Investigation of Expired Ticarcillin and Carbenicillin Drugs for Inhibition of Aluminum Corrosion in Hydrochloric Acid Solution

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Certain expired drugs could be used as proficient inhibitors for the corrosion of metals which have both economic and ecological profits. Thus, two selected expired drugs, namely, Ticarcillin and Carbenicillin were tested to inhibit the corrosion of aluminum in 1.0 M HCl solution. The techniques used in this paper were weight-loss (WL), potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The results illuminated that the inhibition efficiencies (% IEs) of the examined expired drug were increased as the drugs' concentrations increased, while reduced with rising the corrosive solution concentration and temperature. The acquired higher % IEs were declined on the basis of strong adsorption of the drugs' molecules on the aluminum surface and developing protective layer(s) and such adsorption was obeyed Langmuir isotherm. Both thermodynamic and kinetic parameters were determined that confirmed that the nature of adsorption was physical. The kinetics of aluminum corrosion and its inhibition by the employed drugs were studied that confirm the acquired higher % IEs. The examined drugs were set to act as mixed-kind inhibitors with slight anodic predominance. Results obtained from all used techniques revealed that the % IE of Ticarcillin was found to faintly greater than that of Carbenicillin and such used tools were agreed with each others. Finally, the mechanisms of aluminum corrosion in HCl and its inhibition were explained.

Keywords: Aluminum corrosion, Expired drugs, Inhibitors, Thermodynamic and Kinetics, Mechanisms

1. INTRODUCTION

Aluminum is among the most generally used metal in the world [1,2]. An effective thin passive oxide layer is suggested to form on the aluminum surface in aerated environments [3-7]. This oxide layer is inert, stable and adhered that safeguards the aluminum surface from further corrosion [7-9]. This oxide layer is weaken in lower or higher pH media [10,11]. Thus, mineral acids and strong alkaline solutions are thus very corrosive for Aluminum. Acidic solutions especially HCl are generally utilized as a part of corrosive pickling and cleaning of aluminum. Several research works were performed on the corrosion inhibition of Al in HCl solutions [12-16].

Corrosion inhibitors are regarded as significant materials used to prevent metals versus corrosion [17-24]. Corrosion inhibitors are organic compounds having, heteroatoms such as (P, S, N and O), conjugated π-bonds, polar groups and aromatic rings [25-31]. The performances of the organic inhibitors depends on their abilities for adsorption on the metal surface [32-38]. Undesired expired pharmaceutical drugs, that have passed their expiry date, have lately been employed as corrosion inhibitors [39-44]. The choice of expired drugs for employment as corrosion inhibitors was based on various aspects such as their chemical structures which contain O, N and S heteroatoms as the chief active centers as well as aromatic rings, their little or inconsequential influence on the environment compared with the conventional toxic inhibitors and free of cost. Thus, expired drugs when used as corrosion inhibitors they have both economic and environmental benefits. Ticarcillin and Carbenicillin (their structure shown below) are beta-lactam antibiotics that can be used for the treatment of Gram-negative bacteria. These expired drugs could be examined as corrosion inhibitors due to their molecular structures that have aromatic or heterocyclic rings (electron rich) with electroactive O, N and S atoms.

The existing research work targets to evaluate the inhibition effectiveness of two expired: Ticarcillin and Carbenicillin for Al corrosion in 1.0 M HCl solution. Various tools were used in this work. Also, thermodynamic and kinetic features will be investigated. Finally, the mechanisms of Al corrosion in HCl solution and its inhibition will be explained.
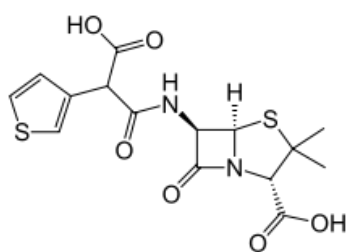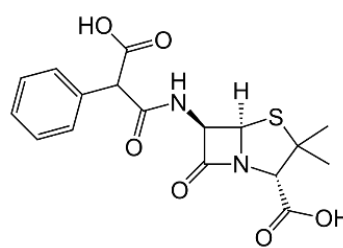
Ticarcillin (Ticar)   Carbenicillin (Carb)

2. EXPERIMENTAL

2.1. Materials

The solutions used in this study were prepared from analytical grade chemicals and the solvent utilized was bidistilled water. The investigated corrosive medium was 1.0 M HCl solution. Ticarcillin and Carbenicillin solutions were prepared utilizing bidistilled water and their examined

concentrations was: 50 to 250 mg/L (ppm). Corrosion tests were carried out on Al samples (99.9 % purity). Al sheets (4 x 2 x 0.2 cm^3) were used for WL tests. For PDP and EIS, cylinder-shaped rod surrounded with araldite with uncovered area of 1.0 cm^2 was used.

2.2. Techniques and Instruments

The techniques used in this paper were WL, PDP, EIS and SEM. Before any experiment the aluminum specimen surface was polished with various grades of emery paper up to 1500.

In WL tests, the polished cleaned aluminum sheets were inserted in a 100 ml of the examined corrosive solution for a period of time of 2 hours. The mean WL (mg/cm^2) for at least two like tests was taken. The corrosion rate (CR, mpy) was determined using Eq. (1) [45]:

$$CR \text{ (mpy)} = \frac{KW}{Atd} \qquad (1)$$

where K is a constant (3.45 x 10^6), W is the WL in grams, A is the aluminum sheet area in cm^2, t is the time in hour and d is the density of aluminum. The % IE values were computed via Eq. (2) [46]:

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

where CR and CR$_{inh}$ are the values of corrosion rates without and with the added drug, respectively.

In both PDP and EIS measurements the aluminum electrode was prepared as reported [24-26] and quickly immersed in the cell containing the corrosive environment (1.0 M HCl) without and with the requested concentration of the examined drug at OCP (open circuit potential) which attained after almost 25 min. of immersion. All electrochemical experiments were recorded utilizing thermostated PGSTAT30 potentiostat/galvanostat. Three compartment cells was employed: aluminum (working electrode), platinum sheet (counter electrode), and saturated calomel (reference electrode). PDP curves (Tafel plots) were recorded in the range of potential of ±250 mV at a scan rate of 2.0 mV/s. The values of % IEs of the examined expired drugs were computed via Eq. (3):

$$\% \text{ IE} = \theta \text{ x } 100 = \left[1 - \frac{i_{corr(inh)}}{i_{corr}} \right] \text{ x } 100 \qquad (3)$$

where, i_{corr} and $i_{corr(inh)}$ are the values of corrosion current densities without and with the added drug, respectively.

