J. Electrochem. Sci. Eng. **15(3)** (2025) 2646; http://dx.doi.org/10.5599/jese.2646

Open Access : : ISSN 1847-9286
www.jESE-online.org

Original scientific paper

Exploring the inhibitory performance of expired moxifloxacin and norfloxacin on copper corrosion in saline environment

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Received: January 17, 2025; Accepted: March 1, 2025; Published: March 9, 2025

Abstract

The reuse of expired drugs has become a challenge in maintaining environmental cleanliness and achieving economic benefits. In this report, two expired drugs, moxifloxacin and norfloxacin, were used as inhibitors for copper corrosion in 3.5 % NaCl solution at different temperatures using several experimental approaches including chemical, electrochemical and spectroscopic techniques. The interaction of these two molecules on the copper surface was also inspected using different adsorption models. Using a dose of 500 mg L^{-1} of these drugs at 298 K, maximum inhibition efficiencies (IE) of 88.7 and 85.2 % were estimated from the potentiodynamic polarization technique for Mox and Nor, respectively., confirming that they can be considered as promising and effective inhibitors. The IE values were enhanced with increasing drug doses and reduced with rising temperature. The higher IE is due to the strong adsorption of these molecules on the copper surface, which is physical in nature and *follows the Langmuir adsorption isotherm. This is due to their unique chemical structures, as they contain a number of functional groups. Polarization experiments confirmed that the drugs were tuned to behave as mixed-type inhibitors with an anodic predominance. All thermodynamic and kinetic parameters were calculated and discussed in details, and the inhibition mechanism was proposed. All experimental results obtained by different techniques were in agreement with each other.*

Keywords
Metal corrosion; salty environment; fluoroquinolone antibiotics; anti-corrosion properties; adsorption

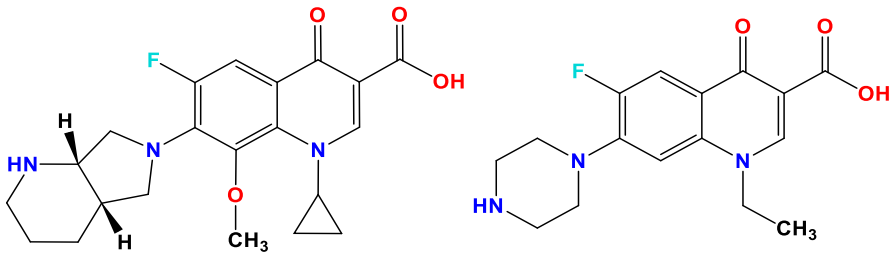
Introduction

Corrosion of metals is the gradual damage of the surfaces of metals and alloys through reactions with the surroundings. This natural phenomenon costs the world's economy a lot of money each year. Such a phenomenon raises economic concerns and causes serious environmental impacts. Copper is a premeditated metal in several industrial areas, including heating and cooling systems, because of its good mechanical properties and low cost. Although copper has appropriate corrosion resistance in the atmosphere and some chemical environments due to the formation of a shielding oxide passive layer on its surface [1], copper is susceptible to corrosion in aggressive media [2,3]. Copper corrosion was set to have a negative impact on the functioning of metals and alloys in the systems formed from it [4,5]. The probability of construction of passive film on copper surface is low in the aggressive media or the existence of corrosive ions such as Cl^- ions. Based on the extensive use of copper in diverse fields, copper corrosion and its protection have attracted voluminous consideration, and many studies have been conducted in this regard [6,7].

One of the preeminent approaches to controlling corrosion is employing corrosion inhibi tors [8-10]. Various inhibitors were examined to protect copper from corrosion in various NaCl solutions, particularly at a concentration of 3.5 % in different conditions. In this regard, some amino acids such as cysteine and methionine were investigated as green inhibitors for copper corrosion in 3.5 % NaCl solution [11] N-acetyl cysteine [12]. Rajkumar *et. al.* constructed of a self-assembled monolayer on the surface of copper in 3.5 % NaCl solution comprising 4-aminothiophenol [13]. Also, pharmaceutical drugs as eco-friendly compounds were tested, such as domperidone drug, which was examined to inhibit copper corrosion in a 3.5 % NaCl solution [14]. Qiang *et al.* [15] used 5-nitroindazole to inhibit copper corrosion in 3 % NaCl solution and found that inhibition efficiency (IE) reached 99 % at 0.4 mM of the inhibitor. Tian *et al*. have synthesized certain derivatives of triazolyl-acylhydrazone [16] and thiadiazole derivatives [17] in order to employ them as corrosion inhibitors in chloride media. In 3.5 % NaCl solution, Khan *et al.* [18] examined the inhibition properties of benzotriazole for copper corrosion in flow conditions, Dheeraj *et. al.* [19] studied 4-amino-5--methyl-4H-1,2,4-triazole-3-thiol, Lie *et. al.* [20] employed polypyrrole-oxalic acid benzotriazole, while Toghan *et. al*. [21] used N-benzylhydrazinecarbothioamide. Finšgar *et al.* reported the adsorption of 4-methyl-2-phenyl-imidazole using the XPS technique [22] and 2-mercaptobenzoxazole [23] on the copper surface in 3.5 % NaCl, while Ezznaydy *et al.* [24] used mono-hydroxamic acid. Glycerol was inspected in 0.5 M NaCl solutions at different pH values [25]. Also, various organic compounds were investigated as inhibitors in several acidic media [26-30] and in other media [31,32].

Unfortunately, most applied corrosion inhibitors are toxic and have high cost. Thus, chemists have focused on eco-friendly corrosion inhibitors [33-35]. Newly expired medications were employed as hopeful, efficient, and eco-friendly corrosion inhibitors instead of outdated toxic or hazardous inhibitors to the environment [36-37]. They have good adsorption capabilities on metallic surfaces because they contain several electronegative functional groups, heteroatoms: N, O and S, π systems and heterocycles [38,39]. This leads to the formation of a defensive layer that protects the metal surfaces from corrosion. Applying expired drugs as corrosion inhibitors was found to have double benefits: economic, where they are free of cost, and environmental, that they contain complex compounds that safeguard the environment from the threat of such compounds if they reach it. Several drugs were examined and were discovered to be as efficient corrosion inhibitors for copper,

such as domperidone in 3.5 % NaCl solution and some pharmaceutical compounds in HNO_3 acid. Moxifloxacin (Mox) and norfloxacin (Nor) are two drugs from the fluoroquinolone antibiotic medications family used to remedy various bacterial infections [40,41]. Moxifloxacin treats a number of infections, including respiratory tract and intra-abdominal infections. They are broad-spectrum antibiotics that are active against both gram-positive and gram-negative bacteria. Figure 1 shows the chemical structures of both drugs, which have extensive π-electron systems, heteroatoms (N and O) and electron-donating methyl groups that enable such compounds to strongly adsorb on the metal surfaces. Therefore, such drugs can be efficient and eco-friendly metallic corrosion inhibitors.



Moxifloxacin (Mox) **Norfloxacin (Nor)**

Figure 1. *Chemical structure of moxifloxacin and norfloxacin*

Based on the above, this paper aims to reuse expired pharmaceuticals and utilize them to control the spread of environmental toxins and harmful chemicals. Therefore, in this report, two expired drugs, moxifloxacin and norfloxacin, were applied as eco-friendly and cost-free inhibitors for the corrosion of copper in 3.5 % sodium chloride solution at different temperatures. Experiments were carried out using several methods, including electrochemical, surface, chemical and adsorption. Thermodynamic and kinetic calculations were studied, and the inhibition mechanism was proposed.

Experimental

Materials and techniques

The investigated metal was copper sheets (Merck, purity 99.93 %) with a composition of 0.0297 wt.% Fe, 0.0230 wt.% Pb, 0.0120 wt.% Ni, 0.0053 wt.% Si, and the remainder is Cu. These sheets were treated before experiments by polishing them with successive emery papers of various grades (200 to 1200). Then, they were washed with bi-distilled water, degreased with acetone, and dried before immersing in the tested medium. The principal corrosive medium (blank) used in all studies was a solution of 3.5 % NaCl (99.99 %) prepared with bi-distilled water. Solutions of the explored expired drugs, moxifloxacin (Fluka, $C_{21}H_{24}FN_3O_4$, 401.438 g mol^{-1}, EXP 03 2022), and norfloxacin (Fluka, $C_{16}H_{18}FN_3O_3$, 319.336 g mol^{-1}, EXP 06 2022) were prepared using bi-distilled water. They were used in the concentration range 100 to 500 mg/L. The techniques used in this investigation were chemical (weight loss (WL)), electrochemical (open circuit potentials (OCP) and potentiodynamic polarization (PDP)), and spectroscopic (scanning electron microscopy (SEM)).

Weight loss measurements

For WL measurements, copper sheets with an area of 15.76 cm^2 (4.2×1.6×0.2 cm) were used. Prior to each experiment, copper sheets were prepared, as reported above. Then, the prepared copper sheets were immersed in 100 mL of the examined solution, in the absence and presence of different concentrations of the explored drugs in the range of 100 to 500 mg L^{-1} for time intervals of 4, 8, 12, 16 and 20 hours, at temperatures of 288, 298, 308 and 318 K. Next, the copper sheets were

cleaned, dried, and weighed. The average weight loss, mg cm^{-2} of copper sheets, was calculated after each experiment.

Electrochemical measurements

Open circuit potential measurements

The change of OCP or E_{OC} with immersion time (t) for copper in 3.5 % NaCl without and with different concentrations of the explored drugs at 298 K was examined over an hour. OCP measurements were performed using a temperature-controlled PGSTAT30 potentiostat-galvanostat with a saturated calomel electrode (SCE) as a reference electrode.

Potentiodynamic polarization measurements

In otentiodynamic polarization (PDP) measurements, a temperature-controlled PGSTAT30 potentiostat - galvanostat was used. For all experiments, a three-electrode cell was used and prepared as reported. The working electrode was a copper sheet with an area of 1.0 cm^2 fixed in an epoxy resin, the counter electrode (CE) was a platinum plate, and SCE served as a reference electrode (RE). Before each exploration, the surface of the copper electrode was pretreated as previously mentioned, then inserted in the tested solution for a time needed to attain stable potential at open circuit potential (OCP). PDP measurements were performed at a scan rate of 1.0 mV s^{-1}.

Scanning electron microscopy study

For SEM examination, at 5.0 kV, a JEOL SEM was used. Before each examination, the uninhibited and inhibited copper sheets were cleaned and dried as mentioned above and then observed by SEM with a magnification of 1200×.

Results and discussion

Weight loss measurements

Effect of inhibitor concentrations

Weight loss experiments were performed for copper sheets in 3.5 % NaCl solution (main corrosive medium, blank) and the presence of the expired drugs Mox and Nor at concentrations of 100 to 500 mg L^{-1}, at 298 K. The weight loss versus immersion time plots are shown in Figure 2.

