, animal extracted and natural extracts are successfully employed as nontoxic corrosion inhibitors. But only limited work is carried out in order to solve the dissolution problem in various industrial sections. Hence, in the current study, we selected expired amitriptyline drug because it is not useful for consumers. The structure of the amitriptyline drug is shown in the Fig. 1. The chemical structure of the amitriptyline shows that it contains nitrogen and double bonds in their moieties, which is expected to show good corrosion inhibition property on the mild steel surface in 3 M HCl solution. The corrosion inhibition property of expired amitriptyline drug was screened by potentiodynamic polarization, alternating current (AC) impedance spectroscopy, atomic absorption spectroscopy and scanning electron microscopy techniques.

Materials and Methods

The mild steel pieces of 99% purity were generally abraded with different grade sand papers for the potentiodynamic polarization, AC impedance spectroscopy, atomic absorption spectroscopy and scanning electron microscopy techniques. The expired amitriptyline drug (obtained from the local medical shop Shivamogga, Karnataka-India) of concentrations 0.5 mg/L, 1 mg/L, 1.5 mg/L and 2 mg/L was used for the present investigation. The mild steel corrosion process in aqueous systems is electrochemical phenomena. The electrochemical technique was used to gain insight into form and rate of dissolution of metal. The electrochemical studies were carried out by using the CHI660C workstation. Generally, electrochemical studies are performed by using the three conventional electrodes namely tested metal as working electrode, platinum as counter electrode and saturated calomel electrode as reference electrode. The mild steel metal was immersed in the 3M HCl solution for about one hour to establish the open circuit potential (steady state). The electrochemical plots were recorded in the aerated solution at ambient temperature. The electrochemical readings were recorded at 1 mV/s scan rate in the potential range of ±250 mV. AC impedance spectroscopy experiment was carried out in the frequency range of 10^5 Hz to 1 Hz with 10 points per decade.

From the corrosion current density value obtained from Tafel plots, the protection efficiency in percentage was calculated as per the following equation:

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

where, I'_{corr} = the value of corrosion current density in the protected system and i_{corr} = the value of corrosion current density value in the unprotected system.

From the impedance spectroscopy, the protection efficiency was calculated as per the below relation:

$$\text{Protection efficiency (\%)} = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100$$

where, R_{ct} = the value of charge transfer resistance in unprotected system and $R_{ct(inh)}$ = the value of charge transfer resistance in protected system.

Atomic absorption spectroscopy (model G8-908, Australia) was used in order to find out the amount of dissolved iron content in the 3M HCl solution without and with inhibitor of four different concentrations (0.5 mg/L, 1 mg/L, 1.5 mg/L and 2 mg/L). The protection efficiency was calculated as per the following equation:

$$\text{Corrosion protection efficiency (\%)} = \frac{B-A}{B} \times 100$$

Where, B = amount of dissolved iron content in unprotected system and A = amount of dissolved iron content in protected solution.

The surface morphology of mild steel in the absence and presence of the expired amitriptyline drug was characterized by scanning electron microscopy technique. The scanning electron microscopy was carried out in order to get insights about the mild steel morphological changes on the electrode in protected and unprotected system. The mild steel metal was immersed in the 3M HCl solution without and with 0.4 mg/L of corrosion inhibitor (expired amitriptyline drug) with contact time of 3 hour.

Results and Discussion

Potentiodynamic polarization technique

Potentiodynamic polarization plots for mild steel in 3M HCl solution without and with expired amitriptyline drug at four concentration levels is shown in Fig. 2. According to the results, the corrosion current density values decreased with the rise in concentration of expired amitriptyline drug. The protection efficiency was also enhanced with rise in the expired amitriptyline drug concentration (Table 1). The differences between corrosion potential (E_{corr}) values in protected and unprotected systems was less than ±85 mV. Hence, expired amitriptyline drug falls under the category of mixed type corrosion inhibitors [11]. The presence of heteroatom's and electron rich groups in the expired amitriptyline drug can form strong resistant barrier film on the cathodic and anodic area of mild steel in 3M HCl solution and retards the dissolution or disintegration reaction. The variation in the cathodic and anodic Tafel slope values indicates that the inhibitor affects both the cathodic and anodic reactions [12]. The cathodic and anodic Tafel slope values do not change in linear manner, indicating the mixed corrosion inhibition property of expired amitriptyline drug. Similar observations were reported by El-Etre in 2008 [13].

