Expired azithromycin and roxithromycin drugs as environmentally friendly inhibitors for mild steel corrosion in H₂SO₄ solutions

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ABSTRACT

The inhibitory impacts of two expired drugs, namely, azithromycin (AZM) and roxithromycin (RXM) towards the corrosion of mild steel (MS) in 1.0 M H₂SO₄ solution were examined exploiting potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss techniques. The results obtained from various employed techniques indicate that increasing the concentration of examined expired drugs and reducing the temperature increased the inhibition efficiencies. Potentiodynamic polarization indicated that the expired AZM and RXM drugs acted as mixed-type inhibitors, but the cathode was highly polarized, β_c > β_a. The inhibiting power of these compounds is interpreted based on their adsorption on the surface of MS. The adsorption process obeys Langmuir isotherm. Impedance data confirmed that MS corrosion is under charge transfer control and the adsorption of both expired drugs on the MS surface led to the formation of protective film. The inhibition efficiency of RXM is greater than that of AZM due to the increased molecular weight and number of electron donating group within the expired drug. Activation and adsorption thermodynamics parameters were computed and interpreted. The adsorption process is spontaneous and endothermic.

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1. Introduction

Corrosion of iron and steel, especially in industrial processes causes serious problems and significant economic losses which affects national income and, therefore, many scientists are interested in reducing or preventing risks. There are many ways to control the corrosion of iron and steel. The most important and effective method is the use of corrosion inhibitors (1). In general, most corrosion inhibitors are organic compounds containing in their chemical structure hetero atoms, aromatic rings, or multiple bonds (2–16). Most of these compounds have an effective inhibitory effect by their adsorption on the metal surface. The intensity
of adsorption was found to depend on the chemical properties of the compound such as the presence of some active groups and the electron density on the donor atoms (17). Unfortunately, these compounds give high inhibition efficiency, but most of them are toxic and non-environmentally friendly. Therefore, scientists turned to the use of some expired drugs to employ them in the inhibition of the corrosion of iron and its alloys. These compounds do not cause any harm to humans or the environment and the use of expired drugs as corrosion inhibitors solves two major environmental and economic problems: reducing environmental pollution with pharmaceutically effective compounds and reducing the costs of disposing of expired drugs. Also, expired drugs, including many active centers, facilitate the adsorption process and give high inhibition efficiencies (18–25). Usually, 1.0 M H₂SO₄ solution is utilized in many industries such as acid pickling scaling, industrial cleaning, but, unfortunately, corrosion of steel has occurred, causing many economic problems. Therefore, the main objective of this manuscript is the economic and environmental benefits of two expired drugs, azithromycin (AZM) and roxithromycin (RXM) as inhibitors for the corrosion of mild steel (MS) in 1.0 M H₂SO₄ solution rather than eliminating and not using them. Three dissimilar techniques were used such as potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and weight loss (WL). Furthermore, the effect of elevated temperatures on the MS corrosion in 1.0 M H₂SO₄ solution containing some concentrations of the expired drugs was investigated and various thermodynamic parameters of activation and adsorption were evaluated and explored.

2. Experimental methods

2.1. Chemical composition of mild steel (MS)

The chemical composition of the inspected MS alloy in percentage weight is: 0.07C, 0.27Mn, 0.012S, 0.021P, 0.07Si and the rest is Fe.

| Drug       | Azithromycin (AZM) | Roxithromycin (RXM) |
|------------|---------------------|----------------------|
| Chemical structure | ![](image1) | ![](image2) |
| Molecular formula | C₃₈H₇₄N₂O₁₃ | C₄₁H₇₆N₂O₁₅ |
| Molecular weight | 767.0 g/mol | 837.047 g/mol |

2.2. Methods

WL method was performed using cylindrical rods of MS with area equal to 9.42 cm². MS rods are polished with different-grade emery papers and then degreased by acetone and washed with distilled water, then dried using filter papers. The method of WL measurements was performed as described previously (26, 27).

