Corrosion Inhibition Effect of Expired Ampicillin and Flucloxacillin Drugs for Mild Steel in Aqueous Acidic Medium

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The inhibition efficiencies of ampicillin and flucloxacillin expired drugs on mild steel (MS) corrosion in 1.0 M sulfuric acid medium was examined at 20°C using weight loss (WL), and electrochemical potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) techniques. Examined expired drugs are set to be efficient inhibitors for MS corrosion in sulfuric acid medium. The experimental outcomes of weight loss technique displayed that the inhibition performances of the investigated expired drugs augmented with increasing concentrations of such drugs and reduced by raising the temperature. The observed high inhibition efficiencies of the studied expired drugs may be owing to powerful adsorption of the drug species on MS surface resulting in formation of protective layers. Adsorption of the tested expired drugs on the MS surface was set to accord with Langmuir adsorption isotherm. The assessed thermodynamic parameters supported the mechanism of physical adsorption of the inhibitors.

1. INTRODUCTION

Pharmaceutical drug are chemical compounds that used in medicines to cure or treat bodies from diseases. Antibiotics are amongst the supreme considerable set of pharmaceutical drugs employed for treating bodies from bacterial and fungal infections. Also, they are employed in food preservation and processing [1,2]. Although, such drugs are essentially required for bodies, they are strange matters to the bodies. Hence, they must be eliminated from the bodies immediately after carrying out their medical action. Therefore, bodies have a natural process to eliminate such drugs through drug metabolism

process taking place in the liver. In addition, drugs are susceptible to expiration if the dates after which drugs might not be suitable for use as manufactured. Expired drugs can decompose, and either be ineffective or even harmful. Therefore, the expired drug must be disposed after the expiration date because such expired drugs may enter the environment and water cycle through different routes such as wastewater effluent, medical waste, etc. This leads to intimidation to the ecosystem and human health and has toxic impacts on the microorganisms because they contain complex organic compounds which are difficult to decompose into simple final products. Thus, they are regarded as one of the supreme dangerous pollutants for the environment and human health [3,4] and their impacts are aggrandizing day by day. Due to their vigorous risks to the environment and humans, variety of methods have been developed to overcome or safe reuse of these pollutants in order to protect the environment and human health.

Fortunately, pharmaceutical drugs are high molecular weight organic compounds and have hetero atoms in their structures which accelerate their adsorption on the steel surface [5-17]. Therefore, such drugs can be employed as good inhibitors for the corrosion of metals. The inhibition efficiencies of drugs have been linked with their structures, high molecular weight, high solubility in water and their safe use. Furthermore, using expired drugs that have no economic value as corrosion inhibitors for metals save large amounts of money in the protection of metals and alloys as well as protection of the environment and human health from these harmful substances. In this regard, drugs were formerly developed as corrosion inhibitors in different media [18-24]. Therefore, in the present study we aimed to recycle some selected expired drugs and reuse them as corrosion inhibitors. The selected expired drugs are two beta-lactam antibiotics of the penicillin class, viz. ampicillin and flucloxacillin (illustrated in Figure 1). Ampicillin (Amp) is one of the most famous antibiotics used to treat or prevent several viral and bacterial infections such as group B streptococcal infection in newborns. It is very effective and safe antibiotic prerequisite in the human health [25]. Flucloxacillin (Flx) is the most commonly antibiotic used for treating infections by inhibiting the synthesis of bacterial cell walls.
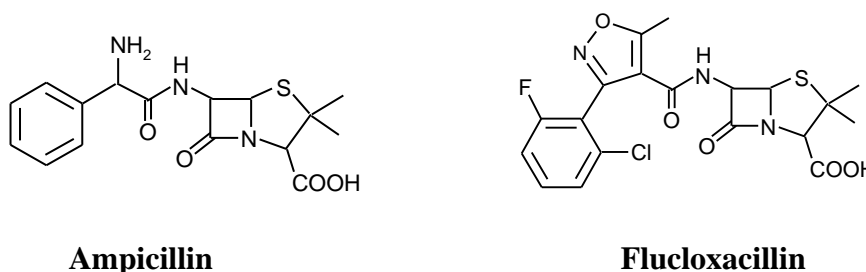

Ampicillin   **Flucloxacillin**

Figure 1. Chemical structures of Ampicillin (Amp) and Flucloxacillin (Flx) drugs.

In view of the above-mentioned aspects, we planned to estimate the inhibition efficiencies of ampicillin and flucloxacillin expired drugs for MS corrosion in aqueous sulfuric acid medium exploiting WL, PDP and EIS techniques.

2. EXPERIMENTAL

2.1. Materials

Ampicillin ($C_{16}H_{19}N_3O_4S$, Mw. 349.41) and flucloxacillin ($C_{19}H_{17}ClFN_3O_5S$, Mw. 453.87) drugs were supplied by Sigma and their solutions were prepared in doubly distilled water. Stock solutions of the corrosive medium (H_2SO_4) were prepared with doubly distilled water and the request concentrations were acquired via dilution. Corrosion experiments were carried out on MS samples having the composition (wt. %): 0.070 C, 0.070 Si, 0.012 S, 0.021 P, 0.270 Mn and the rest is Fe.