The values of corrosion rates (CR) of copper were calculated using Eq. (1) [3, 42]:

$$CR = \frac{KW}{Atd} \quad (1)$$

where K is a constant of 8.76×10^4 for CR in mm $year^{-1}$ (or 3.45×10^6 for CR in mils $year^{-1}$), W / g is weight loss of Cu, A / cm^2 is the exposed area of copper sheet, t / h is the immersion time and d is the density of copper (8.94 g cm^{-3}). The values of IE of the explored drugs and degrees of surface coverage (θ) by the explored drugs were calculated by Eq. (2) [7]:

$$IE = 100\theta = \left[1-\frac{CR_{inh}}{CR}\right]100 \quad (2)$$

where CR and CR_{inh} are corrosion rates in the absence and presence of the explored drugs, respectively.

Based on the gained experimental outcomes, as the concentration of the explored drugs increased, the copper's CR was reduced and the values of IE were enhanced, as illustrated in Figures 3 and 4, respectively. In the existence of 500 mg L^{-1} of the explored drugs, the IE of Mox and

Nor were found to be 89.4 and 83.9 %, respectively. Thus, it could be concluded that the explored drugs act as effective inhibitors for copper corrosion in a 3.5 % NaCl solution.

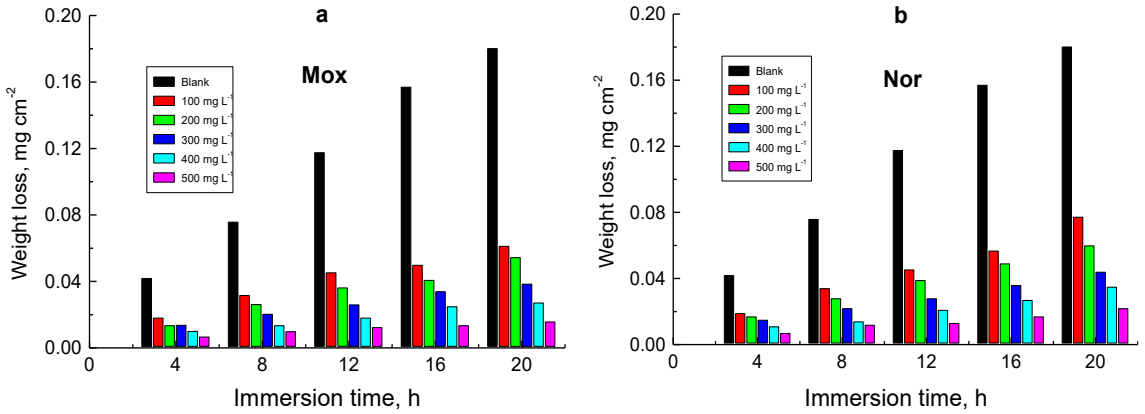


Figure 2. *Weight loss versus immersion time plots for copper corrosion in 3.5 % NaCl solution (blank) and in the presence of different concentrations of expired drugs a - Mox and b - Nor, at 298 K*

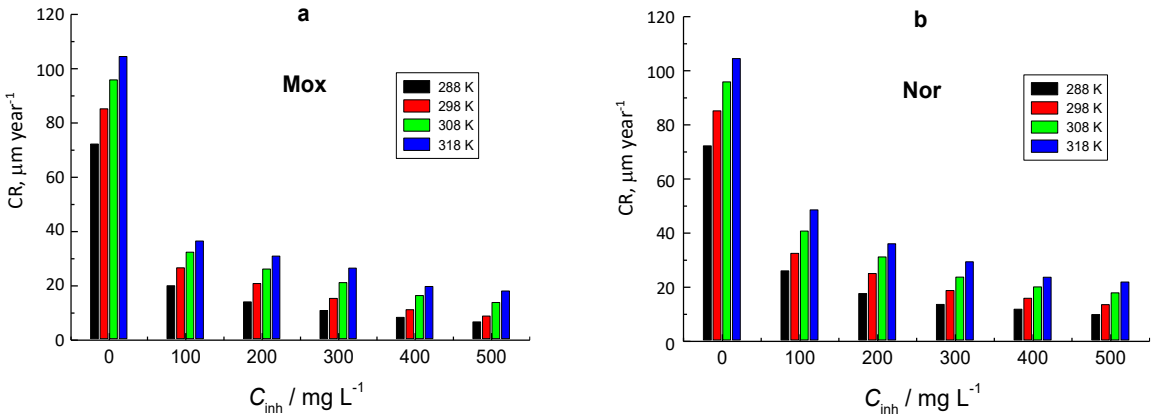


Figure 3. *Variations of the corrosion rates of copper in 3.5 % NaCl solution in the absence and presence of different concentrations of expired drugs a - Mox and b - Nor, at different temperatures*

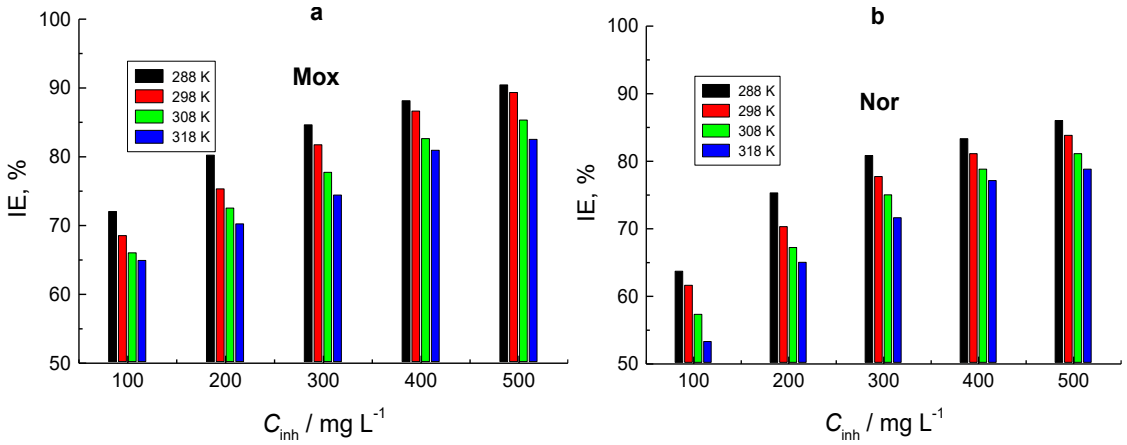


Figure 4. *Variations of inhibition efficiencies with different concentrations of expired drugs a -Mox and b -Nor for corrosion of copper in 3.5 % NaCl solution at different temperatures*

Effect of temperature

The effect of temperature (within 288 to 318 K) was inspected to recognize the type of adsorption of the explored drugs on the copper surface and to evaluate the thermodynamic and kinetic parameters. The results in Table 1 indicate that CR of copper in 3.5 % NaCl solution increases, while the values of IE of the explored drugs decrease with rising temperature, as illustrated in Figures 5 and 6. This behavior suggested that the type of adsorption of these drugs is physical [43].

Table 1. *Corrosion rate (CR, mm year^{-1}), IE and θ of copper in 3.5 % NaCl in absence and presence of different concentrations of expired drugs Mox and Nor, at different temperatures*

Inhibitor	C_{Inh} / mg L^{-1}	Temperature, K											
		288			298			308			318		
		CR, μm year^{-1}	IE, %	θ	CR, μm year^{-1}	IE, %	θ	CR, μm year^{-1}	IE, %	θ	CR, μm year^{-1}	IE, %	θ
None	0	72.39	--	--	85.34	--	--	96.01	--	--	104.65	--	--
Mox	100	20.19	72.1	0.721	26.80	68.6	0.686	32.54	66.1	0.661	36.63	65.0	0.65
	200	14.25	80.3	0.803	20.98	75.4	0.754	26.32	72.6	0.726	31.09	70.3	0.703
	300	11.07	84.7	0.847	15.54	81.8	0.818	21.31	77.8	0.778	26.70	74.5	0.745
	400	8.53	88.2	0.882	11.35	86.7	0.867	16.61	82.7	0.827	19.89	81.0	0.81
	500	6.88	90.5	0.905	9.04	89.4	0.894	14.02	85.4	0.854	18.21	82.6	0.826
Nor	100	26.21	63.8	0.638	32.69	61.7	0.617	4.089	57.4	0.574	48.77	53.4	0.534
	200	17.81	75.4	0.754	25.27	70.4	0.704	31.40	67.3	0.673	36.22	65.1	0.651
	300	13.82	80.9	0.809	18.95	77.8	0.778	23.90	75.1	0.751	29.62	71.7	0.717
	400	12.01	83.4	0.834	16.05	81.2	0.812	20.27	78.9	0.789	23.85	77.2	0.772
	500	10.06	86.1	0.861	13.74	83.9	0.839	18.06	81.2	0.812	22.07	78.9	0.789

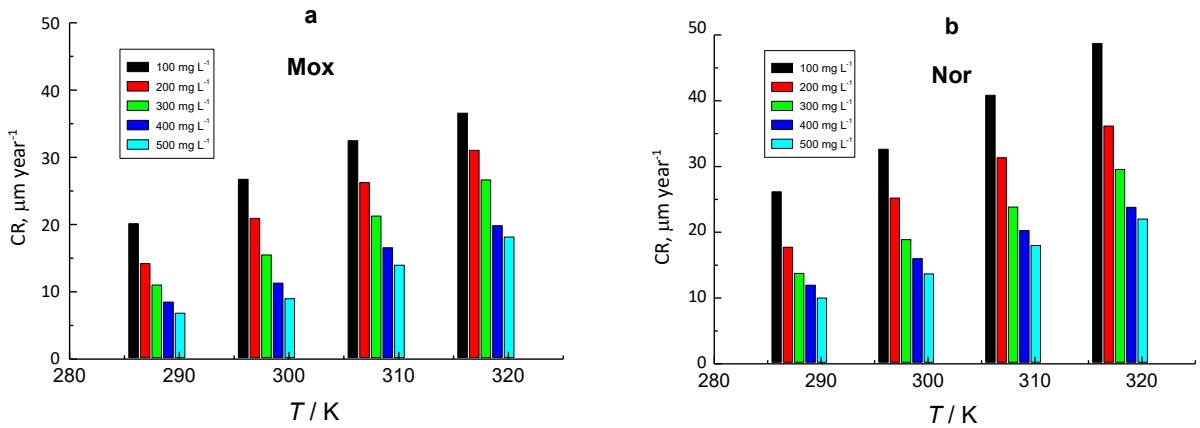


Figure 5. *Variations of corrosion rates of copper in 3.5 % NaCl solution with temperature at various concentrations of expired drugs a - Mox and b - Nor*

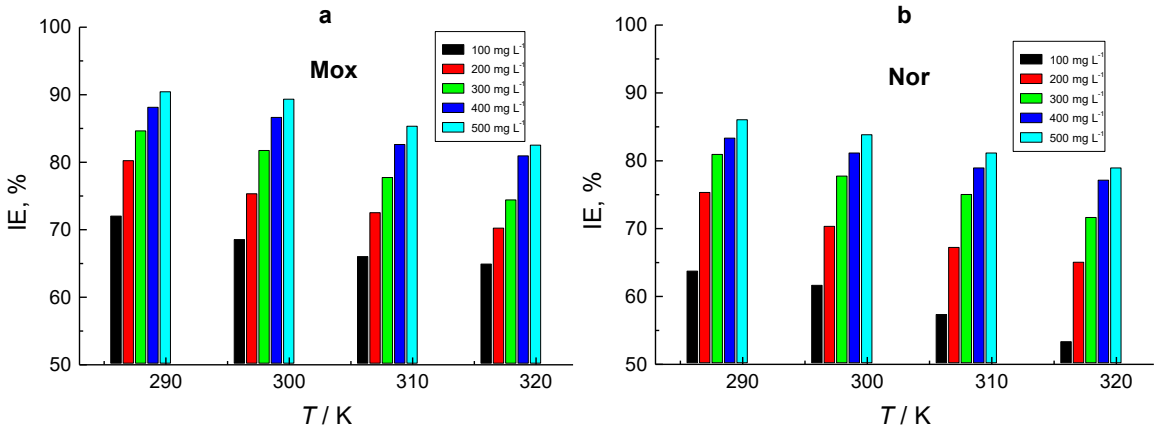


Figure 6. *Variations of inhibition efficiencies with temperature at various concentrations of expired drugs a - Mox and b - Nor for corrosion of copper in 3.5 % NaCl solution*

Effect of NaCl concentration

The effect of the corrosive medium (NaCl) concentration on IEs of the explored drugs at a concentration of 300 mg L^{-1} in the corrosion of copper in NaCl solutions is shown in Figure 7. Figure 7 shows that the IE was decreased with an increment of NaCl concentration (from 1.5 to 4.5 %), indicating that the explored drugs are more effective at lower NaCl concentrations.