PDP and EIS techniques were accomplished exploiting PGSTAT30 potentiostat/galvanostate. In PDP measurements, the electrode potential was automatically changed in a potential range of −200 mV to +200 mV with regard to OCP at a sweep rate of 2.0 mVs⁻¹. EIS technique was performed in ranges of frequency, 100 kHz - 0.1 Hz, and 5 mV amplitude. The experiments were achieved at 25 ± 0.1°C employing a thermostat. In these measurements, a three-part cell containing MS rod with exposed surface area equal to 0.54 cm² used as a working electrode, a reference electrode and an Pt auxiliary electrode. Prior to any experiment, the MS electrode is treated as in WL method. All used chemicals in these measurements were of A.R. quality.

2.3. Inhibitors

Two expired drugs, namely, azithromycin (AZM) and roxithromycin (RXM) produced by Pfizer pharmaceutical company, Egypt, were used as corrosion inhibitors of MS in 1M H₂SO₄ solutions. The chemical structures, molecular formulas and molecular weights of these drugs are inserted in Table 1.

3. Results and discussion

3.1. PDP measurements

Figure 1(a,b) represents the PDP curves for MS in free 1.0 M H₂SO₄ solution and in presence of varying concentrations of the expired AZM and RXM (ranging from 100 to 400 ppm), respectively. Values of anodic (βₐ)
and cathodic ($\beta_c$) Tafel slopes were obtained from the linear region of PDP curves as well as the values of corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$) and % IE were evaluated and were inserted in Table 2. The obtained values of $\beta_a$ and $\beta_c$ were slightly altered with increasing the concentrations of AZM and RXM drugs. This donates that the expired AZM and RXM drugs act as inhibitors of the mixed type, but the cathode is more polarized, where the values of $\beta_c$ is more than $\beta_a$ (28). Also, the variation in $E_{corr}$ values is less than ±85 mV confirming that the expired AZM and RXM are also considered as mixed inhibitors (10). $i_{corr}$ values were decreased resulting in increase in the inhibitory effect of expired AZM and RXM drugs. The value of % IE of AZM was found to be larger than that of RXM. These expired drugs were found to be good inhibitors for the corrosion of MS in H$_2$SO$_4$ solutions where they exhibit higher inhibition efficiencies than other reported drugs (19,23).

### 3.2. EIS measurements

The Nyquist plots of MS in free 1.0 M H$_2$SO$_4$ solution and with several concentrations of the expired AZM and RXM drugs were clarified in Figure 2(a,b). The electrical equivalent circuit model is shown in Figure 3. It used to analyze the obtained impedance data. The circuit consists of the solution resistance ($R_s$), the charge-transfer resistance of the interfacial corrosion reaction ($R_{ct}$) and the double layer capacitance ($C_{dl}$). Excellent fit with this model was obtained with our experimental data. Under equilibrium conditions, although here is no net power vector globally, the phase is on both sides of the interface / boundaries equally and vice versa (ionic on the electrolyte and the electron on the electrode), which leads to the potential difference at the interface. This builds up the charge separation between the two phases. For the electron transfer process; two dominant processes can be imagined taking place in parallel. The first is the capacitive behavior of the separation of charges at the interface and the second is the resistive behavior of the electron transfer process. The combination of these two processes leads to a semicircle response to the Nyquist plot which observed in both free 1.0 M H$_2$SO$_4$ solution and with AZM and RXM expired drugs. This indicates that the corrosion of MS is controlled by the process of charge transfer (29). The diameter of the capacitive ring increases with increasing concentration of expired drugs which indicates enhancing the inhibition film formed on the MS surface.

### Table 2. PDP data for MS corrosion in a free 1.0 M H$_2$SO$_4$ solution and with AZM and RXM expired drugs at 25°C.

| Inhibitor | Conc. (ppm) | $E_{corr}$ (mV(SCE)) | $\beta_a$ (mV/decade) | $\beta_c$ (mV/decade) | $i_{corr}$ (µA/cm$^2$) | % IE |
|-----------|-------------|----------------------|------------------------|------------------------|------------------------|------|
| AZM       | 0           | 487                  | 67                     | 98                     | 411                    | 64.47|
|           | 100         | 488                  | 69                     | 102                    | 146                    | 64.47|
|           | 200         | 483                  | 77                     | 99                     | 117                    | 75.91|
|           | 300         | 462                  | 87                     | 119                    | 110                    | 84.67|
|           | 400         | 458                  | 98                     | 118                    | 63                     | 88.32|
| RXM       | 100         | 482                  | 73                     | 124                    | 167                    | 59.37|
|           | 200         | 477                  | 72                     | 121                    | 112                    | 72.75|
|           | 300         | 472                  | 78                     | 118                    | 74                     | 82.00|
|           | 400         | 463                  | 93                     | 120                    | 62                     | 84.91|
The electrochemical parameters acquired from EIS technique, $R_{ct}$, $C_{dl}$ and %IE are calculated and are listed in Table 3. Values of capacity of double layer $C_{dl}$ were calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_{ct}}$$