2.2. Methods

Measurements of WL were carried out in a temperature-controlled system. MS samples used for WL experiments were rods with areas equal to 14 cm^2 and were prepared for these measurements as mentioned formerly [7,8].

Both PDP and EIS techniques were achieved exploiting temperature-controlled PGSTAT30 potentiostat/galvanostat. The working electrode was a rod of MS with exposed area of 0.6 cm^2. Prior to each experiment, the working electrode was processed as in WL technique, and then it was immersed in the corrosive medium (blank, 1.0 M H_2SO_4) and/or the required concentration of the drug at OCP up to achieving the steady state. In a PDP technique, the electrode potential was changed in a potential range of -200 mV to +200 mV vs. OCP at a sweep rate of 2.0 mV/s. Electrochemical impedance spectroscopy measurements were done in a frequency range of 100 kHz to 0.1 Hz with an amplitude of 4.0 mV peak-to-peak exploiting AC signals at OCP.

3. RESULTS AND DISCUSSION

3.1. WL Measurements

3.1.1. Influence of Drugs Concentrations at Various Temperatures

WL measurements for MS corrosion in the blank solution (1.0 M H_2SO_4) and in the media with several concentrations of the examined drug inhibitors in the range of 100 – 400 ppm were conveyed out at four temperatures (293, 303, 313 and 323 K). Study the impact of inhibitor concentrations at various temperatures aims to evaluate the efficiencies of the inhibitors and to verify the stability of the protective films that can be constructed on the surface of MS as well as assessment of thermodynamic and activation parameters of the corrosion process. Similar weight-Loss curves illustrated in Figure 2 (at 293 K) were acquired at other temperatures but not shown here. The assessed values of the corrosion rates of MS, inhibition efficiencies (% IE) and degrees of surface coverage (θ) of the inhibitors were also inserted in Table 2. Values of % IE were assessed using the next equation [26]:

$$\% \text{ IE} = \theta \text{ x } 100 = \left[1 - \frac{CR_{inh}}{CR} \right] \text{ x } 100 \tag{1}$$

where CR and CR_{inh} (in mpy) are corrosion rates in devoid of and containing the inhibitor, respectively.
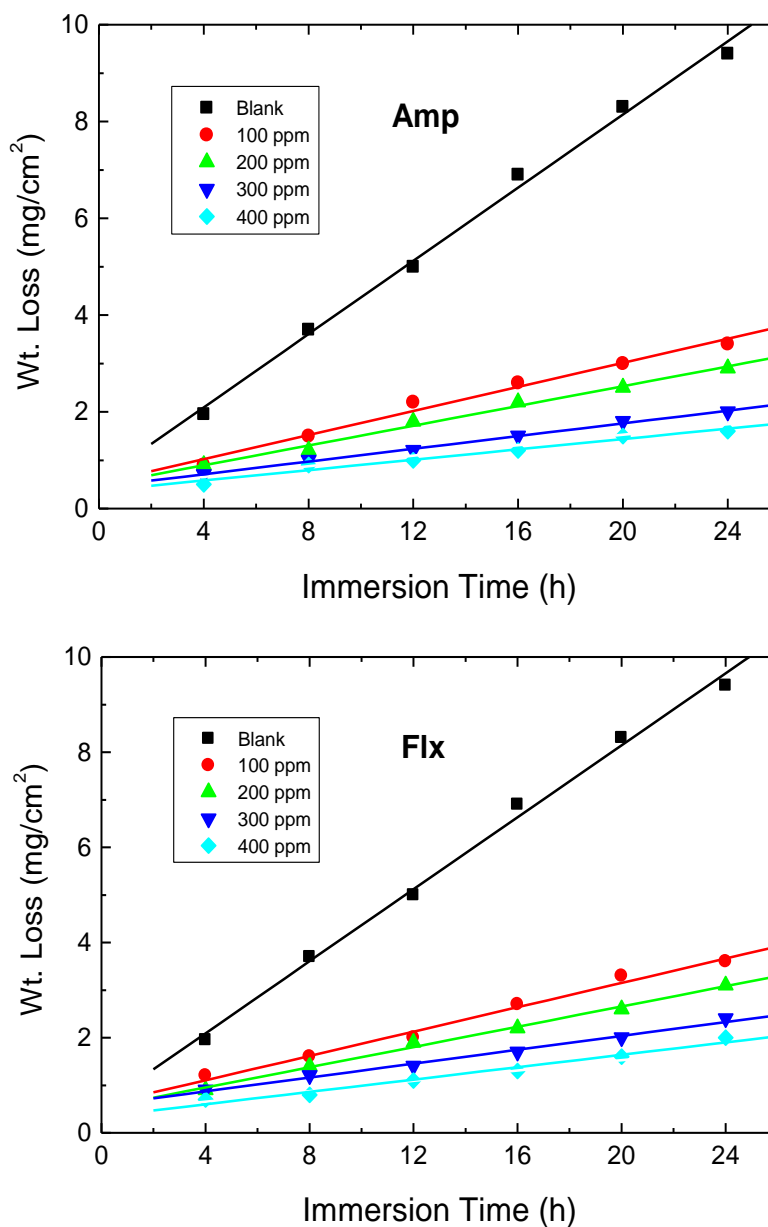
Figure 2. WL vs. time plots for the corrosion of MS in 1.0 M H_2SO_4 medium at 20°C in devoid of and containing some concentrations of ampicillin (Amp) and flucloxacillin (Flx).