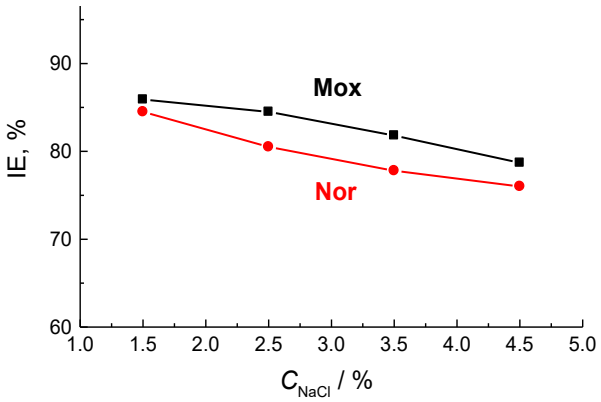


Figure 7. *Variations of the inhibition efficiency of 300 mg L^{-1} of expired drugs on corrosion of copper in different concentrations of NaCl solution at 298 K*

Effect of immersion time

It has already been reported [44] that the corrosion rate of a metal is affected by the immersion time and, therefore, it is very significant to illuminate the impact of immersion time on corrosion inhibition. The effect of immersion time (2 to 20 h) on IE of the explored drugs (300 mg L^{-1}) in the corrosion of copper in 3.5 % NaCl solution was investigated at 298 K, Figure 8. The results indicated that the explored drugs inhibit the corrosion of copper at all immersion times, but the IE increased greatly at the initial stage up to 4 h, then reduced by increasing the immersion time. Increasing IEs at the initial stage can be ascribed to the adsorption of multi-layers of drug molecules on the copper surface, which enhances copper corrosion inhibition. After about 4 h, some adsorbed inhibitor molecules are proposed to leave the copper surface, decreasing the effective area covered by such molecules causing a reduction of IE.

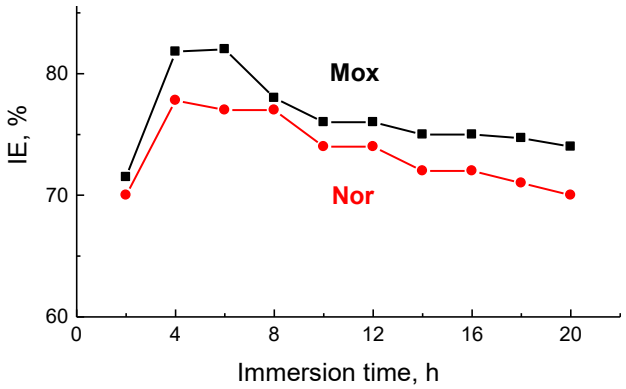


Figure 8. *Variations of inhibition efficiency for 300 mg L^{-1} of expired drugs with immersion time for copper corrosion in 3.5 % NaCl solution, at 298 K*

Adsorption isotherm examination

It was reported [45] that organic corrosion inhibitors exert their inhibitive action by their adsorption on the metal surfaces. Therefore, examination of the adsorption isotherms is a significant way to identify the adsorption nature of the inhibitor molecules on the metal surface. Therefore, experiments were carried out to fit the obtained data with different adsorption isotherms such as Temkin, Langmuir, Freundlich, Frumkin, and Flory-Huggins. The results gained at different temperatures indicated that the best fit was attained for Langmuir adsorption isotherm, where linear plots of C_{inh} / θ *vs.* C_{inh} (Eq. 3) with about unit slopes were obtained, as shown in Figure 9. This signified that the adsorption of the explored drugs on the copper surface in NaCl solution obeyed Langmuir isotherm [3]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (3)$$

where K_{ads} is the adsorption constant, while C_{inh} is the inhibitor concentration.

Generally, Eq. (3) is represented graphically as a linear relationship, y = a + bx, where a = intercept and b = slope, while the goodness of fit is usually measured by the coefficient of determination (R^2). These values for linear relations shown in Figure 9 are listed in Table 2. By Eq. (3) describing Langmuir isotherm, K_{ads} is defined as reciprocal intercepts of linear lines with the C_{inh}/θ axis. Since C_{inh} is expressed in mg L^{-1}, the expected unit for K_{ads} should be L mg^{-1}, the unit of Kads is assumed to be L mg^{-1} directly, however it was converted to mL mol-1 as displayed in Table 2. The higher K_{ads} values indicate strong and spontaneous adsorption of drug molecules. Such adsorption is considered physical because the value of Kads was reduced by rising temperature.

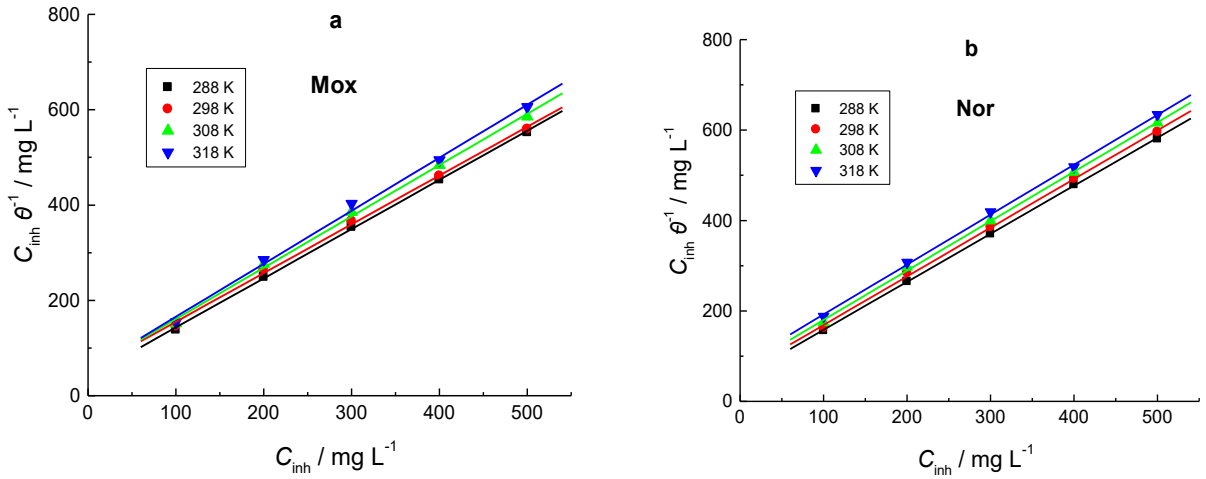


Figure 9. *Langmuir adsorption isotherms for the expired drugs a - Mox and b -Nor adsorbed on the copper surface in 3.5 % NaCl, at different temperatures*

Thermodynamic parameters

Calculation of thermodynamic parameters is very important to understand the corrosion inhibition mechanism. The free energy of adsorption (ΔG_{ads}) can be calculated *via* the following the equation [46]:

$$\Delta G_{ads} = -RT \ln (55.5\, K_{ads}) \quad (4)$$

Using Eq. (4) and K_{ads} values from Table 2, ΔG_{ads} values were calculated and listed in Table 2. The obtained values between -29.55 and -31.84 kJ mol^{-1} indicate that the nature of adsorption is a merge of physical and chemical types, *i.e.* a mixed type (physicochemical adsorption). The adsorption is a spontaneous process that appears from negative values of $\Delta G_{ads.}$ [47]. Also, the results show that the values of ΔG_{ads} for the expired drug Mox are slightly higher than those of the drug Nor, signifying that more Mox was adsorbed on the copper surface than Nor. This behavior is in agreement with the gained values of IE for both explored drugs.

The heat of adsorption (ΔH_{ads}) was gained from Van't Hoff equation, Eq. (5) [48]:

$$\ln K_{ads} = \frac{-\Delta H_{ads}}{RT} + \text{constant} \quad (5)$$

Figure 10 illustrates the linear plots of ln K_{ads} *vs.* 1/T. As seen in Table 2, the computed ΔH_{ads} values are negative, proposing that the adsorption of drug molecules is an exothermic process of physical type [49,50].

The values of adsorption entropy (ΔS_{ads}) were computed using Eq. (6):

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (6)$$

The computed values ΔS_{ads} are inserted in Table 2, signifying increasing in the disorder of the adsorption of drug molecules. Such behavior may be due to the desorption of more H_2O molecules from the copper surface and their replacement by drug molecules [51].