(1)

where $R_{ct}$ is the charge transfer resistance and $f_{\text{max}}$ is the maximum frequency.

Values of %IE were computed from $R_{ct}$ according to the following relation below:

$$\% \text{IE} = \left[1 - \frac{(R_{ct})_{\text{in}}}{(R_{ct})_{\text{un}}} \right] \times 100$$

(2)

where, $(R_{ct})_{\text{un}}$ and $(R_{ct})_{\text{in}}$ are the values of $R_{ct}$ in free 1.0 M H$_2$SO$_4$ solution and with the expired drugs, respectively.

As shown in Table 3, as the concentrations of the expired AZM and RXM drugs increase the values of $R_{ct}$ and %IE increase indicated the formation of a protective film on the MS/solution interface. This denotes that the corrosion of MS is controlled by a charge transfer process (30). On the other hand, the $C_{dl}$ values are reduced resulting from the water molecules at the electrode interface are substituted by examined expired drug of lower dielectric constant through adsorption which form adsorbed film on the surface of MS. Thus, the lowest values of the local dielectric constant of the MS/solution interface. The values of %IE gained from EIS measurements decreases as follows: AZM > RXM. The sequence of %IE obtained from the EIS technique are coincides with that obtained from PDP measurements.

Table 3. Values of $R_{ct}$, % IE and $\theta$ of several concentrations of the expired AZM and RXM drugs for MS corrosion in 1.0 M H$_2$SO$_4$ solution at 25°C.

| Inhibitor | Inhibitor Conc. (ppm) | $R_{ct}$ ohm cm$^{-2}$ | $C_{dl} \times 10^{-3}$ µFcm$^{-2}$ | % IE |
|-----------|-----------------------|---------------------|-------------------------------|------|
| AZM       | 0                     | 51                  | 104                           | –    |
|           | 100                   | 128                 | 86                            | 60.16|
|           | 200                   | 205                 | 74                            | 75.12|
|           | 300                   | 312                 | 66                            | 83.65|
|           | 400                   | 403                 | 58                            | 87.20|
| RXM       | 100                   | 105                 | 82                            | 51.43|
|           | 200                   | 190                 | 70                            | 73.16|
|           | 300                   | 330                 | 64                            | 84.51|
|           | 400                   | 385                 | 52                            | 86.75|
3.3. WL measurements

3.3.1. Effect of inhibitor concentrations at various temperatures

Figure 4(a,b) displays the relationship between immersion time and weight loss of MS coupons in free 1.0 M H$_2$SO$_4$ solution and with several concentrations of the expired AZM and RXM drugs (ranging from 100 to 400 ppm) at 25°C, respectively. Similar curves were also obtained at different temperatures (15, 35 and 45°C) but not appeared, while the corrosion parameters were computed and were listed in Table 4. It is noted that in Figure 3 the WL varied linearly with the immersion time in free and in the presence of the expired AZM and RXM drugs. This denotes that devoid of insoluble surface films during corrosion. In the sense that the expired drugs are first adsorbed on the MS surface and thus inhibit the corrosion either by blocking the anodic and cathode reaction sites or by changing the mechanism of the anodic and cathodic processes.

Values of corrosion rate (CR), % IE and the degree of surface coverage ($\theta$) were calculated from the equations (31):

$$\text{CR(mpy)} = \frac{KW}{Atd}$$

(3)

$$\%\text{IE} = \left[1 - \frac{CR_{in}}{CR_{un}}\right] \times 100$$

(4)

$$\theta = \frac{\%\text{IE}}{100}$$

(5)

where $K$ is a constant, $W$ is the WL in grams, $A$ is the surface area in cm$^2$, $t$ is the immersion time in hours, $d$ is the density of MS and $CR_{un}$, $CR_{in}$ are corrosion rates in free and with the expired drug, respectively.