The acquired outcomes showed that CR values reduced with increasing [inhibitor]. This behavior is owing to augmented adsorption of the drugs over vacant sites onto the MS surface with raising the inhibitor concentration resulting in a rebate in the dissolution rate of MS and thus higher % IE values. Therefore, the examined expired drugs can be considered as good inhibitors for MS corrosion in 1.0 M of H_2SO_4 medium. On the other hand, with raising temperature, so do the corrosion rates in both the blank solution and the inhibited ones. Consequently, the values of % IE were found to be reduced with a temperature as listed in Table 2. This decrease in % IE suggests physical adsorption of the expired drug on the MS surface [27].

Table 1. Values of CR of MS, % IE and θ of various concentrations of ampicillin (Amp) and flucloxacillin (Flx) in 1.0 M H_2SO_4 medium at various temperatures.

Inh.	Inh. Concn. (ppm)	Temperature (K)											
		293			303			313			323		
		CR	% IE	θ	CR	% IE	θ	CR	% IE	θ	CR	% IE	θ
	0	161	--	--	180	--	--	196	--	--	213	--	--
Amp	100	50	68.94	0.69	63	65.00	0.65	80	59.18	0.59	94	55.87	0.56
	200	31	80.74	0.81	41	77.22	0.77	55	71.94	0.72	70	67.14	0.67
	300	18	88.81	0.89	25	86.11	0.86	33	83.16	0.83	47	77.93	0.78
	400	11	93.17	0.93	22	87.78	0.88	27	86.22	0.86	43	79.81	0.80
Flx	100	56	65.21	0.65	74	58.89	0.59	94	52.04	0.52	111	47.89	0.48
	200	34	78.88	0.79	49	72.78	0.73	65	66.84	0.67	79	62.91	0.63
	300	23	85.71	0.86	32	82.22	0.82	43	78.06	0.78	58	72.77	0.73
	400	19	88.20	0.88	27	27.00	0.85	37	81.12	0.81	51	76.07	0.76

Table 1 illuminated the inhibition efficiencies change of the studied expired drugs with the drug concentrations at various temperatures. The data listed in the table indicated that, at the same inhibitors concentration, the % IE values are increased in the sequence : ampicillin > flucloxacillin designating that the steric impacts and the extent of the electronic density of donor atoms involved in the inhibitor molecule are regarded as the main role in adsorption.

3.1.2. Adsorption considerations

It was reported [28] that organic compounds introduce their inhibition characteristic via adsorption on the MS surface, and several isotherms such as Frumkin, Langmuir, Temkin, Freundlich and others. have been utilized to investigate the interpretation of corrosion inhibition. The investigation outcomes in the existing study designated that the adsorption of the tested expired drugs on the surface of MS in sulfuric acid solution accord with the Langmuir adsorption isotherm, given in Figure 3, which is presented by [29]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{2}$$

where K_{ads} is the adsorption equilibrium constant values (Table 2).

3.1.3. Thermodynamic Parameters

The standard free energy of adsorption (ΔG^o_{ads}) is regarded to K_{ads} regarding to the equation [30],