The measurements of impedance studies were carried out in the frequency range of 100 kHz to 0.1 Hz, and the amplitude of 5.0 mV (peak to peak) using AC signals at OCP. Also, the values of % IEs were evaluated using Eq. (4) [46]:

$$\% \text{ IE} = \left[1 - \frac{R_{ct}}{R_{ct(inh)}} \right] \text{ x } 100 \qquad (4)$$

where R_{ct} and $R_{ct(inh)}$ are the charge transfer resistances without and with the added drug, respectively.

For the surface examination (SEM), the Al sheets were immersed in 1.0 M HCl solution without and with the examined drugs (250 mg/L) for 12 hours immersion period then dried, and submitted to SEM examination.

3. RESULTS AND DISCUSSION

3.1. WL Measurements

3.1.1. Effect of [HCl] on the CRs

The effect of [HCl] (corrosive medium) on the values of corrosion rates (CRs) of aluminum, WL experiments for aluminum sheets were carried out in various concentrations of HCl solutions, namely, from 0.25 M to 2.0 M at 298 K as shown in Figure 1. The figure showed that the values of weight loss of aluminum sheets and, thus, the values of CRs were increased with increasing the concentration of HCl solution. This can be explained on the basis of the increased concentration of the aggressive Cl^- ions with increasing [HCl] which accelerates the dissolution of the aluminum [47,48].
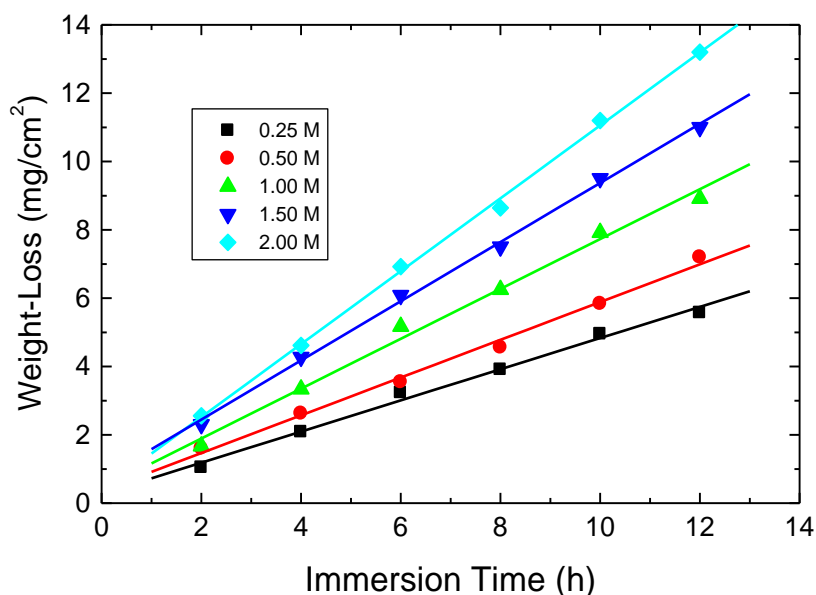

Figure 1. WL versus immersion time for the corrosion of aluminum in various [HCl] solutions at 298 K

3.1.2. Effect of Drugs' Concentrations

Figure 2 illustrates the plots of WL versus immersion time for Al sheets in 1.0 M HCl solution without and with different concentrations (50 – 250 mg/L) of Ticarcillin and Carbenicillin at 298 K. The CR values of aluminum and those of % IEs and θs of the drugs were calculated and are recorded in Table 1. The recorded results signified that the values of the CRs of aluminum were reduced and the values of

both % IEs and θs of the drugs were enhanced with rising the drugs' concentrations as shown in Figure 3. This can be ascribed to the increased adsorption of the drugs' molecules on the Al surface with increasing concentrations leading to a reduction of the values of CRs and, thus, increasing the values of both % IEs and θs. Hence, the examined drugs are regarded as proficient inhibitors for the corrosion of Al in 1.0 M HCl solution. Also, the results indicated that the values of % IEs of Ticarcillin were found to be slightly higher than those of Carbenicillin.
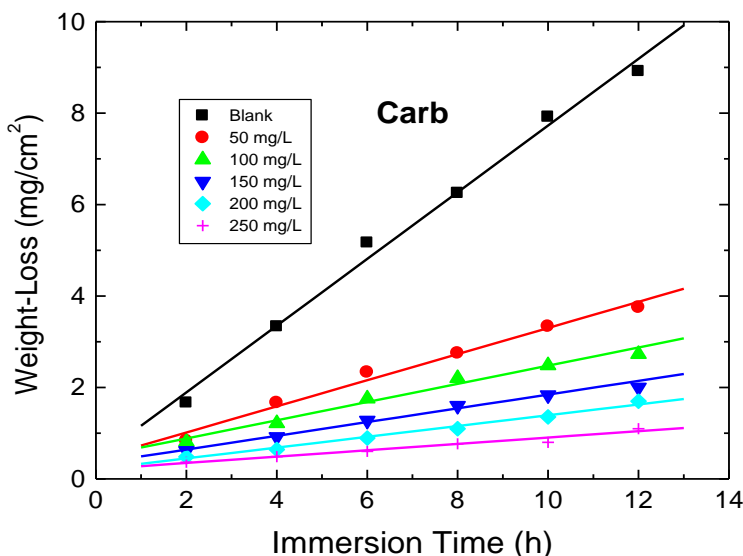

Figure 2. WL versus immersion time for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.

Table 1. Values of CRs of Al in 1.0 M HCl solution, %IEs and θs of various concentrations of Ticarcillin (Ticar) and Carbenicillin (Carb) at diverse temperatures.