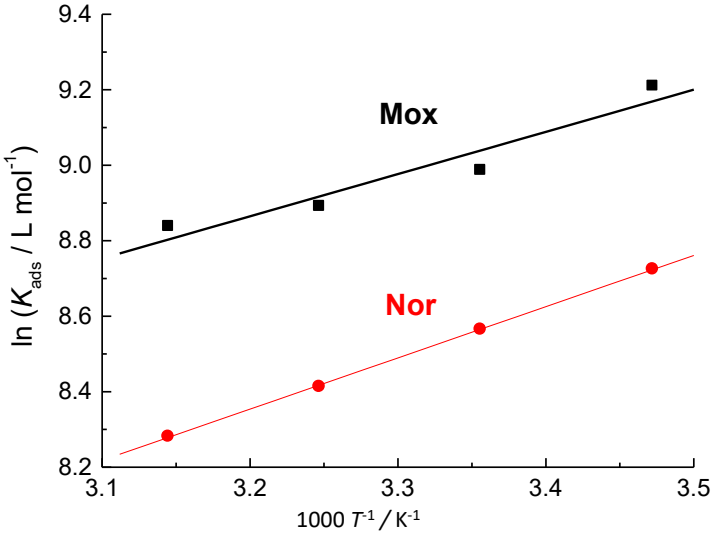


Figure 10. *Van't Hoff plots for expired drugs adsorbed on the copper surface in 3.5 % NaCl*

Table 2. *Thermodynamic parameters and K_{ads} for copper corrosion in 3.5 % NaCl with expired drugs at different temperatures*

Inhibitor	T / K	a	b	R^2	K_{ads} / 10^3 L mol^{-1}	ΔG_{ads} / kJ mol^{-1}	ΔH_{ads} / kJ mol^{-1}	ΔS_{ads} / J mol^{-1} K^{-1}
Mox	288	39.98	1.032	0.99971	10.03	-31.68	-9.29	75.94
	298	52.74	1.022	0.99894	7.98	-32.21		75.18
	308	53.37	1.041	0.99871	7.27	-33.06		75.47
	318	54.35	1.072	0.99884	6.90	-33.99		76.04
Nor	288	51.62	1.047	0.99912	6.15	-30.51	-11.28	79.09
	298	61.18	1.053	0.99934	5.25	-31.18		78.68
	308	70.85	1.078	0.99959	4.51	-31.83		78.26
	318	81.80	1.082	0.99948	3.95	-32.52		77.94

Kinetic parameters

The values of activation energy (E_a*) were evaluated from Arrhenius equation, Eq. (7) [52]:

$$\ln \mathrm{CR} = \ln A - \frac{E_a^*}{RT} \quad (7)$$

where A is the Arrhenius constant.

The results shown in Figure 11 indicate that the plots of ln CR versus 1/T are linear, from which slopes, the values of E_a* were evaluated and inserted in Table 3.

The values of E_a* in the presence of the explored drugs were higher than that gained in the blank solution, signifying strong physical adsorption of drug molecules on the copper surface and the formation of a barrier that separates such a surface from the corrosive medium [53]. Furthermore, the acquired values of E_a* were lesser than 80 kJ mol^{-1}, which is a prerequisite for chemical adsorption, suggesting that the adsorption type is physical [54]. These findings are in agreement with the results of both ΔG_{ads} and ΔH_{ads}, proving the actuality of the obtained results.

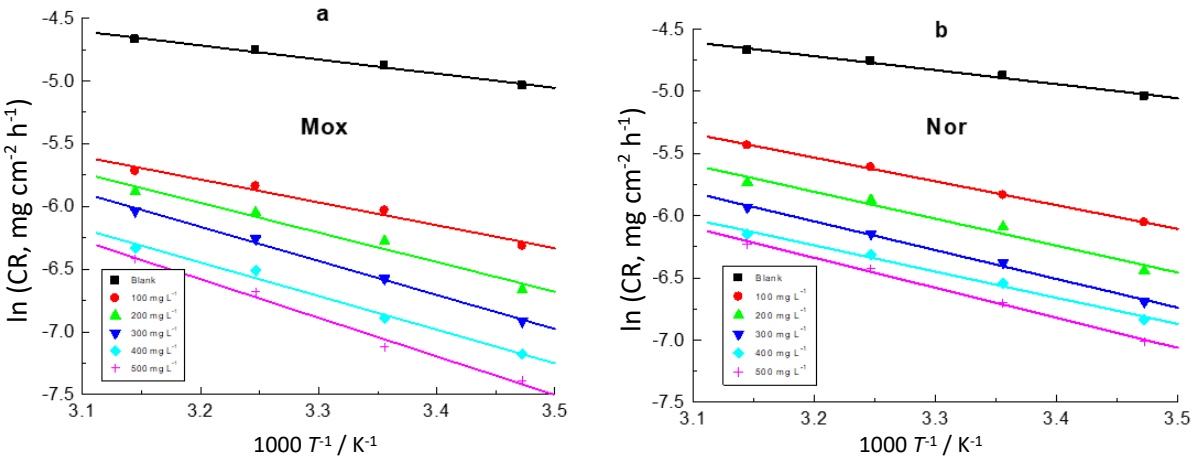


Figure 11. *Arrhenius plots for copper corrosion in 3.5 % NaCl (blank) and in presence of different concentrations of expired drugs a - Mox and b - Nor*

Table 3. *Activation parameters for copper corrosion in 3.5 % NaCl (blank) and with expired drugs Mox and Nor*

3.5 % NaCl +	C_{inh} / mg L^{-1}	E_a* / kJ mol^{-1}	ΔH* / kJ mol^{-1}	ΔS / J mol^{-1} K^{-1}
Blank	0	9.33	6.83	-41.49
Mox	100	15.17	12.62	-31.76
	200	19.62	17.02	-19.29
	300	22.57	20.08	-11.06
	400	22.20	19.73	-14.55
	500	25.52	23.06	-5.07
Nor	100	15.89	13.34	-27.43
	200	17.99	15.52	-22.53
	300	19.22	16.64	-21.20
	400	17.51	14.82	-28.68
	500	20.07	17.65	-20.37

Enthalpy (ΔH*) and entropy (ΔS*) of activation were evaluated from the transition state equation, Eq. (8) [55]:

$$\ln\left(\frac{CR}{T}\right)=\left(\ln\frac{R}{Nh}+\frac{\Delta S^*}{R}\right)-\frac{\Delta H^*}{R}\frac{1}{T} \quad (8)$$

where R is the gas constant, N is Avogadro's number and h is Planck's constant. The plots of ln CR *vs*. 1/T are linear, as shown in Figure 12.

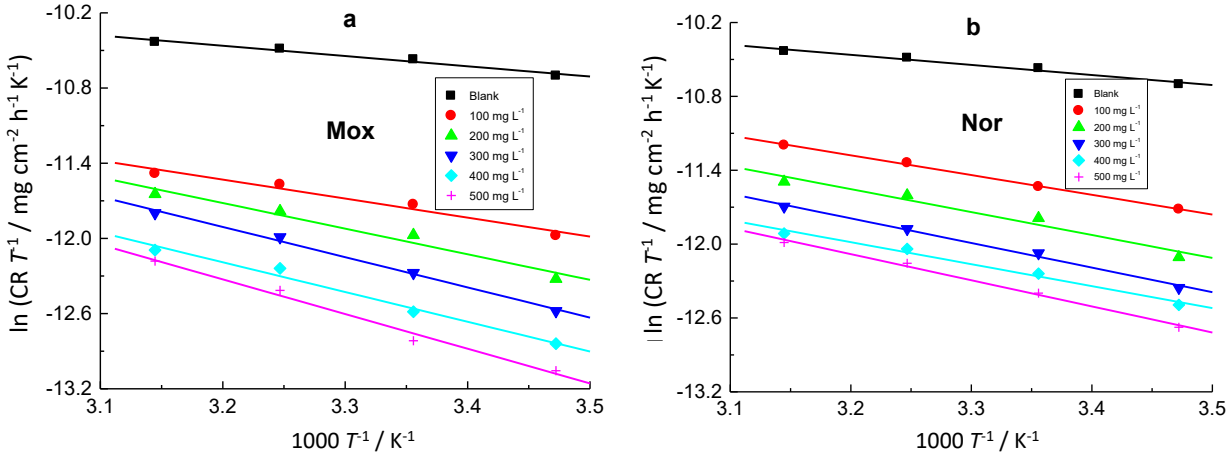


Figure 12. *Transition state plots for copper corrosion in 3.5 % NaCl (blank) and in presence of different concentrations of expired drugs a - Mox and b - Nor*

The values of both Δ*H** and Δ*S** were evaluated from these plots and listed in Table 3. Values of Δ*H** are positive, signifying that the corrosion is endothermic, while the obtained negative values of Δ*S** signify a decrease in the randomness due to the formation of the activated complexes [56]. The higher value of Δ*H** in the existence of the explored drugs suggests greater difficulty for the corrosion process to occur, which eventually signifies higher inhibition. Adsorption of drug molecules on the copper surface increases the values of Δ*H**, enhancing IE.

Figure 13 shows a matching of the trend of the values of E_a* with those of Δ*H** for all examined concentrations of both drugs.

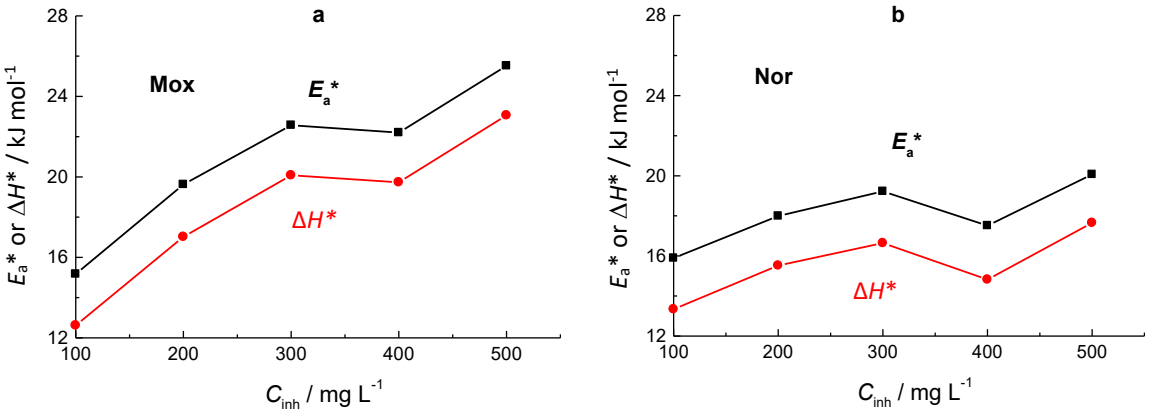


Figure 13. *Variations of activation parameters with concentrations of expired drugs a - Mox and b - Nor for the corrosion of copper in 3.5 % NaCl solution*

Kinetics of copper corrosion and its inhibition

The kinetics of copper corrosion in 3.5 % NaCl and its inhibition by different concentrations of expired drugs Mox and Nor, at 298 K were investigated. The obtained results showed that the corrosion of copper and its inhibition follow the first-order kinetics according to Equation (9):

$$-\ln WL = k_1 t - \ln W_0 \quad (9)$$

where k_1 is the first order rate constant, and W_0 is the initial weight of the copper sheet.

The plots of -ln WL *vs*. *t* are linear, as shown in Figure 14, signifying that the kinetics of copper corrosion and its inhibition by the explored drugs in 3.5 % NaCl is negative first order.