$$\Delta G^o_{ads} = -RT \ln(55.5\, K_{ads}) \tag{3}$$

The assessed values of ΔG^{o}_{ads} for the examined drugs at various temperatures were listed in Table 3. The higher negative values of ΔG^{o}_{ads} specify spontaneity of the adsorption process and stability of the adsorbed layer on the MS surface [31].
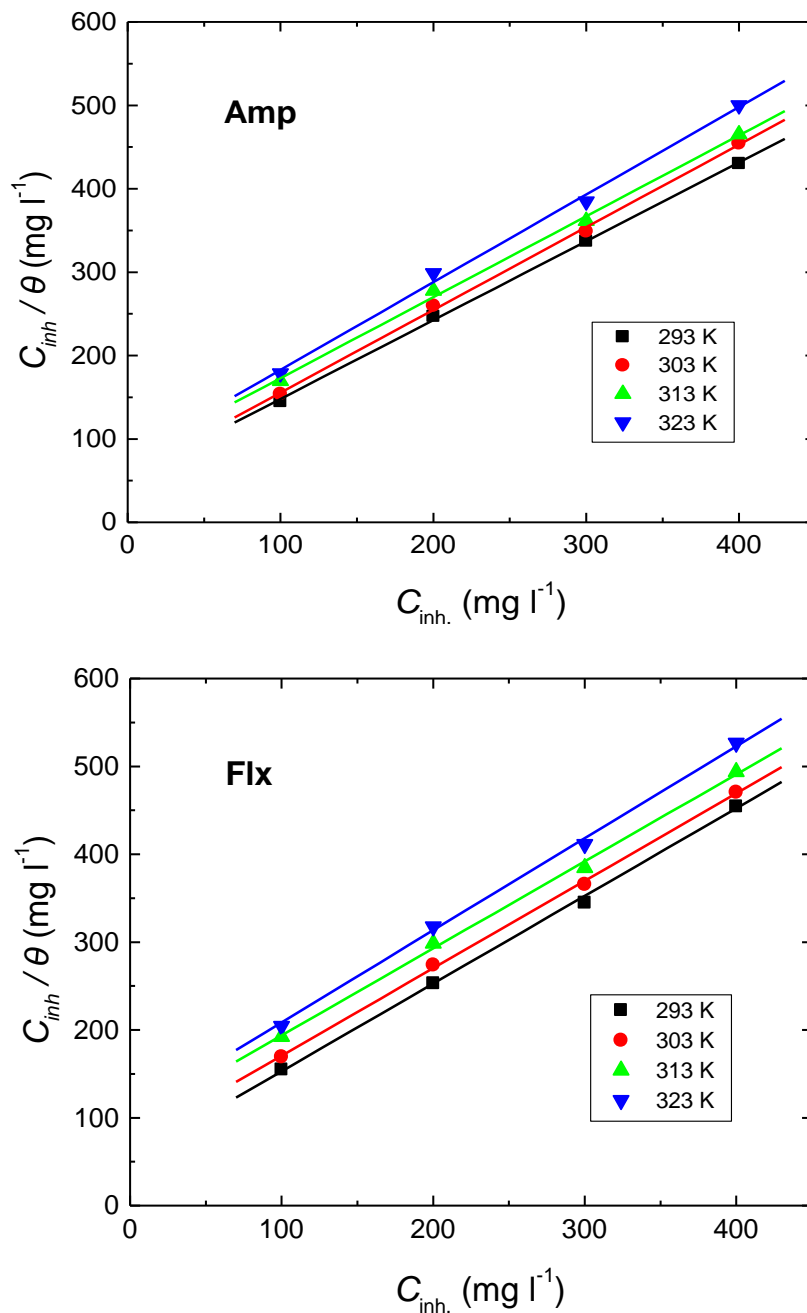

Figure 3. Langmuir isotherms for ampicillin (Amp) and flucloxacillin (Flx), adsorbed on the MS surface in 1.0 M H_2SO_4 medium at various temperatures.

Table 2. Thermodynamic parameters and adsorption constant (K_{ads}) for MS corrosion in 1.0 M H_2SO_4 medium with various concentrations of ampicillin (Amp) and flucloxacillin (Flx) at various temperatures.

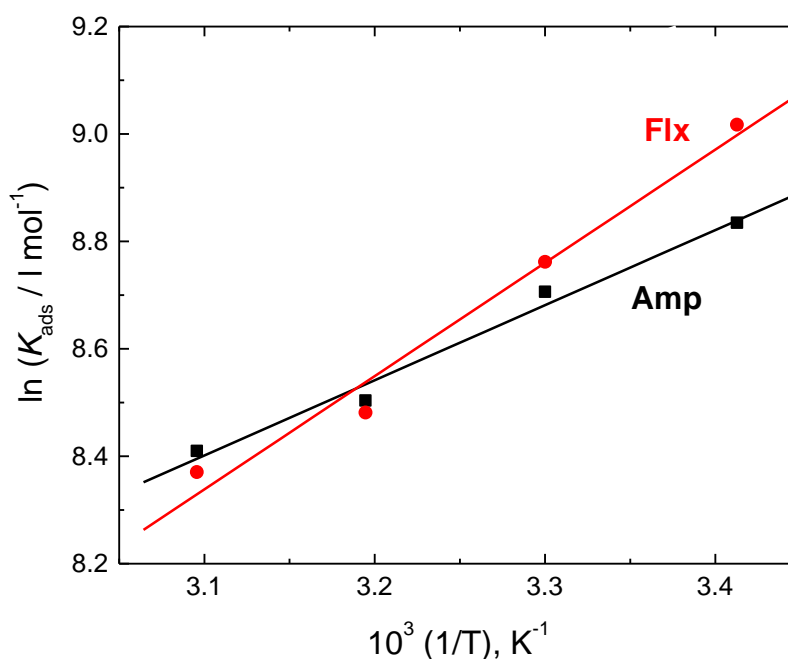| Inhibitor	Temp. (K)	$10^{-3} K_{ads}$ l mol^{-1}	ΔG^o_{ads} kJ mol^{-1}	ΔH^o_{ads} kJ mol^{-1}	ΔS^o_{ads} J mol^{-1} K^{-1}
Amp	293	6.86	-31.31		67.12
	303	6.03	-32.05	-11.64	69.66
	313	4.93	-32.58		71.48
	323	4.49	-33.37		74.18
Flx	293	8.24	-31.75		48.78
	303	6.38	-32.19	-17.46	50.28
	313	4.82	-32.53		51.42
	323	4.31	-33.26		53.94

Figure 4. Van't Hoff plots for ampicillin (Amp) and flucloxacillin (Flx) adsorbed on MS surface in 1.0 M H_2SO_4 medium.