Drugs	Conc. (mg/L)	Temperature (K)											
		288			298			308			318		
		CR	% IE	θ	CR	% IE	θ	CR	% IE	θ	CR	% IE	θ
	0	335	--	--	366	--	--	389	--	--	411	--	--
Ticar	50	97	71	0.71	124	66	0.66	144	63	0.63	169	59	0.59
	100	60	82	0.82	92	75	0.75	105	73	0.73	123	70	0.70
	150	40	88	0.88	62	83	0.83	78	80	0.80	99	76	0.76
	200	27	92	0.92	44	88	0.88	58	85	0.85	82	80	0.80
	250	20	94	0.94	33	91	0.91	51	87	0.87	70	83	0.83
	50	114	66	0.66	135	63	0.63	152	61	0.61	185	55	0.55

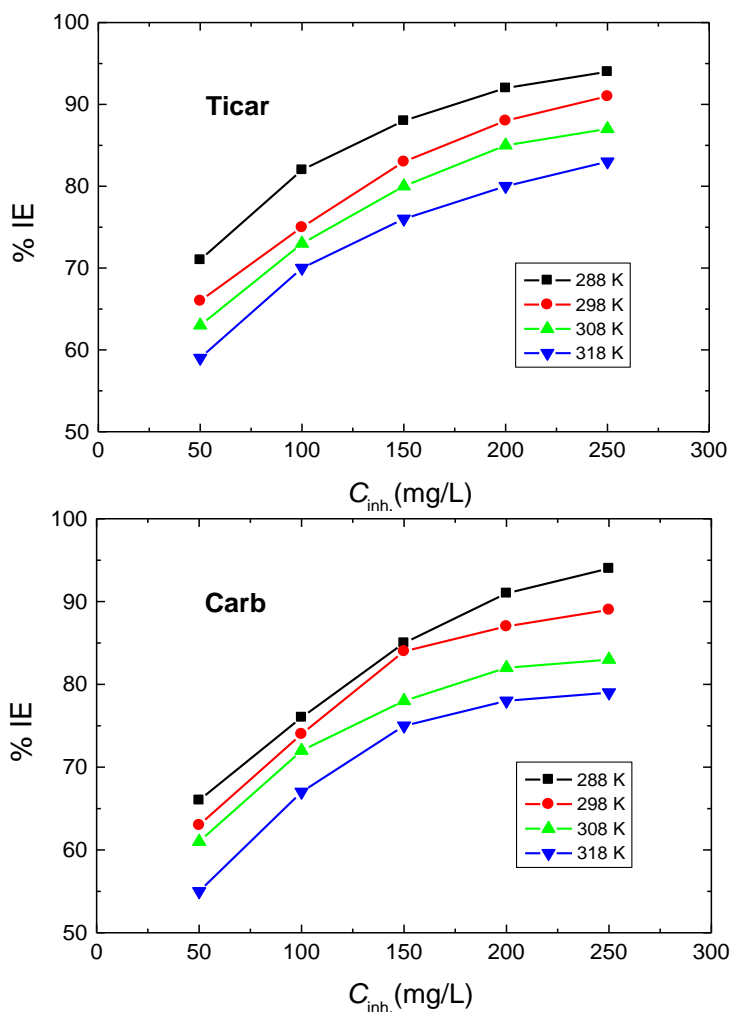| **Carb**	**100**	80	76	0.76	95	74	0.74	109	72	0.72	136	67	0.67
	150	50	85	0.85	59	84	0.84	86	78	0.78	103	75	0.75
	200	30	91	0.91	48	87	0.87	70	82	0.82	90	78	0.78
	250	20	94	0.94	40	89	0.89	66	83	0.83	86	79	0.79

Figure 3. Dependence of % IEs of Ticarcillin (Ticar) and Carbenicillin (Carb) on their concentrations in the corrosion of Al in 1.0 M HCl solution at various temperatures.

3.1.3. Effect of [HCl] on the % IEs

Figure 4 represents the effect of HCl concentration (from 0.25 M to 2.0 M) on the values of % IEs of 250 mg/L of the examined expired drugs at 298 K. From Figure 4 it is obvious that the values of % IEs were reduced with rising [HCl] solution signifying that such drugs are more efficient at low concentration of the corrosive medium. This can be ascribed to the increased aggressiveness of the HCl with increasing its concentration.
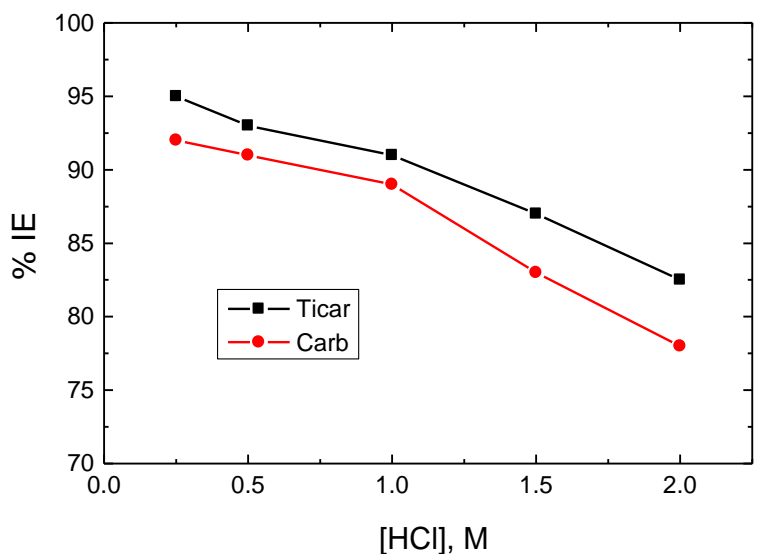
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7

Figure 4. Dependence of % IEs of Ticarcillin (Ticar) and Carbenicillin (Carb) on [HCl] in the corrosion of Al in HCl solution at 298 K.