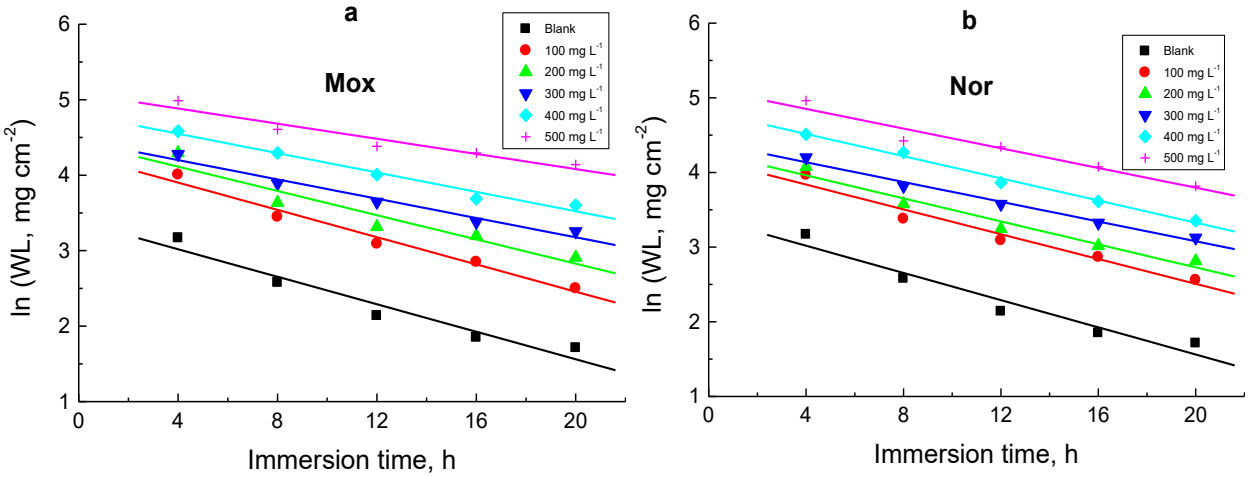


Figure 14. *First-order rate constant plots for copper corrosion in 3.5 % NaCl (blank) and in presence of different concentrations of expired drugs a - Mox and b - Nor, at 298 K*

From Figure 14, the values of k_1 were evaluated and listed in Table 4. Moreover, the values of half-life time, $t_{1/2}$, of such process were calculated (Table 4) from k_1 values *via* Eq. (10) [57]:

$$t_{1/2} = \frac{0.693}{k_1} \quad (10)$$

Table 4. *Values of k_1 and $t_{1/2}$ for copper corrosion in 3.5 % NaCl (blank) and in presence of different concentrations of expired drugs Mox and Nor at 298 K*

C_{inh} / mg L^{-1}	Mox		Nor	
	k_1 / h^{-1}	$t_{1/2}$ / h	k_1 / h^{-1}	$t_{1/2}$ / h
0	0.091	7.62	0.091	7.62
100	0.089	7.79	0.083	8.35
200	0.080	8.66	0.077	9.01
300	0.063	11.00	0.065	10.66
400	0.065	10.66	0.074	9.36
500	0.051	13.59	0.066	10.50

The values of the order of corrosion inhibition (*n*) enabled by the presence of expired drugs were computed *via* Eq. (11) [58] and listed in Table 5.

$$\log CR = \log k + n \log C_{inh.} \quad (11)$$

Table 5. *Values of the order of corrosion inhibition of copper in 3.5 % NaCl by expired drugs Mox and Nor at different temperatures*

Temperature, K	*n*	
	Mox	Nor
288	-0.658	-0.587
298	-0.674	-0.544
308	-0.523	-0.519
318	-0.441	-0.505

Also, the plots of log CR *vs*. log C_{inh} for the expired drugs Mox and Nor were linear, as illustrated in Figure 15. The obtained values of *n* (Table 5) indicate that the inhibition of copper corrosion is negative fractional-first order regarding C_{inh}. The negative sign of *n* values and the opposite reliance of the values of corrosion rates with C_{inh} signified good IE of the explored drugs [59].

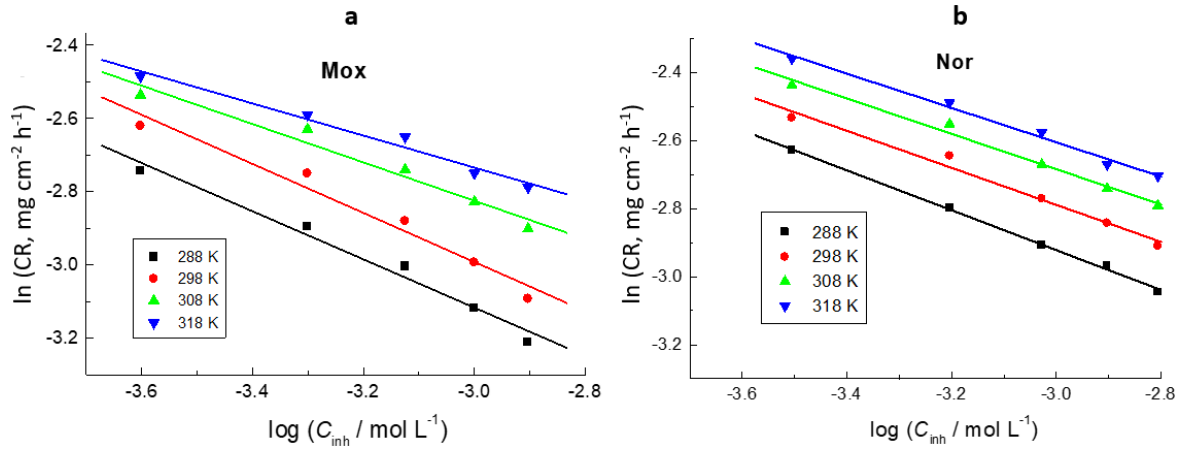


Figure 15. *Plots of log CR* vs. *log C_{inh} for the inhibition of copper corrosion in 3.5 % NaCl by expired drugs a - Mox and b -N or at different temperatures*

Electrochemical studies

Open circuit potential measurements

Figure 16 shows the variation of open circuit potentials (OCP or E_{OC}) as a function of immersion time for copper in 3.5 % NaCl without and with different concentrations of the explored drugs at

298 K over an hour (3600 s). The addition of the explored drugs shifted the values of open circuit potentials towards more positive values, signifying the construction of corrosion products or the adsorption of species on the copper surface. The E_{OC} in the blank solution was initially shifted in the cathodic direction before a steady state, suggesting dissolution of the oxide layer formed on the copper surface and attack of the metal. In the presence of the explored drugs, the steady state was attained faster compared with that in the blank, and this behavior was increased with increasing the concentration of the added drugs, indicating modification of the E_{OC} behavior of copper *via* adsorption of drug molecules on the copper surface and construction of surface films that protect the metal surface. Also, the explored drugs were suggested to act as mixed-type inhibitors with anodic predominance (the shifts in E_{OC} were less than ±85 mV) [60].

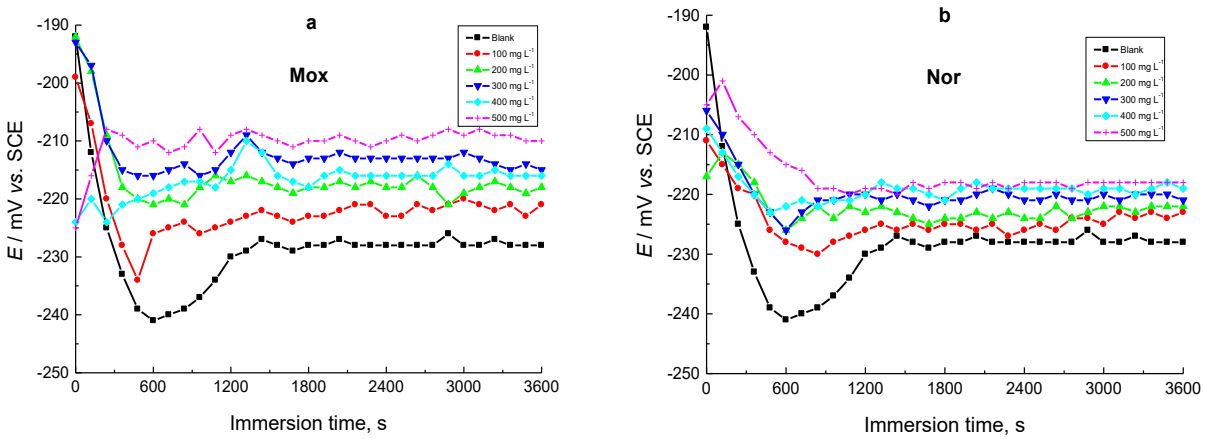


Figure 16. *OCP vs. immersion time measurements for copper in 3.5 % NaCl solution (blank) and in presence of different concentrations of expired drugs a - Mox and b - Nor at 298 K*

Potentiodynamic polarization measurements

The results obtained from PDP measurements for copper corrosion in 3.5 % NaCl and with the explored drugs Mox and Nor at 298 K were used to plot the Tafel curves, presented in Figure 17. The figure indicated that the addition of the explored drugs to the corrosive solution (3.5 % NaCl) shifted both the anodic and cathodic branches of the Tafel curves towards lower i_{corr} values, suggesting a reduction in the corrosion rate of copper and, thus, corrosion inhibition. Extrapolation of both branches of the Tafel curves was used to evaluate the corrosion parameters, including corrosion potential (E_{corr}), anodic (β_a) and cathodic (β_c) Tafel slopes, corrosion current density (i_{corr}) and polarization resistance (R_p), which are inserted in Table 6. Also, *via* Eq. (12), the values of IE and θ were computed [61] and listed in Table 6.

Table 6. *PDP corrosion parameters of copper corrosion in 3.5 % NaCl (blank) and in presence of different concentrations of expired drugs Mox and Nor at 298 K*

Inhibitor	C_{inh} / mg L^{-1}	E_{corr} / mV *vs.* SCE	β_a / mV dec^{-1}	$-\beta_c$ / mV dec^{-1}	i_{corr} / μA cm^{-2}	R_p / Ω cm^2	IE, %	θ
None	0	-228	52	116	6.20	2518	--	--
Mox	100	-222	55	157	1.85	5573	70.2	0.702
	200	-217	58	125	1.36	12665	78.0	0.780
	300	-212	66	151	1.09	18319	82.4	0.824
	400	-215	61	141	0.92	20122	85.1	0.851
	500	-209	53	115	0.70	22534	88.7	0.887
Nor	100	-225	56	114	2.03	8034	67.3	0.673
	200	-223	62	115	1.65	10614	73.4	0.734
	300	-219	54	114	1.26	12644	79.7	0.797
	400	-218	52	110	1.00	15352	83.9	0.839
	500	-217	51	118	0.92	16828	85.2	0.852

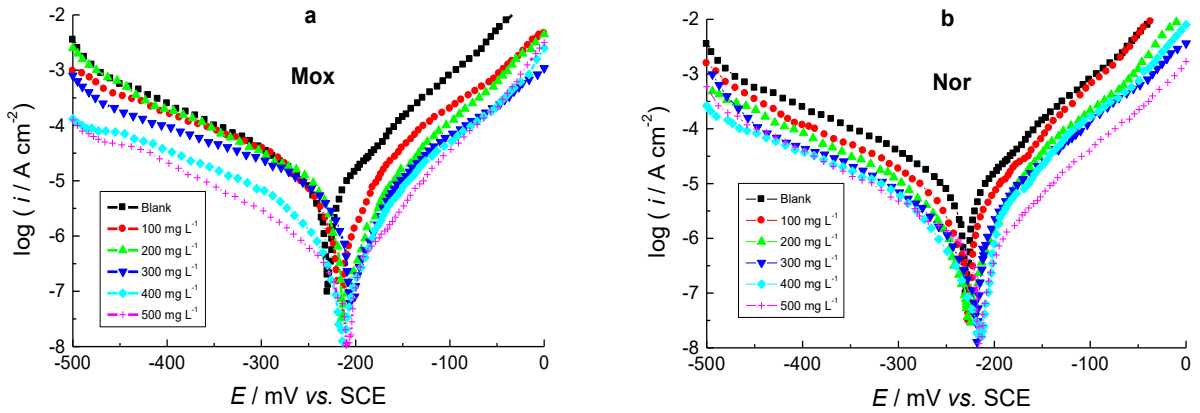


***Figure 17**. PDP plots for copper corrosion in 3.5 % NaCl (blank) and in presence of different concentrations of expired drugs a - Mox and b -Nor at 298 K*

$$IE = 100\,\theta = \left(1 - \frac{i_{corr(inh)}}{i_{corr}}\right)100 \qquad (12)$$

In Eq. (12), $i_{corr(inh)}$ and i_{corr} are the values of the current density in the inhibited and uninhibited systems, respectively.