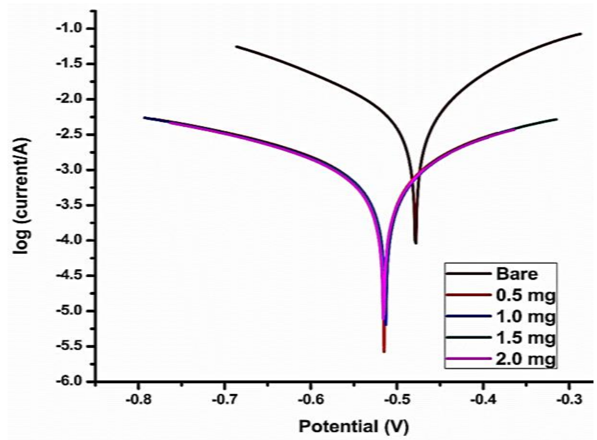

Fig. 2 Tafel plot with and without amitriptyline drug as corrosion inhibitor of mild steel used at four different concentrations.

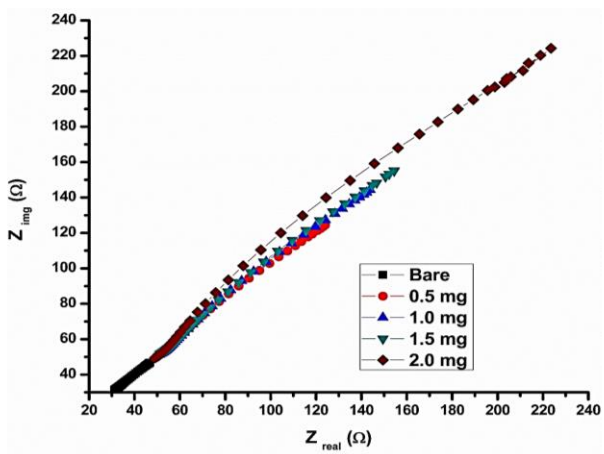

Fig. 3 Nyquist plot with and without amitriptyline drug as corrosion inhibitor of mild steel used at four different concentrations.

AC impedance spectroscopy technique

The impedance studies were carried out on the mild steel in 3M HCl solution without and with expired amitriptyline drug at four concentration levels. The Nyquist plot is shown in the Fig. 3. The results obtained from the impedance techniques are shown in the Table 2. The results showed that the charge transfer resistance values increased with the rise in expired amitriptyline drug concentration. This proves the formation of protective layer on the surface of mild steel in 3M HCl solution. The electron rich elements in the expired amitriptyline drug were adsorbed on the mild steel surface which

Table 1 Tafel plot results of mild steel in 3M HCl solution in protected and unprotected systems.

Concentration (mg/L)	Corrosion potential (mV)	Cathodic Tafel slope (V/dec)	Anodic Tafel slope (V/dec)	Corrosion current (A)	Protection efficiency (%)
Bare	-478	5.792	7.183	0.0064	-
0.5	-515	4.686	5.518	0.00088	86.273
1.0	-513	4.737	5.537	0.00084	86.795
1.5	-515	4.701	5.573	0.00084	86.881
2.0	-516	4.780	5.659	0.00079	87.577

reduced the attack of corrosive ions and protected it from the dissolution or disintegration process.

Each Nyquist plot shape is very similar in the absence and presence of the corrosion inhibitor, which indicates that introduction of corrosion inhibitor caused no change in the mild steel corrosion mechanism. Similar observations were reported by Raghavendra and Bhat [14]. Analysis of Nyquist plot shows that the impedance plots were larger in the presence of expired amitriptyline drug as compared to the bare system. The diameter of the Nyquist plot enhanced with rise in the concentration of the expired amitriptyline drug and it is the result of adsorption of corrosion inhibitor on the surface of mild steel, consequently corrosion inhibition property increased. The higher anticorrosive properties of expired amitriptyline drug can be related to the formation of homogenous and strong film on the surface of mild steel by continuous adsorption. The maximum corrosion inhibition property obtained from the AC impedance spectroscopy technique was 82.3%.

Atomic absorption spectroscopy technique

The results of atomic absorption spectroscopy are shown in the Table 3. From the table, it is clear that the amount of iron content of the mild steel decreased with rise in the concentration of the expired amitriptyline drug, which is due to the formation of protective layer on the mild steel surface in 3M HCl solution. This clearly indicates the corrosion inhibition property of expired amitriptyline drug on the mild steel surface in 3M HCl solution. These results are attributed to the increase in the surface coverage due to the greater adsorption of expired drug molecules on the mild steel in the 3M HCl solution. The presence of electron rich elements in the expired drug produced the high protection efficiency. The maximum protection efficiency obtained was 94%. The results obtained from the atomic absorption spectroscopy are in good agreement with the results of potentiodynamic polarization and AC impedance spectroscopy studies.