The acquired values of ΔG^o_{ads} specified that the adsorption process is a mixed amongst physical and chemical adsorption [32].

The standard adsorption heat (ΔH^o_{ads}) can be assessed exploiting Van't Hoff Eq. [33]:

$$\ln K_{ads} = \frac{-\Delta H^o_{ads}}{RT} + \text{Constant} \tag{4}$$

The relationship between ln K_{ads} vs. 1/T yielded clear straight lines as shown in Figure 4. Values of ΔH^o_{ads} were assessed and were also inserted in Table 3. The negative values of ΔH^o_{ads} approved that the adsorption of the examined drugs is an exothermic process [34].

The standard adsorption entropy (ΔS^o_{ads}) can be acquired from Gibbs–Helmholtz equation:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \tag{5}$$

The obtained values of ΔS^o_{ads} are inserted in Table 3. The obtained positive values of ΔS^o_{ads} showed the increased disorder of the expired drugs during their adsorption on the MS surface [35].

3.1.4. Kinetic Parameters

The dependence of CR (mg cm^{-2} h^{-1}) on temperature is explained by Arrhenius equation [36]:

$$\ln CR = \ln A - \frac{E_a^*}{RT} \tag{6}$$
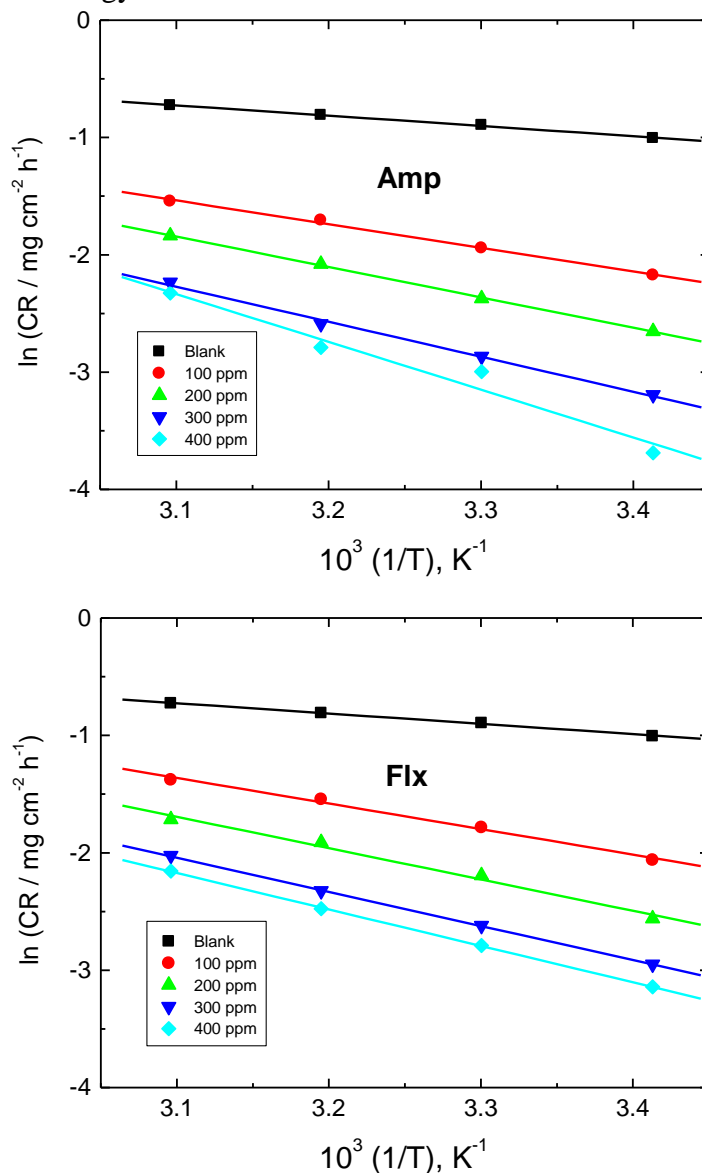
where, E_a^* is the activation energy.

Figure 5. Arrhenius plots for MS corrosion in 1.0 M H$_2$SO$_4$ medium in devoid of and containing some concentrations of ampicillin (Amp) and flucloxacillin (Flx).