Figure 17 and the corrosion parameters listed in Table 6 signify that adding the explored drugs to the corrosive medium slightly moved the value of E_{corr} in the positive or anodic direction signifying that the added drugs exhibited mixed-type inhibitory properties with anodic supremacy. With increasing drugs' concentrations, the obtained values of both β_a and β_c showed small changes in their values (in most cases), indicating that the kinetics of the corrosion process was not affected by the added drugs. The value of i_{corr} of copper was reduced while the R_p value was augmented with the rising concentration of the added drugs, proving corrosion inhibition.

Finally, comparing the IE of the explored drugs Mox and Nor at 298 K gained from the employed techniques (WL and PDP), a good agreement was achieved designating the authenticity of the used techniques, as shown in Figure 18.

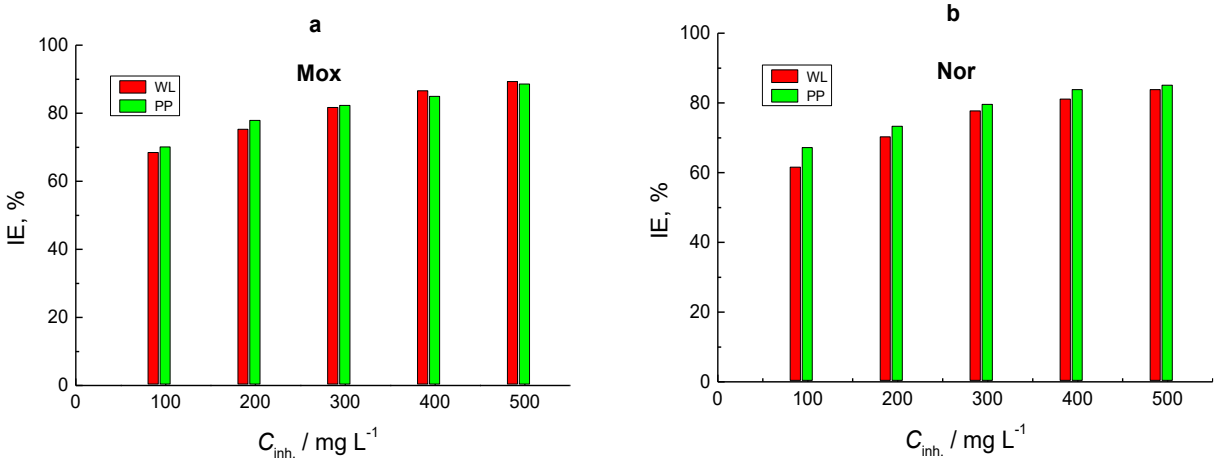


***Figure 18.** Comparing between % IE values obtained by PDP and WL techniques for different concentrations of expired drugs a - Mox and b -Nor for copper corrosion in 3.5 % NaCl, at 298 K*

Surface analysis

SEM micrographs of the copper surfaces before and after 20 hours of immersion in a 3.5 % NaCl solution and in the presence of 500 mg L^{-1} of the expired drugs Mox and Nor are shown in Figure 19.

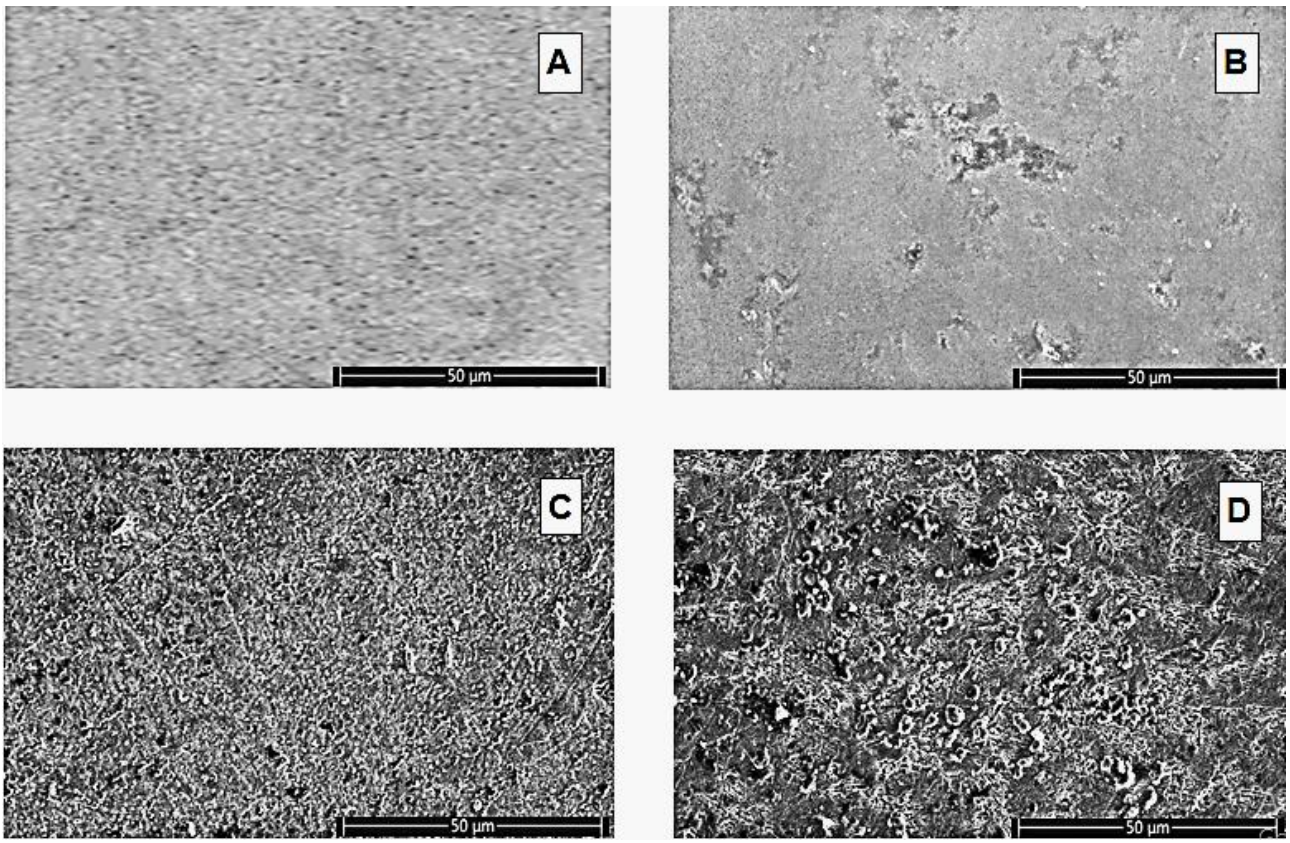


Figure 19. *SEM images of copper surfaces before (A) and after 20 hours of immersion in (B) 3.5 % NaCl; (C) and (D) 3.5 % NaCl with 500 mg/L of expired drugs Mox and Nor*

Figure 19(A) shows the polished copper surface prior to immersion, while Figure 19(B) shows the copper surface after immersion in 3.5 % NaCl. It is obvious that after immersion, copper manifests damage to the surface and appearance of numerous pits due to the aggressiveness of the corrosive medium (NaCl). Figures 19 (C) and (D) show the elimination of damaged characteristics and pits from the copper surfaces and the formation of protective films on them. This is due to the strong adsorption of the drug molecules on the copper surfaces, the construction of adhesive and protective films, and the demonstration of excellent inhibition properties. Hence, the results of the SEM study agree with the experimental outcomes collected from different techniques.

Corrosion-inhibition mechanism

For copper in aerated neutral media, the cathodic reaction has been stated [62] to be a reduction of either water molecules or dissolved oxygen (Eqs. (13 and (14))with formation of hydroxide,

$$2H_2O + 2e^- = H_2 + 2OH^- \quad (13)$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \quad (14)$$

The anodic reaction is the dissolution of Cu to Cu^+ and Cu^{2+} ions, as presented by Eqs. (15) and (16) [63]:

$$Cu = Cu^+ + e^- \text{ (fast)} \quad (15)$$

$$Cu^+ = Cu^{2+} + e^- \text{ (slow)} \quad (16)$$

Cu^+ reacts with Cl^- in a fast reaction to form an unstable insoluble film of CuCl on the copper surface, Eq. (17) [64]:

$$Cu^+ + Cl^- = CuCl \quad (17)$$

Then, the formed CuCl turns to the soluble $CuCl_2^-$, Eq. (18)[65]:

$$CuCl + Cl^- = CuCl_2^- \quad (18)$$

The formed $CuCl_2^-$ oxidizes, leading to the dissolution of copper, Eq. (19):

$$CuCl_2^- = Cu^{2+} + 2Cl^- + e^- \quad (19)$$

The obtained higher IE of the explored drugs are proposed to result from the substitution of Cl^- ions or water molecules adsorbed on the copper surface by drug molecules [66] according to the exchange reaction, Eq. 20:

$$Inh_{(sol)} + nH_2O_{(ads)} \leftrightarrow Inh_{(ads)} + nH_2O_{(sol)} \quad (20)$$

The physical adsorption (electrostatic) and the chemical adsorption (formation of chemical bonds) are probably combined. Physical adsorption occurs due to the presence of charged inhibitor molecules in the medium and the charged metal surface, while chemical adsorption is due to the creation of coordinate bonds due to sharing or transferring charges between the inhibitor molecules and the metal surface. Because the explored drugs Mox and Nor contain extensive π-electron systems heteroatoms (N and O) in their structures, they can form coordinate bonds with the vacant orbitals on the copper surface, resulting in an enhancement of their adsorption on the metal surface [67], according to Eq. (21):

$$Cu + Inh. = [Cu - Inh]_{(ads)} \quad (21)$$

Such adsorption leads to the formation of a strong surface layer that protects the copper surface from the aggressiveness of the corrosive medium, leading to a retardation in the dissolution rate of copper.