3.1.4. Effect of Temperature

WL tests were performed at different temperatures, namely, 288, 298, 308 and 318 K in order to examine the efficiencies of the added drugs to the corrosive medium at higher temperatures and to justify the strength of the adsorption film(s) which was proposed to form on the aluminum surface and to determine the thermodynamic and activation parameters.
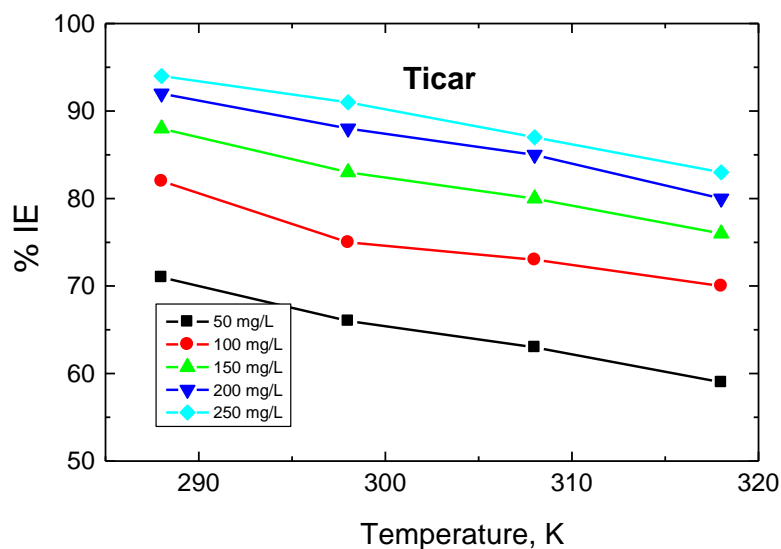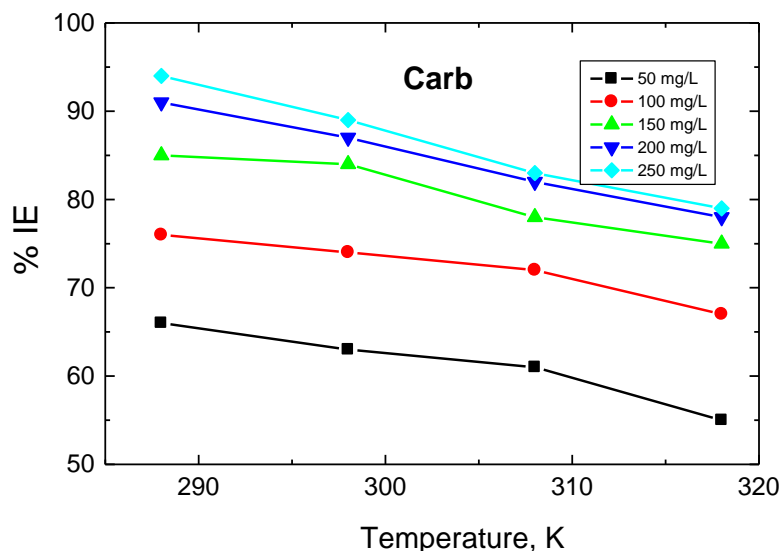
Figure 5. Dependence of % IEs of Ticarcillin (Ticar) and Carbenicillin (Carb) on temperature in the corrosion of Al in 1.0 M HCl solution.

The values of CRs of Al, and those of both % IEs and θs in the presence of various concentrations of the examined drugs were calculated and are presented in Table 1. The outcomes showed that increasing temperature led to increasing the values of CRs of Al and, thus, reducing the values of % IEs of the examined drugs at all tested concentrations as shown in Figure 5. This behavior can be ascribed to desorption of the drugs' molecules from the Al surface with rising temperature that confirms physical adsorption of the examined drugs on the aluminum surface [49].

3.1.5. Adsorption Isotherms

In order to explain the adsorption mechanism of the examined drugs on the aluminum surface in this study, the values of surface coverage (θ) of the examined drugs at different concentrations and temperatures were introduced in diverse adsorption isotherms such as Langmuir, Frumkin, Temkin, Freundlich, etc. The existing outcomes were set to obey Langmuir adsorption isotherm as shown in Figure 6 and defined by Eq. (5) [50],

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad\qquad (5)$$

where K_{ads} is the adsorption constant. Values of K_{ads} were calculated from the plots in Figure 6 and are given in Table 2.
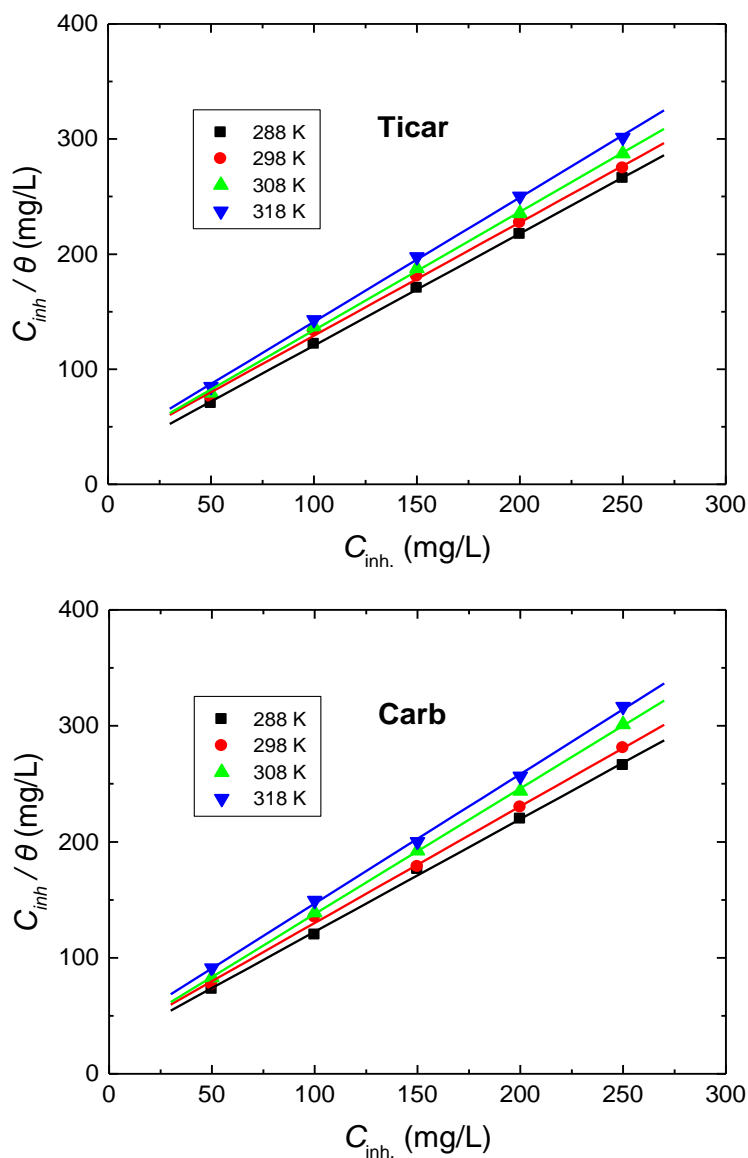
Figure 6. Langmuir adsorption isotherms for Ticarcillin (Ticar) and Carbenicillin (Carb) adsorbed on Al surface in 1.0 M HCl solution at diverse temperatures.