Figure 5 represents Arrhenius graphs for MS in 1.0 M H_2SO_4 solution in the free and with several concentrations of the examined drugs. The assessed values of E_a^* in the presence of the drugs were higher than those in the blank solution (Table 4) confirming vigor adsorption of the drug molecules, thus reducing the corrosion rates. Additionally, the range of E_a^* values suggested the physical adsorption of the drugs [37]. These observations are in accord with those based on the values of both ΔG^o_{ads} and ΔH^o_{ads} approving the validity of the acquired outcomes.
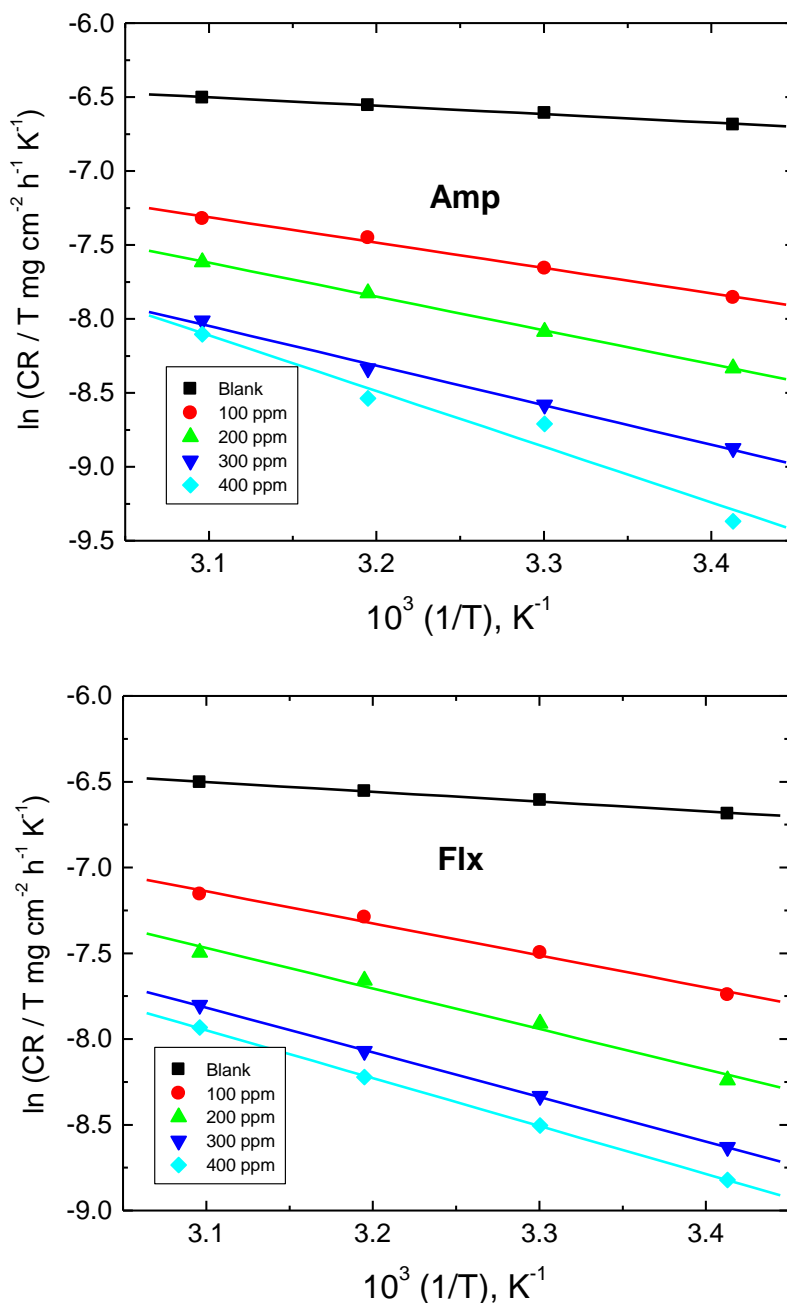

Figure 6. Transition state plots for the corrosion of MS in free 1.0 M H_2SO_4 medium in devoid of and containing some concentrations of ampicillin (Amp) and flucloxacillin (Flx).

Table 3. Activation parameters for MS corrosion in free 1.0 M H_2SO_4 medium in devoid of and containing some concentrations of ampicillin (Amp) and flucloxacillin (Flx).

Inhibitor	Inhibitors Concn. (mg l^{-1})	E_a^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}
	0	**7.23**	**4.74**	**-39.08**
Amp	**100**	16.79	14.22	-16.63
	200	21.62	18.96	-4.57
	300	24.94	22.00	-2.08
	400	33.84	31.26	-29.93
Flx	**100**	18.04	15.55	-11.22
	200	22.12	19.62	-1.16
	300	24.11	21.62	-1.99
	400	25.77	23.28	-5.82

The enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for MS corrosion are assessed exploiting Eq. 7 [38]:

$$\ln\left(\frac{CR}{T}\right) = \left(\ln\frac{R}{Nh} + \frac{\Delta S^*}{R}\right) - \frac{\Delta H^*}{R}\frac{1}{T} \tag{7}$$

where, N is Avogadro's number and h is Planck's constant.

Values of ΔH^* and ΔS^* were obtained from the graphs of $\ln(CR/T)$ vs. $1/T$ (Fig. 6) are inserted in Table 4. The positive values of ΔH^* reflect the endothermic nature of the corrosion process. The negative value of ΔS^* illuminated association of the drug molecules rather than dissociation resulting in a rebate in the disorder [39].