Conclusions

1. Two expired drugs, Mox and Nor, were investigated as inhibitors of copper corrosion in 3.5 % NaCl medium.
2. Maximum IE of 89.4, 83.9, 88.7 and 85.2 % using WL and PDP measurements were achieved for expired Mox and Nor, respectively. IE was enhanced with increasing drug doses while reduced with rising temperature. Higher IE were suggested to be due to good adsorption of drug molecules on the copper surface and such adsorption was proposed to be physical and followed Langmuir isotherm.
3. Both expired drugs behave as mixed inhibitors with anodic predominance.
4. The investigational outcomes collected from all used techniques were principally consistent with each other's.
5. Based on the results reported here, expired Mox and Nor can be proposed as promising candidates for inhibiting copper corrosion.

Acknowledgments: *This work was supported and funded by the Deanship of Scientific Research at Imam Mohammad Ibn Saud Islamic University (IMSIU) (grant number IMSIU-RG23086).*

References

[1] E. Touzé, C. Cougnon, Study of the air-formed oxide layer at the copper surface and its impact on the copper corrosion in an aggressive chloride medium, *Electrochimica Acta* **262** (2018) 206-213. https://doi.org/10.1016/j.electacta.2017.12.187

[2] K. F. Khaled, Guanidine derivative as a new corrosion inhibitor for copper in 3 % NaCl solution, *Materials Chemistry and Physics* **112**(2008) 104-111. https://doi.org/10.1016/j.matchemphys.2008.05.052

[3] A. Fawzy, A. Toghan, O. K. Alduaij, N. Alqarni, A. M. Eldesoky, A. A. Farag, Electrochemical, spectroscopic, kinetic and surface analysis of the inhibitory performance of Alcian blue dye for copper corrosion in sulfuric acid solution, *International Journal of Electrochemical Science* **19** (2024) 100429. https://doi.org/10.1016/j.ijoes.2023.100429

[4] Y. Qiang, S. Zhang, L. Guo, X. Zheng, B. Xiang, and S. Chen, Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid, *Corrosion Science* **119** (2017) 68-78. https://doi.org/10.1016/j.corsci.2017.02.021

[5] D. Kumar, N. Jain, V. Jain, B. Rai, Amino acids as copper corrosion inhibitors: A density functional theory approach, *Applied Surface Science* **514** (2020) 145905. https://doi.org/10.1016/j.apsusc.2020.145905

[6] A. Fawzy, O. K. Alduaij, A. Al-Bahir, D. A. Alshammari, N. Alqarni, A. M. Eldesoky, A. A. Farag, A. Toghan, A comparative study of pyridine and pyrimidine derivatives based formamidine for copper corrosion inhibition in nitric acid: Experimental and computational exploration, *International Journal of Electrochemical Science* **19** (2024) 100403. https://doi.org/10.1016/j.ijoes.2023.100403

[7] F. García-Ávila, G. Bonifaz-Barba, S. Donoso-Moscoso, L. F. del Pino, L. Ramos-Fernández, Dataset of copper pipes corrosion after exposure to chlorine, *Data in Brief* **19** (2018) 170-178. https://doi.org/10.1016/j.dib.2018.05.023

[8] A. Toghan, A. Fawzy, A. I. Alakhras, A. A. Farag, Electrochemical and theoretical examination of some imine compounds as corrosion inhibitors for carbon steel in oil wells formation water, *International Journal of Electrochemical Science* **17** (2022) 2212108. https://doi.org/10.20964/2022.12.94

[9] Y. Qiang, S. Zhang, L. Wang, Understanding the adsorption and anticorrosive mechanism of DNA inhibitor for copper in sulfuric acid, *Applied Surface Science* **492** (2019) 228-238. https://doi.org/10.1016/j.apsusc.2019.06.190

[10] N. M. El-Basiony, M. H. Sliem, A. A. Abd-Elaal, Theoretical and experimental insights into the C-steel aqueous corrosion inhibition at elevated temperatures in 1.0 M HCl via multicarbonyl Gemini cationic surfactants, *Zeitschrift für Physikalische Chemie* **237** (2023) 707-736. https://doi.org/10.1515/zpch-2023-0219

[11] G. Kilinççeker, H. Demir, The inhibition effects of cysteine on the corrosion behaviour of copper in 3.5% NaCl solution, *Anti-Corrosion Methods and Materials* **60** (2013) 134-142. DOI:10.1108/00035591311315256

[12] X. D. Chen, M. Gong, Q. S. Fu, X. W. Zheng, X. S . Feng, [Omim][Pro] amino acid ionic liquids as a corrosion inhibitor for copper in 3.5 % NaCl solution, *Applied Mechanics and Materials* **496-500** (2014) 47-50. https://doi.org/10.4028/www.scientific.net/AMM.496-500.47

[13] G. Rajkumar, R. Sagunthala, M. G. Sethuraman, Investigation of inhibiting properties of self-assembled films of 4-aminothiophenol on copper in 3.5 % NaCl, *Journal of Adhesion Science and Technology* **29** (2015) 1107-1117. https://doi.org/10.1080/01694243.2015.1019391

[14] D. Wang, B. Xiang, Y. Liang, S. Song, C. Liu, Corrosion control of copper in 3.5 wt.% NaCl Solution by domperidone: experimental and theoretical study, *Corrosion Science* **85** (2014) 77-86. https://doi.org/10.1016/j.corsci.2014.04.002

[15] Y. Qiang, S. Zhang, S. Xu, L. Yin, The effect of 5- nitroindazole as an inhibitor for the corrosion of copper in a 3.0% NaCl solution, *RSC Advances* **5** (2015) 63866-63873. https://doi.org/10.1039/C5RA12933H

[16] H. Tian, Y. F. Cheng, W. Li, B. Hou, Triazolyl-acylhydrazone derivatives as novel inhibitors for copper corrosion in chloride solutions, *Corrosion Science* **100** (2015) 341-352. https://doi.org/10.1016/j.corsci.2015.08.022

[17] H. Tian, W. Li, K. Cao, B. Hou, Potent inhibition of copper corrosion in neutral chloride media by novel non-toxic thiadiazole derivatives, *Corrosion Science* **73** (2013) 281-291. https://doi.org/10.1016/j.corsci.2013.04.017

[18] P. F. Khan, V. Shanthi, R. K. Babu, S. Muralidharan, R. C. Barik, Effect of benzotriazole on corrosion inhibition of copper under flow conditions, *Journal of Environmental Chemical Engineering* **3** (2015) 10-19. https://doi.org/10.1016/j.jece.2014.11.005

[19] S. C. Dheeraj, M. A. Quraishi, C. Carrière, A. Seyeux, P. Marcus, A. Singh, Electrochemical, ToF-SIMS and computational studies of 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol as a novel corrosion inhibitor for copper in 3.5% NaCl, *Journal of Molecular Liquids* **289** (2019) 111113. https://doi.org/10.1016/j.molliq.2019.111113

[20] Y. H. Lei, N. Sheng, A. Hyono, M. Ueda, T. Ohtsuka, Effect of benzotriazole (BTA) addition on polypyrrole film formation on copper and its corrosion protection, *Progress in Organic Coatings* **77** (2014) 339-346. https://doi.org/10.1016/j.porgcoat.2013.10.009

[21] A. Toghan, O. K. Alduaij, A. Fawzy, A. M. Eldesoky, A. A. Farag, Physicochemical, electrochemical, and theoretical study of the corrosion inhibition performance of copper using N-benzylhydrazinecarbothioamide in a 3.5% NaCl solution, *Journal of Electrochemical Science and Engineering* **14** (2024) 231-245. https://doi.org/10.5599/jese.2181

[22] M. Finšgar, The first X-ray photoelectron spectroscopy surface analysis of 4-methyl-2-phenyl-imidazole adsorbed on copper, *Analytical Methods* **7** (2015) 6496-6503. https://doi.org/10.1039/C5AY00896D

[23] M. Finšgar, D. Kek Merl, 2-Mercaptobenzoxazole as a copper corrosion inhibitor in chloride solution: electrochemistry, 3D-profilometry, and XPS surface analysis, *Corrosion Science* **80** (2014) 82-95. https://doi.org/10.1016/j.corsci.2013.11.022

[24] G. Ezznaydy, A. Shaban, J. Telegdi, B. Ouaki, S. El Hajjaji, Inhibition of copper corrosion in saline solution by mono-hydroxamic acid, *Journal of Materials and Environmental Science* **6** (2015) 1819-1823. https://www.jmaterenvironsci.com/Document/vol6/vol6_N7/215.JMES-2015-Ezznaydi.pdf

[25] S. L. Chi-Ucan, A. Castillo-Atoche, P. C. Borges, J. A. Manzanilla-Cano, G. Gonzalez-Garcıa, R. Patino, L. Dıaz-Ballote, Inhibition effect of glycerol on the corrosion of copper in NaCl solutions at different pH values, *Journal of Chemistry* **2014** (2014) 396405. https://doi.org/10.1155/2014/396405

[26] A. Toghan, O. K. Alduaij, A. Fawzy, A. M. Mostafa, A. M. Eldesoky, A. A. Farag, Effect of adsorption and interactions of new triazole-thione-Schiff bases on the corrosion rate of carbon steel in 1 M HCl solution: Theoretical and experimental evaluation, *ACS Omega* **9** (2024) 6761-6772. https://doi.org/10.1021/acsomega.3c08127

[27] G. Quartarone, M. Battilana, L. Bonaldo, T. Tortato, Investigation of the inhibition effect of indole-3-carboxylic acid on the copper corrosion in 0.5 M H_2SO_4, *Corrosion Science* **50** (2008) 3467-3474. https://doi.org/10.1016/j.corsci.2008.09.032

[28] M. M. Shaban, N. M. El Basiony, A. B. Radwan, Electrochemical investigation of C-steel corrosion inhibition, in silico, and sulfate-reducing bacteria investigations using Pyrazole derivatives, *ACS Omega* **8** (2023) 30068-30080. https://doi.org/10.1021/acsomega.3c02333

[29] S. Y. Sayed, M. S. El-Deab, B. E. El-Anadouli, B. G. Ateya, Synergistic effects of benzotriazole and copper ions on the electrochemical impedance spectroscopy and corrosion behavior of iron in sulfuric acid, *The Journal of Physical Chemistry B* **107**(2003) 5575. https://doi.org/10.1021/jp034334x

[30] R. A. Anaee, I. Hameed R. Tomi, M. H. Abdulmajeed, S. A. Naser, M. M. Kathem, Expired Etoricoxib as a corrosion inhibitor for steel in acidic solution, *Journal of Molecular Liquids* **279** (2019) 594-602. https://doi.org/10.1016/j.molliq.2019.01.169