3.1.6. Thermodynamic Parameters

Values of standard free energy of adsorption (ΔG°_{ads}) were computed at diverse temperatures via Eq. (6) [51]:

$$\Delta G^o_{ads} = -RT \ln(55.5\, K_{ads}) \qquad (6)$$

The obtained greater negative values of ΔG^o_{ads} (inserted in Table 2) designated spontaneity of the adsorption and solidity of the film(s) adsorbed on the Al surface. Also, these values showed that the nature of adsorption process was a mixed between physical and chemical adsorption [52].

Values of standard adsorption heat (ΔH^o_{ads}) were evaluated via Van't Hoff equation [53]:

$$\ln K_{ads} = \frac{-\Delta H^{o}_{ads}}{RT} + \text{Constant} \qquad (7)$$

The plots of ln K_{ads} against 1/T were straight lines as shown in Figure 7 from which the values of ΔH^{o}_{ads} were evaluated and are listed also in Table 2. The negative values of ΔH^{o}_{ads} signified that the nature of adsorption is exothermic [54].

The standard adsorption entropy (ΔS^{o}_{ads}) values were evaluated using Gibbs–Helmholtz equation:

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T\Delta S^{o}_{ads} \qquad (8)$$

The acquire positive values of ΔS^{o}_{ads} (enclosed in Table 2) indicated increasing disorder of the drugs' molecules during their adsorption on the aluminum surface [55].

Table 2. Values of K_{ads} and thermodynamic parameters of the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at diverse temperatures.

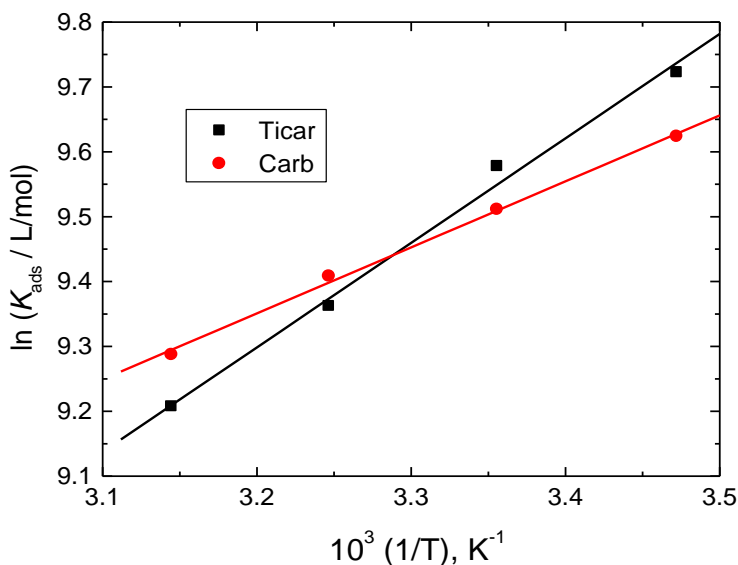| Drugs	Temp. (K)	$10^{-3} K_{ads}$ L/mol	ΔG^{o}_{ads} kJ/mol	ΔH^{o}_{ads} kJ/mol	ΔS^{o}_{ads} J/mol K
Ticar	**288**	16.69	-32.90		67.74
	298	14.44	-33.63	-13.39	67.92
	308	11.64	-34.26		67.76
	318	9.97	-34.96		67.83
Carb	**288**	15.12	-32.66		84.06
	298	13.51	-33.52	-8.45	84.13
	308	12.19	-34.38		84.19
	318	10.80	-35.17		84.02

Figure 7. Van't Hoff plots for Ticarcillin (Ticar) and Carbenicillin (Carb) adsorbed on the Al surface in 1.0 M HCl solution.

3.1.7. Kinetic Parameters

The values of activation energy (E_a^*) in the absence and presence of diverse concentrations of the examined expired drugs were evaluated from Arrhenius plots expressed by following equation [56]:

$$\ln CR = \ln A - \frac{E_a^*}{RT} \qquad (9)$$

The Arrhenius plots were found to be linear (Figure 8) specifying the rationality of the utilized kinetic mode. The computed values of E_a^* (Table 3) were discovered to be higher than that obtained for the drug-free corrosive solution. This behavior confirms strong adsorption of the drugs' molecules resulting in reduction in the corrosion rates. Also, the gained E_a^* values were in the range of physical adsorption mode [57]. The obtained values of E_a^* accord with the obtained values of both ΔG^o_{ads} and ΔH^o_{ads} confirming the rationality of the present investigation.
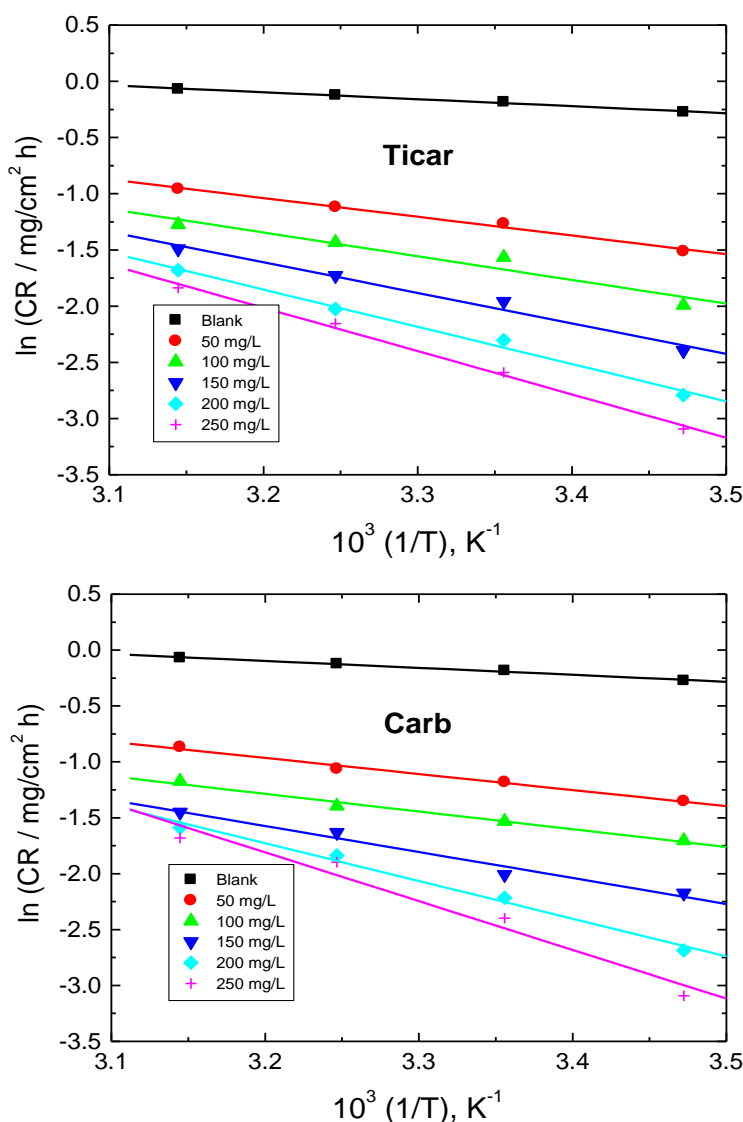