3.3. PDP Measurements

3.3.1. Influence of Expired Drugs Concentrations

The acquired PDP curves for the corrosion of MS in 1.0 M H_2SO_4 solution, in devoid of and containing several concentrations of the tested drugs are presented in Figure 7, and the corrosion parameters are given in Table 4. The outcomes showed that supplementation of the drugs to the blank solution shifted the anodic and cathodic branches of the polarization curves to lesser current densities and then corrosion of MS was inhibited. Therefore, it could be stated that such the investigated drugs performed as mixed-type inhibitors with anodic predominance [40].
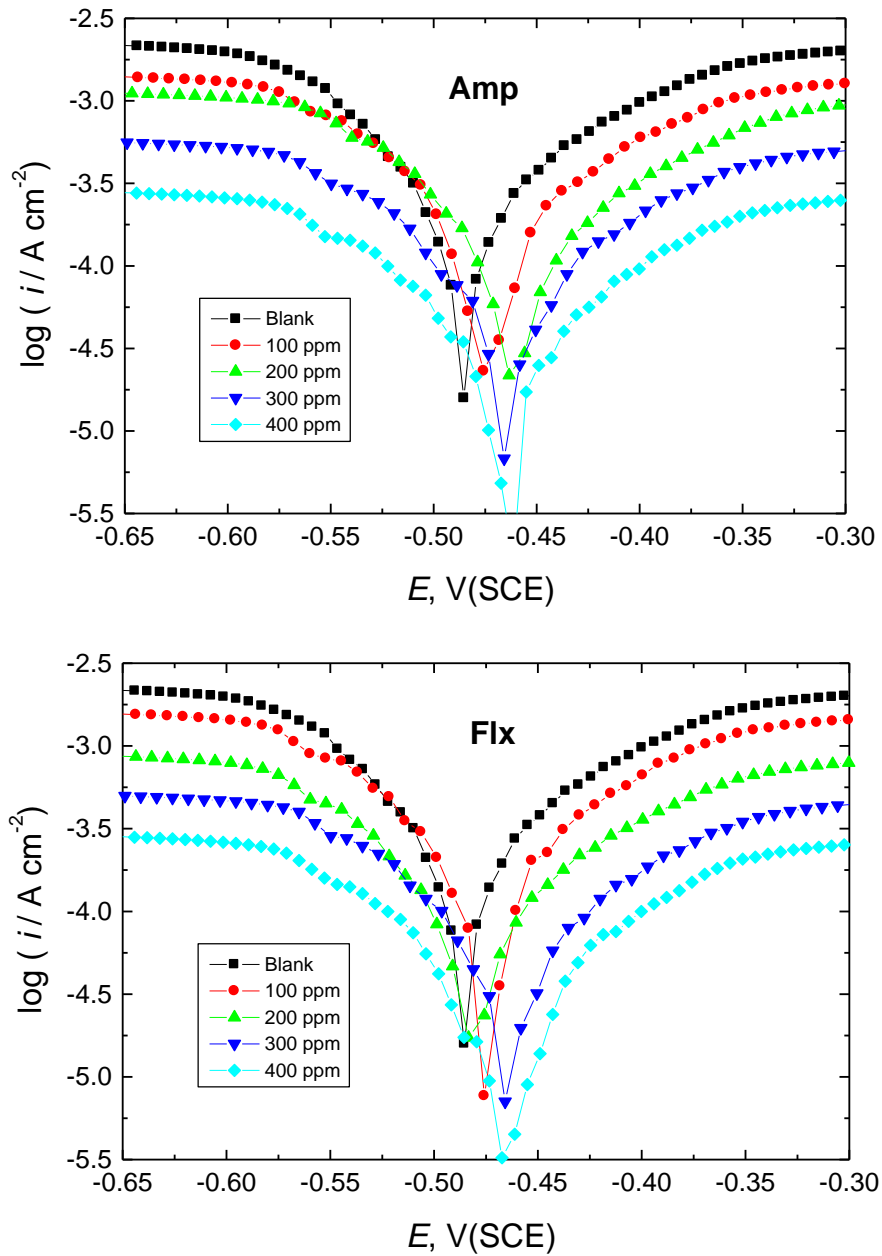
Figure 7. PDP curves for MS corrosion in 1.0 M H₂SO₄ medium at 20 °C in devoid of and containing some concentrations of ampicillin (Amp) and flucloxacillin (Flx).

Table 4. Polarization data for MS corrosion in 1.0 M H_2SO_4 medium at 20 °C in devoid of and containing some concentrations of ampicillin (Amp) and flucloxacillin (Flx).

Inh.	Inh. Concn. (ppm)	$-E_{corr}$ (mV(SCE))	β_a (mV/decade)	$-\beta_c$ (mV/decade)	i_{corr} (µA/cm^2)	% IE	θ
	0	489	85	76	397	--	--
Amp	100	481	102	86	115	71.03	0.71
	200	472	99	93	71	82.11	0.82
	300	467	96	105	36	90.93	0.91
	400	464	103	109	24	93.95	0.94
Flx	100	479	104	83	147	62.97	0.63
	200	478	109	86	87	78.09	0.78
	300	469	98	107	52	86.90	0.87
	400	468	107	113	36	90.93	0.91

3.4. Electrochemical Impedance Spectroscopy Measurements

Figure 8 displays the Nyquist graphs for MS corrosion in 1.0 M H_2SO_4 without and with several concentrations of the examined drugs at 298 K. The impedance spectra in the blank solution and with the presence of tested drugs showed single depressed capacitive loops anticipating that MS corrosion is noteworthy governed by the process of charge transfer. The values of R_{ct} and % IE were given in Table 5. It has been noted that R_{ct} augmented greatly with raising drug concentrations resulting in a rebate in the corrosion rates.