[31] M. Finšgar, I. Milošev, Inhibition of copper corrosion by 1,2,3-benzotriazole: a review, *Corrosion Science* **52** (2010) 2737-2749. https://doi.org/10.1016/j.corsci.2010.05.002
[32] H. A. Abdullah, R. A. Anaee, A. A. Khadom, A. T. Abd Ali, A. H. Malik, M. M. Kadhim, Experimental and theoretical assessments of the chamomile flower extract as a green corrosion inhibitor for aluminum in artificial seawater, *Results in Chemistry* **6** (2023) 101035. https://doi.org/10.1016/j.rechem.2023.101035
[33] A. Toghan, A. Fawzy, Unraveling the adsorption mechanism and anti-corrosion functionality of dextrin and inulin as eco-friendly biopolymers for the corrosion of reinforced steel in 1.0 M HCl: A thermodynamic and kinetic approach, *Polymers* **15** (2023) 3144. https://doi.org/10.3390/polym15143144
[34] K. Dahmani, M. Galai, M. Ouakki, M. Cherkaoui, R. Touir, S. Erkan, S. Kaya, B. El Ibrahimi, Quantum chemical and molecular dynamic simulation studies for the identification of the extracted cinnamon essential oil constituent responsible for copper corrosion inhibition in acidified 3.0 wt% NaCl medium, *Inorganic Chemistry Communications* **124** (2021) 108409. https://doi.org/10.1016/j.inoche.2020.108409
[35] A. Toghan, A. Fawzy, A. I. Alakhras, N. Alqarni, M. E. A. Zaki, M. M. S. Sanad, A. A. Farag Experimental exploration, RSM modeling and DFT / MD simulations of the anticorrosion performance of naturally occurring amygdalin and raffinose for aluminum in NaOH solution, *Coatings* **13** (2023) 704. https://doi.org/10.3390/coatings13040704
[36] A. M. Al-Ghaban, H. A. Abdullah, R. A. Anaee, S. A. Naser, A. A. Khadom, Expired butamirate drug as eco-friendly corrosion inhibitor for aluminum in seawater: Experimental and theoretical studies, *Journal of Engineering Research* **12** (2024) 299-309. https://doi.org/10.1016/j.jer.2023.11.020
[37] K. H. Rashid, A. A. Khadom, S. H. Abbas, K. F. Al-Azawi, H. B. Mahood, Optimization studies of expired mouthwash drugs on the corrosion of aluminum 7475 in 1 M hydrochloric acid: Gravimetrical, electrochemical, morphological and theoretical investigations, *Results in Surfaces and Interfaces* **13** (2023) 100165. https://doi.org/10.1016/j.rsurfi.2023.100165
[38] H. M. Elabbasy, A. Toghan, H. S. Gadow, Cysteine as an Eco-Friendly Anticorrosion Inhibitor for Mild Steel in Various Acidic Solutions: Electrochemical, Adsorption, Surface Analysis, and Quantum Chemical Calculations, *ACS Omega* **9** (2024) 13391-13411. https://doi.org/10.1021/acsomega.3c10522
[39] H. S. Gadow, M. M. Motawea, H. M. Elabbasy, Investigation of myrrh extract as a new corrosion inhibitor for K-brass in 3.5 % NaCl solution polluted by 16 ppm sulfide, *RSC Advances* **7** (2017) 29883-29898. https://doi.org/10.1039/C7RA04271J
[40] Y. Tokura, Quinolone photoallergy: Photosensitivity dermatitis induced by systemic administration of photohaptenic drugs, *Journal of Dermatological Science* **18** (1998) 1-10. https://doi.org/10.1016/S0923-1811(98)00026-7
[41] V. Yadav, P. Talwar, Repositioning of fluoroquinolones from antibiotic to anti-cancer agents: An underestimated truth, *Biomedicine & Pharmacotherapy* **111** (2019) 934-946. https://doi.org/10.1016/j.biopha.2018.12.119.
[42] S. Y. Peng, Z. N. Jiang, Y. R. Li, C. F. Dong, H. F. Liu, G. A. Zhang, A new exceptional imidazoline derivative corrosion inhibitor for carbon steel in supercritical CO_2 environment, *Corrosion Science* **245** (2025) 112663. https://doi.org/10.1016/j.corsci.2024.112663
[43] A. Toghan, O. K Alduaij, N. Alqarni, E M. Masoud, H. Alhussain, A. M. Mostafa, A. A. Farag, A. Fawzy, Mathematical, electrochemical, spectroscopic and microscopic monitoring of the adsorption effect of expired drugs on zinc corrosion in 3.5% NaCl solution, *Results in Chemistry* **13** (2025) 102006. https://doi.org/10.1016/j.rechem.2024.102006

[44] X. Li, S. Deng, G. Mu, H. Fu, F. Yang, Inhibition effect of nonionic surfactant on the corrosion of cold rolled steel in hydrochloric acid, *Corrosion Science* **50** (2008) 420-430. https://doi.org/10.1016/j.corsci.2007.08.014

[45] M. Christov, A. Popova, Adsorption characteristics of corrosion inhibitors from corrosion rate measurements, *Corrosion Science* **46** (2004) 1613-1620. https://doi.org/10.1016/j.corsci.2003.10.013

[46] .K. Shukla, M. A. Quraishi, Cefotaxime sodium: a new and efficient corrosion inhibitor for mild steel in hydrochloric acid solution, *Corrosion Science* **51** (2009) 1007-1011. https://doi.org/10.1016/j.corsci.2009.02.024

[47] M. Behpour, S. M. Ghoreishi, N. Soltani, M. Salavati-Niasari, M. Hamadanian, A. Gandomi, Electrochemical and theoretical investigation on the corrosion inhibition of mild steel by thiosalicylaldehyde derivatives in hydrochloric acid solution, *Corrosion Science* **50** (2008) 2172-2181. https://doi.org/10.1016/j.corsci.2008.06.020

[48] T. Zhao, G. Mu, The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid, *Corrosion Science* **41** (1999) 1937-1944. https://doi.org/10.1016/S0010-938X(99)00029-3

[49] A. S. Fouda, S. A. Abd el-Maksoud, E. H. El-Sayed, H. A. Elbaz, A. S. Abousalem, Effectiveness of some novel heterocyclic compounds as corrosion inhibitors for carbon steel in 1 M HCl using practical and theoretical methods, *RSC Advances* **11** (2021) 19294-19309. https://doi.org/10.1039/D1RA03083C

[50] T. K. Sarkar, M. Yadav, I. B. Obot, Mechanistic evaluation of adsorption and corrosion inhibition capabilities of novel indoline compounds for oil well/tubing steel in 15% HCl, *Chemical Engineering Journal* **431** (2022) 133481. https://doi.org/10.1016/j.cej.2021.133481

[51] W. Durnie, R. D. Marco, A. Jefferson, B. Kinsella, Development of a structure-activity relationship for oil field corrosion inhibitors, *Journal of The Electrochemical Society* **146** (1999) 1751-1758. https://doi.org/10.1149/1.1391837

[52] M. Elachouri, M. S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert, E. Essassi, Some nonionic surfactants as inhibitors of the corrosion of iron in acid chloride solutions, *Corrosion* **52** (1996) 103-108. https://doi.org/10.5006/1.3292100

[53] B. Xu, Y. Liu, X. Yin, W. Yang, Y. Chen, Experimental and theoretical study of corrosion inhibition of 3-pyridinecarbozalde thiosemicarbazone for mild steel in hydrochloric acid, *Corrosion Science* **74** (2013) 206-213. https://doi.org/10.1016/j.corsci.2013.04.044

[54] X. Huang, H. Jiang, K. Cao, W. Huang, J. Liu, B. Liu, H. Wang, Corrosion inhibition of tetrabutylphosphonium benzotriazolate on carbon steel in acidic medium, *International Journal of Electrochemical Science* **19** (2024) 100824. https://doi.org/10.1016/j.ijoes.2024.100824

[55] A. Toghan, H. M. Dardeer, H. S.Gadow, H. M. Elabbasy: New promising halogenated cyclic imides derivatives as potential corrosion inhibitors for carbon steel in acidic environment, *Journal of Molecular Liquids* **325** (2021) 115136-115156. https://doi.org/10.1016/j.molliq.2020.115136

[56] J. Marsh, *Advanced Organic Chemistry*, 3rd ed. Wiley, Eastern New Delhi, 1988. ISBN 978-0-471-72091-1

[57] N. O. Eddy, A. E Patricia, P. A. P. Mamza, Ethanol extract of Terminalia catappa as a green inhibitor for the corrosion of mild steel in H_2SO_4, *Green Chemistry Letter Review* **2** (2009) 223-231. https://doi.org/10.1080/17518250903359941

[58] E. A. Noor, The inhibition of mild steel corrosion in phosphoric acid solutions by some N-heterocyclic compounds in the salt form, *Corrosion Science* **47** (2005) 33-53. https://doi.org/10.1016/j.corsci.2004.05.026

[59] S. B. Aoun, Highly Efficient corrosion inhibition of carbon steel in aggressive acidic media with a pyridazinium-based ionic liquid, *International Journal of Electrochemical Science* **8** (2013) 10788-10804. https://doi.org/10.1016/S1452-3981(23)13148-8

[60] H. Huang, Y. Fu, X. Wang, Y. Gao, Z. Wang, S. Zhang, H. Li, F. Gao, L. Chen, Nano- to Micro-Self-Aggregates of New Bisimidazole-Based Copoly(ionic liquid)s for Protecting Copper in Aqueous Sulfuric Acid Solution, *ACS Applied Materials Interfaces* **11** (2019**)** 10135-10145. https://doi.org/10.1021/acsami.8b19993

[61] H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, Inhibition of copper corrosion by several Schiff bases in aerated halide solutions, *Journal of Applied Electrochemistry* **32** (2002) 65-72. https://doi.org/10.1023/A:1014242112512

[62] K. F. Khaled, Studies of the corrosion inhibition of copper in sodium chloride solutions using chemical and electrochemical measurements, *Materials and Chemistry Physics* **125** (2011) 427-433. https://doi.org/10.1016/j.matchemphys.2010.10.037

[63] E.-S. M. Sherif, Inhibition of copper corrosion reactions in neutral and acidic chloride solutions by 5-ethyl-1,3,4- thiadiazol-2-amine as a corrosion inhibitor, *International Journal of Electrochemical Science* **7** (2012) 2832-2845. https://doi.org/10.1016/S1452-3981(23)13918-6

[64] A. L. Bacarella, J. C. Griess, The anodic dissolution of copper in flowing sodium chloride solutions between 25° and 175°C, *Journal of The Electrochemical Society* **120** (1973) 459-465. https://doi.org/10.1149/1.2403477

[65] F. K. Crundwell, The anodic dissolution of copper in hydrochloric acid solutions, *Electrochimica Acta* **37** (1992) 2707-2714. https://doi.org/10.1016/0013-4686(92)85197-S

[66] A. A. Farag, A. Toghan, Unravelling the adsorption and anti-corrosion potency of newly synthesized thiazole Schiff bases on C-steel in 1 M HCl: Computational and experimental implementations, *Results in Engineering* (2025) 104504. https://doi.org/10.1016/j.rineng.2025.104504

[67] C. Deslouis, B. Tribollet, G. Mengoli, M. M. Musiani, Electrochemical behaviour of copper in neutral aerated chloride solution. I. Steady-state investigation, *Journal of Applied Electrochemistry* **18** (1988) 374-383. https://doi.org/10.1007/BF01093751