Figure 8. Arrhenius plots for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb).
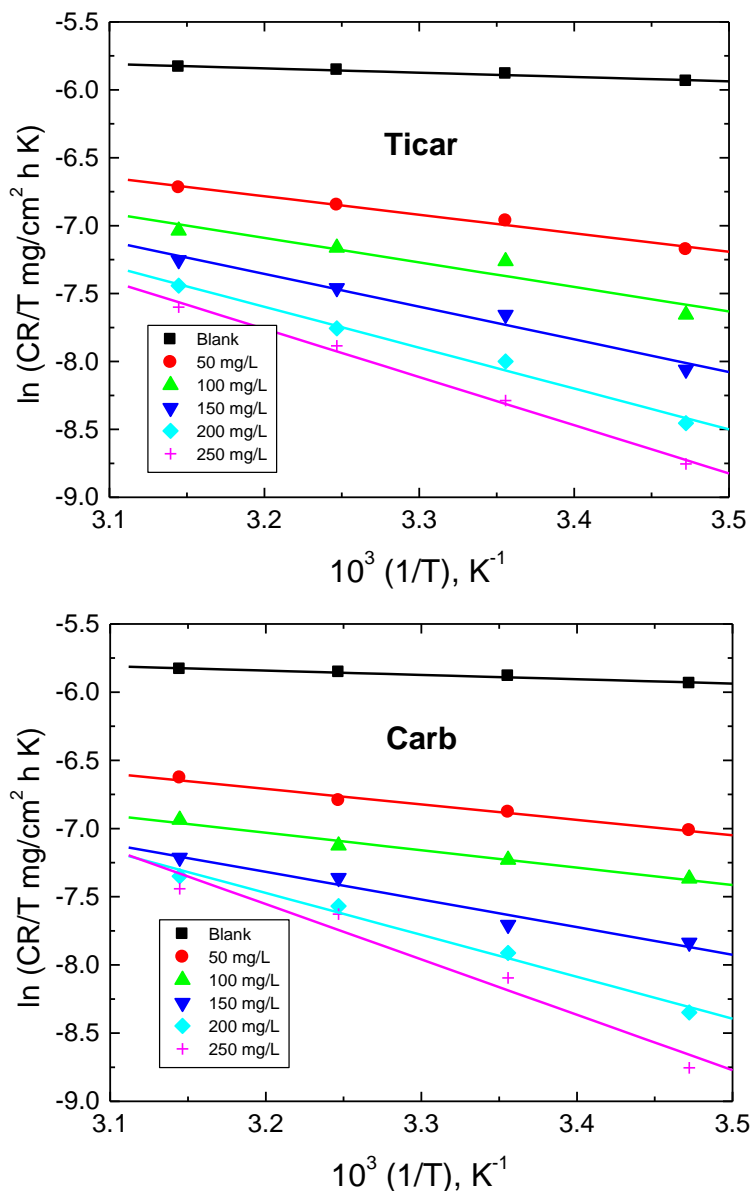
Figure 9. Transition state plots for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb).

Values of enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for the corrosion process were calculated via Eq. (10) [58]:

$$\ln\left(\frac{CR}{T}\right) = \left(\ln\frac{R}{Nh} + \frac{\Delta S^*}{R}\right) - \frac{\Delta H^*}{R}\frac{1}{T} \qquad (10)$$

where, N is Avogadro's number (6.022×10^{23}) and h is Planck's constant (6.626×10^{-34} Js). The values of both ΔH^* and ΔS^* were calculated and listed in Table 3. The obtained positively values of ΔH^* and ΔS^* in the presence of the examined drugs proposed endothermic type of corrosion inhibition, and increase in the drugs' molecules disorder, correspondingly [59].

Table 3. Values of the activation parameters for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb).

Drugs	Drug conc. (mg/L)	E_a^* kJ/mol	ΔH^* kJ/mol	ΔS^* J/mol K
	0	**5.11**	**2.58**	**-16.21**
	50	13.85	11.31	3.74
	100	17.46	14.97	12.89
Ticar	**150**	22.53	19.96	26.61
	200	27.52	24.94	40.33
	250	32.01	29.52	53.63
	50	11.89	9.43	-1.91
	100	13.05	10.57	-0.75
Carb	**150**	19.29	16.82	15.38
	200	28.02	25.56	43.32
	250	36.25	33.72	68.85

3.1.8. Kinetics of Al Corrosion and Its Inhibition

The kinetics of Al corrosion in 1.0 M HCl solution and its inhibition by the examined expired drugs were studied. The plots of –ln(weight-loss) versus time at 298 K showed a linear variation confirming a first order reaction kinetics regarding to the corrosion of Al and its inhibition as illustrated in Figure 10. The first order rate constant values, k_1 (in h^{-1}) were calculated such plots and are introduced in Table 4. The values of half-life times ($t_{1/2}$, h) were acquired from the obtained values of k_1 using Eq. (11) [60] and are listed in Table 4,

$$t_{1/2} = \frac{0.693}{k_1} \qquad\qquad (11)$$

The results illuminated that there is a decrease in the values of the rate constants and an increase in the half-life times ($t_{1/2}$) with increasing the drugs' concentrations that support more protection or inhibition of aluminum corrosion by the examined expired drugs.