Table 2 Alternating current (AC) impedance spectroscopy results with and without amitriptyline drug as corrosion inhibitor of mild steel used at four different concentrations.

Concentration (mg/L)	Charge transfer resistance (Ω)	Protection efficiency (%)
Bare	37.8	-
0.5	127.4	70.3
1.0	148.8	74. 6
1.5	162.1	76.7
2.0	214.1	82.3

Table 3 Atomic absorption spectroscopy results of mild steel metal in 3M HCl solution treated with and without amitriptyline drug as corrosion inhibitor of mild steel used at four different concentrations.

Concentration (mg/L)	Dissolved iron content in 3M HCl solution	Protection efficiency (%)
Bare	0.050	-
0.5	0.020	60
1.0	0.010	80
1.5	0.005	90
2.0	0.003	94

Scanning electron microscopy technique

The results of scanning electron microscopy are shown in the Fig. 4. In unprotected system, irregular damaged surface with pores and cavities can be observed clearly, which is due to the mild steel dissolution because of direct attack of hydrochloric acid ions. The photograph of protected (with 2 g/L of expired amitriptyline drug) mild steel showed the smooth surface which is due to the protection property of adsorbed film on the mild steel surface in hydrochloric acid system. The differences in the surface morphology in unprotected and protected systems prove the corrosion inhibition property of expired amitriptyline drug on the mild steel surface in 3 M HCl solution.

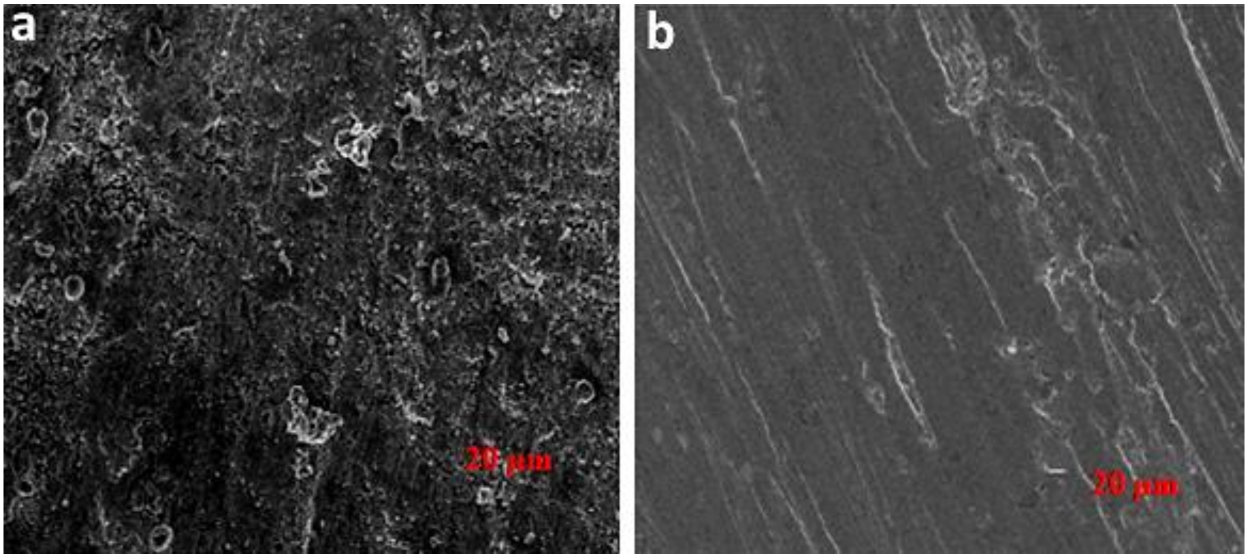

Fig. 4 Scanning electron microscropy images of mild streel surface in 3M HCl solution without (**a**) and with (**b**) amitriptyline drug as corrosion inhibitor used at four different concentrations.

Conclusions

The results of the current study showed that expired amitriptyline drug act as good corrosion inhibitor for mild steel in 3M HCl solution. The protection efficiency enhanced with rise in the expired amitriptyline drug concentration. The results of Tafel plots showed that expired amitriptyline drug act as mixed type corrosion inhibitor by controlling the both cathodic and anodic mild steel corrosion reactions. Impedance studies shows that charge transfer resistance process plays vital role in the inhibition of mild steel dissolution process in 3M HCl solution. Atomic absorption spectroscopy results showed that the amount of dissolved iron in 3M HCl solution was inversely proportional to concentration of expired amitriptyline drug. Scanning electron microscopy results fully support the potentiodynamic polarization, AC impedance spectroscopy and atomic absorption spectroscopy results.

Conflict of interest

The authors declare that they have no conflict of interest.

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