The calculated values of CR, %IE and $\theta$ obtained from WL at various temperatures are registered in Table 4. It is shown that by increasing the concentration of AZM and RXM expired drugs minimized the CR values. The values of %IE and $\theta$ are rise indicate a rise in the inhibitory action of the investigated expired drugs towards the dissolution of MS in 1.0 M H$_2$SO$_4$. Otherwise, as the temperature rises the values of CR increase and the %IE, $\theta$ are decreased indicating the best %IE is observed at 15°C. This can be interpreted on the basis of desorption of the inhibitor molecules at elevated temperature. This behavior proves that the adsorption of expired AZM and RXM on the MS surface is physical. At one and the similar concentration of the expired drugs, the %IE of AZM is higher than RXM, this behavior will be discussed later.

Figure 5(a,b) displays the variation of %IE of the expired AZM and RXM drugs with their concentrations at various temperatures for MS corrosion in 1.0 M H$_2$SO$_4$ solution, respectively. Obviously, values of %IE were found to increase with the increase in the concentrations of the two expired drugs and with decrease temperature. This indicates that the highest %IE was found to be at the lowest temperature proves the adsorption of expired drugs on the surface MS is physical. It is also noted that, the %IE increased rapidly at concentrations up to 300 ppm and when the concentration increases, the increase in %IE was limited. This may be because of the high concentration of the drug is limited adsorbed on the surface of MS.

3.3.2. Kinetic parameters

The effect of CR on the temperature can be determined by the Arrhenius equation (32, 33):

$$\ln CR = \ln A - \frac{E_a}{RT}$$

(6)
where $A$, $R$ and $E_a$ are the Arrhenius constant, the gas constant and the activation energy for the corrosion process, respectively.

Table 4. Values of $CR$ of MS, %IE and $\theta$ of several concentrations of the expired AZM and RXM drugs in 1.0 M $H_2SO_4$ solution at different temperatures.

| Inhibitor | Inhibitor Conc. (ppm) | 288 | 298 | 308 | 318 |
|-----------|-----------------------|-----|-----|-----|-----|
| AZM       | 0                     | 156 |     |     |     |
|           | 100                   | 65  | 58.33| 0.58|     |
|           | 200                   | 37  | 76.28| 0.76|     |
|           | 300                   | 23  | 85.26| 0.85|     |
|           | 400                   | 20  | 87.05| 0.87|     |
| RXM       | 100                   | 56  | 64.10| 0.64|     |
|           | 200                   | 34  | 78.00| 0.78|     |
|           | 300                   | 20  | 87.05| 0.87|     |
|           | 400                   | 14  | 91.02| 0.91|     |

Figure 5. Change of the % IE with the concentrations of the expired drugs at various temperatures for MS corrosion in 1.0 M $H_2SO_4$ solution: (a) AZM and (b) RXM.

Figure 6. Arrhenius plots for MS corrosion in a free 1.0 M $H_2SO_4$ solution and with the expired drugs: (a) AZM and (b) RXM.
the expired AZM and RXM drugs, respectively. Values of $E_a$ for the corrosion reaction were evaluated from the slopes of the straight lines of Figure 6 and were given in Table 5. At all concentrations of the expired drugs, the values of $E_a$ were found to be higher than that of the free acidic solution. The value of $E_a$ range from 13.83–30.23 kJ mol$^{-1}$ for AZM and range from 13.39–25.84 kJ mol$^{-1}$ for RXM. This denotes the physical adsorption of the two expired drug on the surface of MS by making a barrier for mass and charge transfer (34). So, the examined expired drugs were performed as good inhibitors at lower temperature.

Values of enthalpy of activation ($\Delta H^*$) and the entropy of activation ($\Delta S^*$) can be calculated from the transition state equation (32, 33):

$$ \ln \left( \frac{C_{\text{inh}}}{T} \right) = \left( \ln \frac{R}{Nh} + \frac{\Delta S^*}{R} \right) - \frac{\Delta H^*}{R} \frac{1}{T} $$

(7)

where, $N$ is the Avogadro’s number and $h$ is the Planck’s constant.