Table 4. Values of the first-order rate constant (k_1) and half-life time ($t_{1/2}$) for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.

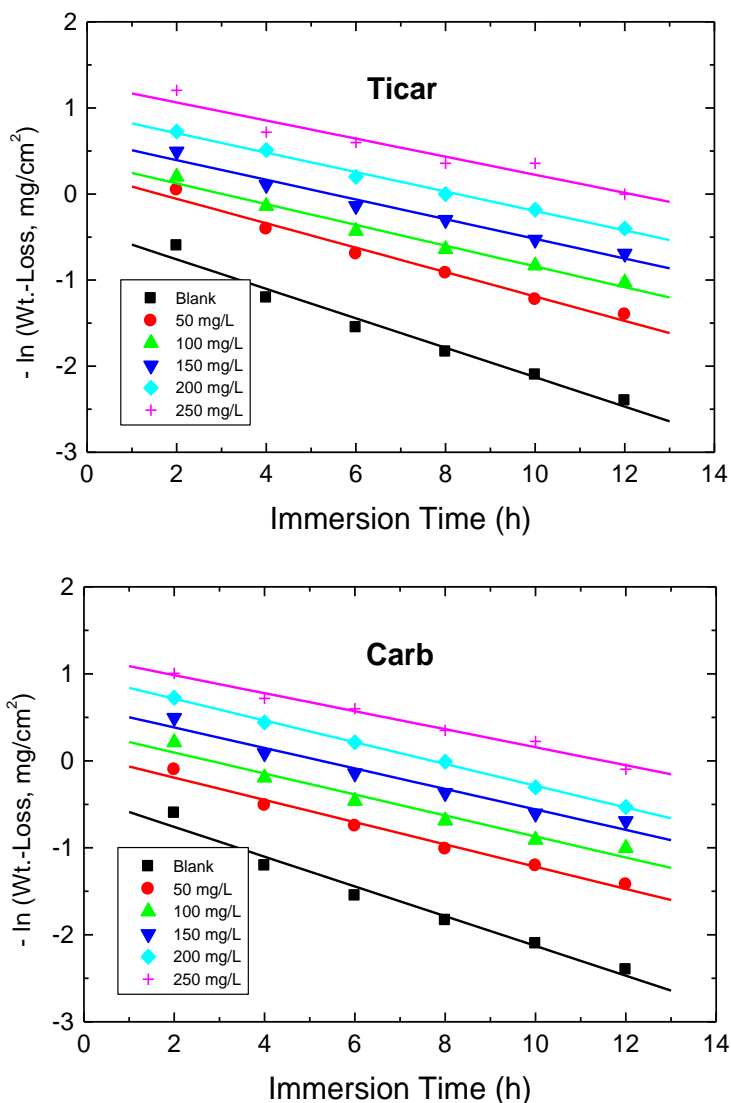| Drug conc. (mg/L)	Ticar		Carb	
	$10^3 k_1$, h^{-1}	$t_{1/2}$, h	$10^3 k_1$, h^{-1}	$t_{1/2}$, h
Blank	171	**4.05**	**171**	**4.05**
50	142	4.88	127	5.46
100	126	5.52	126	5.49
150	114	6.08	118	5.87
200	112	6.18	124	5.59
250	104	6.66	102	6.79

Figure 10. First-order rate constant plots in the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.

Also, the values of the order (*n*) of corrosion inhibition were evaluated via Eq. (12) [61]:

$$\log CR = \log k + n \log C_{inh.} \qquad\qquad (12)$$

where, *k* is the specific rate constant (mg/cm^2 h). The plots of log CR against log C_{inh} for the examined expired drugs at 298 K were linear as illustrated in Figure 11. Values of *n* were discovered to be -0.97 and -0.86 for Ticar and Carb, correspondingly. The gained value of *n* proposed that the corrosion inhibition was negatively fractional-first order process regarding to the drugs' concentrations. The negatively *n* values and the opposite dependence of the CRs on the drugs' concentrations (Figure 11) refers to good % IEs of the examined drugs [62,63].
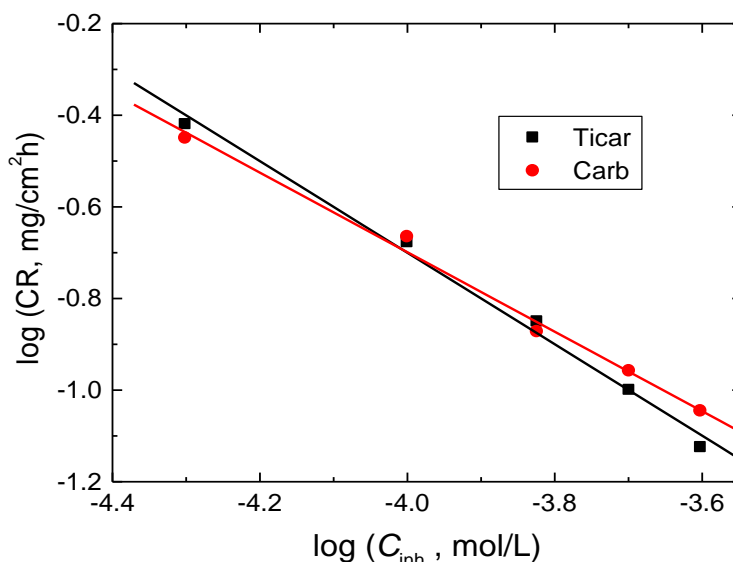
Figure 11. Plots of log CR vs. log C_{inh} for the inhibition of Al corrosion in 1.0 M HCl solution by Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.