Table 5. Values of R_{ct}, % IE and θ of various concentrations of ampicillin (Amp) and flucloxacillin (Flx) for MS corrosion in 1.0 M H_2SO_4 medium at 20 °C.

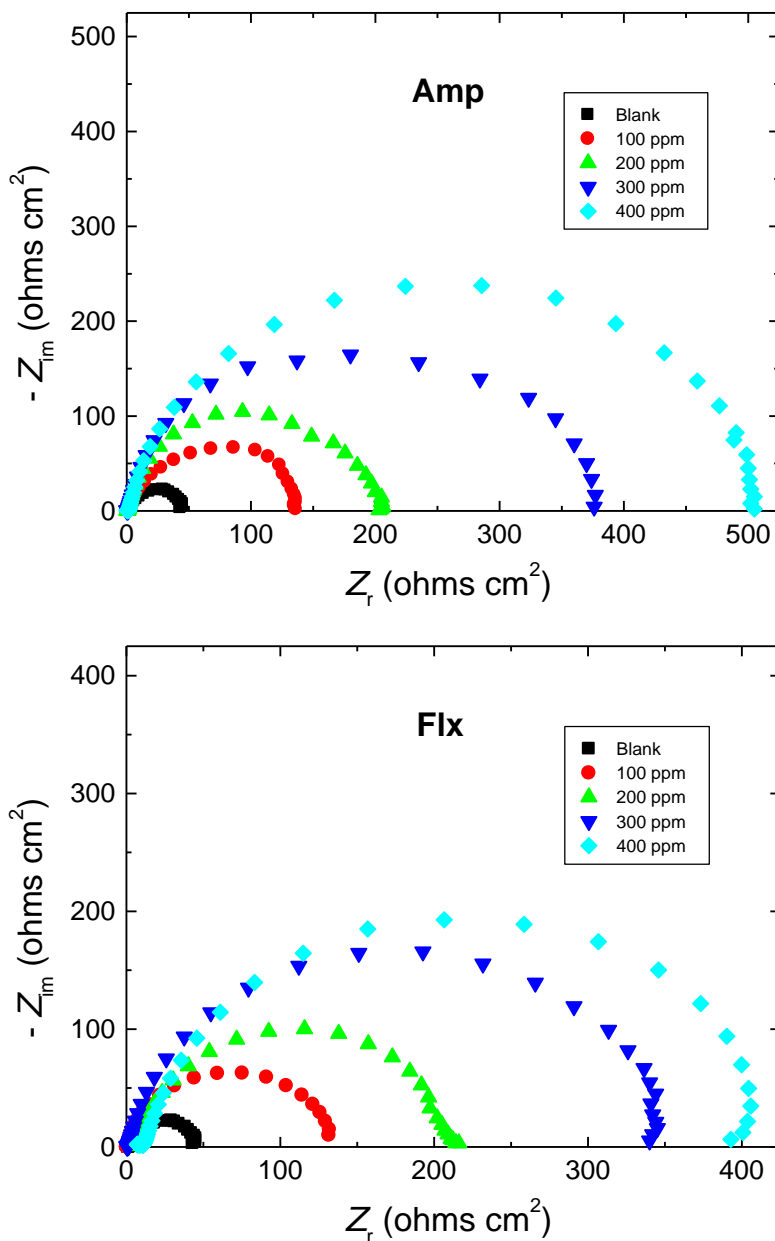| Inhibitor	Inhibitor Concn. (ppm)	R_{ct}	% IE	θ
	0	45	--	--
Amp	100	136	66.91	0.67
	200	205	78.05	0.78
	300	375	88.01	0.88
	400	503	91.02	0.91
Flx	100	132	65.91	0.66
	200	215	79.07	0.79
	300	346	86.99	0.87
	400	409	88.99	0.89

Figure 8. Nyquist plots for MS corrosion in 1.0 M H_2SO_4 medium at 20 ^{o}C in devoid of and containing some concentrations of ampicillin (Amp) and flucloxacillin (Flx).

4. CONCLUSIONS

1) The investigated expired drugs (ampicillin and flucloxacillin) are set to be effective inhibitors for MS corrosion in 1.0 M H_2SO_4 solution.

2) Adsorption of expired drugs on MS surface obeys Langmuir isotherm.

3) Examined expired drugs are acted as mixed type inhibitors with greatly anodic-type ones.

4) The type of the adsorption process of the drugs was set to be physical.

5) The acquired outcomes from all employed techniques were in good accordance.

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