Figure 7(a,b) shows the relation between the values of log CR/ T versus 1/T for MS in a free 1.0 M H$_2$SO$_4$ solution and with various concentrations of the tested expired AZM and RXM drugs, respectively. The computed values of $\Delta H^*$ and $\Delta S^*$ are inserted in Table 5. The acquired positive sign of $\Delta H^*$ reflects the endothermic nature of the MS corrosion while the negative sign of $\Delta S^*$ indicated that the activated complex in the rate determining step symbolizes a combination rather than a segregation (35).

3.3.3. Adsorption isotherm and mechanism of inhibition

The inhibitory effect of the examined expired AZM and RXM drugs towards the corrosion of MS in 1.0 M H$_2$SO$_4$ solution has been interpreted in terms of adsorption of these compounds on the MS surface. The adsorption capacity depends on the chemical structure and the molar mass of the expired drug, the presence of the active center of the chemical structure, the concentration of corrosive acidic solutions and other factors (36). The adsorption process may be regarded as a one alternative process where the expired drug (Ex. D), in the aqueous phase replaces ‘n’ adsorbed on the surface of MS

$$ \text{Ex. D}_{(aq)} + n \text{H}_2\text{O}_{(surf)} \rightarrow \text{Ex. D}_{(surf)} + n \text{H}_2\text{O}_{(aq)} \quad (8) $$

where, $n$ is the number of water molecules that have been replaced by one expired drug inhibitor.

The inhibition of the two studied expired drugs can be ascribed to the presence of hetro atoms such as N, O, the presence of electron donating groups e.g. CH$_3$ and OCH$_3$ in their chemical structures which enhances the adsorption link between the drug and MS surface and, hence, the %IE increases. The sequence of %IE was found to decrease as follows: RXM > AZM. This has coincided with the increase of the molecular weight and the number of the electron donating group within the expired drugs.

To select the most suitable isotherm for adsorption of the expired drugs, a value of (8) was placed in some isotherms e.g. Freundlich, Frumkin, Temkin Langmuir and others. We found that the Langmuir isotherm is the suitable isotherm and can be represented using the following equation (37):

$$ \frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} $$

(9)

where, $C_{\text{inh}}$ is the concentration of the expired drug, $K_{\text{ads}}$ is the equilibrium constant of the adsorption.

Figure 8 represents the plots of $C_{\text{inh}} / \theta$ versus $C$ for the adsorption of the expired drugs (AZM and RXM) on the MS surface in 1.0 M H$_2$SO$_4$ solution at various temperatures. Straight lines are obtained with the slope and correlation coefficient are approximately equal unity. This demonstrates the adsorption of expired drugs to the surface of the MS being obeyed Langmuir isotherm at all temperatures used.

3.3.4. Thermodynamic parameters for adsorption process

The values of $K_{\text{ads}}$ can be determined from the intercepts of Figure 7. The standard free energy values for adsorption, $\Delta G_{\text{ads}}^o$ at different temperatures are related to the values of $K_{\text{ads}}$ and were computed from the following equation (38):

$$ \Delta G_{\text{ads}}^o = -RT \ln (55.5K_{\text{ads}}) $$

(10)

The computed valued of $K_{\text{ads}}$ and $\Delta G_{\text{ads}}^o$ are listed in Table 6. The high values of $K_{\text{ads}}$ demonstrated the vigorous adsorption of the examind expired RXM and AZM.

| Inhibitor | Conc. (mg l$^{-1}$) | $E_a^*$ (kJ mol$^{-1}$) | $\Delta H^*$ (kJ mol$^{-1}$) | $\Delta S^*$ (J mol$^{-1}$ K$^{-1}$) |
|-----------|---------------------|------------------------|-----------------------------|---------------------------------|
| AZM       | 0                   | 6.58                   | 4.07                        | -41.57                          |
|           | 100                 | 13.83                  | 11.27                       | -24.94                          |
|           | 200                 | 20.67                  | 17.46                       | -8.31                           |
|           | 300                 | 26.25                  | 23.61                       | -9.98                           |
|           | 400                 | 30.23                  | 27.69                       | -30.79                          |
| RXM       | 100                 | 13.39                  | 10.92                       | -24.94                          |
|           | 200                 | 18.04                  | 15.55                       | -13.31                          |
|           | 300                 | 24.94                  | 22.53                       | -6.65                           |
|           | 400                 | 25.84                  | 22.78                       | -5.82                           |
drugs on the MS surface. This adsorption is the spontaneous return of the negative values of the values of $\Delta G^{\circ}_{\text{ads}}$. These values ranged from $-32.21$ to $-34.49 \text{ kJ mol}^{-1}$ proving the adsorption of RXM and AZM drugs on the MS surface is a physical due to the values of $\Delta G^{\circ}_{\text{ads}} < 40 \text{ kJ mol}^{-1}$ (39).

Table 6. Thermodynamic adsorption parameters for MS corrosion in a free 1.0 M H$_2$SO$_4$ solution and with the expired AZM and RXM drugs at various temperatures.

| Inhibitor | (1) Temp. (K) | $10^{-3} K_{\text{ads}}$ l mol$^{-1}$ | $\Delta G^{\circ}_{\text{ads}}$ kJ mol$^{-1}$ | $\Delta H^{\circ}_{\text{ads}}$ kJ mol$^{-1}$ | $\Delta S^{\circ}_{\text{ads}}$ J mol$^{-1}$ K$^{-1}$ |
|-----------|---------------|-------------------------------|--------------------------------|-----------------|-------------------|
| AZM       | 288           | 12.50                         | $-32.21$                       | $-10.28$        | 76.14             |
|           | 298           | 11.36                         | $-33.09$                       | $-33.84$        | 76.54             |
|           | 308           | 9.87                          | $-33.49$                       |                | 76.49             |
|           | 318           | 8.33                          |                                 |                | 76.13             |
| RXM       | 288           | 11.26                         | $-31.98$                       | $-8.73$         | 80.72             |
|           | 298           | 9.92                          | $-32.71$                       |                | 80.47             |
|           | 308           | 8.77                          | $-33.50$                       |                | 80.43             |
|           | 318           | 8.01                          | $-34.44$                       |                | 80.84             |
The standard enthalpy of the adsorption (Δ\text{H}_{\text{ads}}^o) can be obtained from the van’t Hoff equation (40):

\[ \ln K_{\text{ads}} = -\frac{\Delta H_{\text{ads}}^o}{RT} + C \]  

(11)

Figure 9 represents the relation between \( \ln K_{\text{ads}} \) vs. \( 1/T \). Straight lines were obtained with slopes equal to \( -\Delta H_{\text{ads}}^o/R \). The values of \( \Delta H_{\text{ads}}^o \) are determined and inserted in Table 6. The negative sign of \( \Delta H_{\text{ads}}^o \) proved that the adsorption of the expired RXM and AZM drugs on the MS surface is an exothermic process.

From the values of \( \Delta H_{\text{ads}}^o \) and \( \Delta G_{\text{ads}}^o \), the values of standard entropy of adsorption (\( \Delta S_{\text{ads}}^o \)) can be obtained from the following equation:

\[ \Delta G_{\text{ads}}^o = \Delta H_{\text{ads}}^o - T\Delta S_{\text{ads}}^o \]  

(12)

The values obtained of \( \Delta S_{\text{ads}}^o \) are listed in Table 6. The positive values of \( \Delta S_{\text{ads}}^o \) indicate the adsorption of the expired RXM and AZM drugs on the MS surface is randomized.

4. Conclusions

(1) The inhibitory effects of azithromycin (AZM) and roxithromycin (RXM) towards the corrosion of mild steel in 1.0 M \( \text{H}_2\text{SO}_4 \) solution were examined exploiting potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss techniques.

(2) The investigated expired drugs were found to act as effective inhibitors for the corrosion of mild steel in 1.0 M \( \text{H}_2\text{SO}_4 \) solutions.

(3) The percentage inhibition efficiency increases with increasing the concentration of the expired azithromycin and roxithromycin and with decreasing the temperature.

(4) Potentiodynamic polarization proves that the studied expired drugs are mixed-type inhibitors with mainly cathodic.

(5) Adsorption of the expired drugs on the surface of mild steel follows the Langmuir adsorption isotherm.

(6) The adsorption process is spontaneous and endothermic, and the adsorption type is physical.

(7) The results obtained from all employed chemical and electrochemical techniques were in good agreement.

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