3.2. PDP Measurements

The PDP curves or Tafel plots for the corrosion of aluminum in 1.0 M HCl solution in the absence and presence of numerous concentrations of the examined expired drugs at 298 K are illustrated in Figure 12. Values of the corrosion parameters extracted from PDP curves: corrosion potentials (E_{corr}), anodic and cathodic slopes (β_a, β_c), corrosion current densities (i_{corr}), polarization resistance (R_p), and the values of both % IEs and θs of the drugs are listed in Table 5. Figure 12 illuminated that addition of the examined drugs shifted the PDP curve of the corrosive solution to lower i_{corr} values indicating reduction of the corrosion rates of aluminum as inserted in Table 5 and, thus, inhibition of aluminum corrosion. The values of β_a and β_c were set to decrease with increasing addition of the examined drugs indicating that these drugs are mixed-type inhibitors. i.e. reduce the anodic dissolution of aluminum and retard the cathodic hydrogen evolution reaction. The value of E_{corr} recorded for aluminum in the absence of the added dugs was slightly moved to positive or anodic direction upon adding the examined drugs signifying that such drugs are mixed-kind inhibitors with anodic priority [64]. Also, the values of % IEs of the examined drugs were increased with increasing their concentrations and the trend of % IEs was: Ticar > Carb which are consistent with those obtained from WL method.
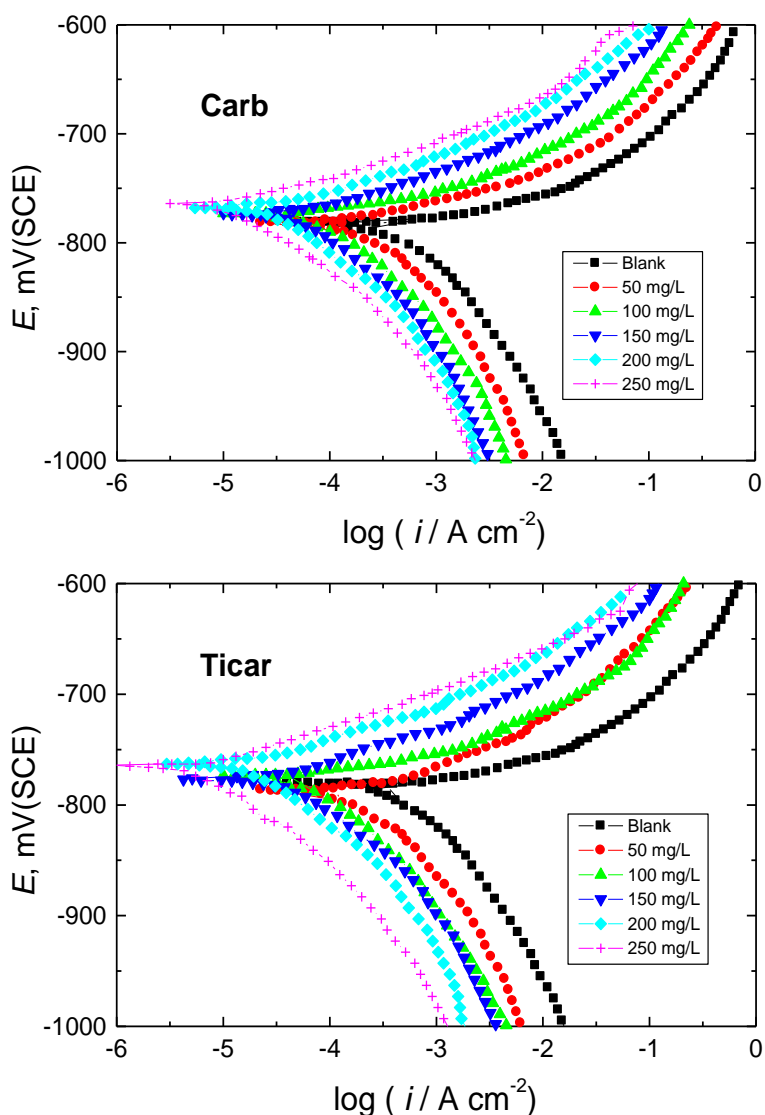
Figure 12. PDP curves for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.

Table 5. PDP results for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.

Drugs	Drug conc. (mg/L)	$-E_{corr}$ (mV(SCE))	β_a (mV/dec.)	$-\beta_c$ (mV/dec.)	i_{corr} ($\mu A/cm^2$)	% IE	θ
	0	**778**	**42**	**143**	**632**	**--**	**--**
Ticar	**50**	780	45	131	234	63	0.63
	100	775	39	123	152	76	0.76
	150	776	41	116	114	82	0.82
	200	769	36	114	70	89	0.89
	250	771	34	111	63	90	0.90

	50	776	34	118	240	62	0.62
	100	771	40	114	171	73	0.73
Carb	**150**	767	41	111	126	80	0.80
	200	763	38	107	107	83	0.83
	250	761	35	121	95	85	0.85

3.3. EIS Measurements

The corrosion of aluminum in 1.0 M HCl solution and its inhibition by the examined drugs were also investigated by EIS technique. Figure 13 showed Nyquist plots for the corrosion of aluminum in 1.0 M HCl solution in the absence and presence of the expired Ticarcillin and Carbenicillin drugs at 298 K. It can be seen from the Nyquist plots that the general shape of the curves was the same in the absence and presence of the drugs signifying no change in the mechanism of corrosion [65]. Also, the gained impedance spectra were found to comprise of one capacitive loops proposing that adsorption of the examined drugs occurs through covering the aluminum surface and the corrosion is mainly controlled by charge transfer process [66]. The size of the capacitive loop of aluminum in the corrosive solution was enhanced with rising the concentrations of the added drugs revealing a reduction in the corrosion rates and enhancement of the % IEs values.

The impedance parameters like solution resistance (R_s), charge transfer resistance (R_{ct}) and constant phase element (CPE) were computed by the aid of the equivalent circuit model illustrated in Fig. 14 and are inserted in Table 6. It is apparent from the values of R_{ct} listed in Table 6 that adding the examined drugs to the corrosive solution led to an increase in the R_{ct} value and this behavior was enhanced by increasing the drugs' concentrations. This designates that the examined drugs act as inhibitors through adsorption at the metal/solution interface which decrease their electrical capacities as they displace water molecules and other ions initially adsorbed on the metal surface [67]. Finally, the results of the % IEs values of the examined expired drugs obtained at 298 K (listed in Tables 1, 5 and 6) designated a good accordance among all applied tools (WL, PDP and EIS) as shown in Figure 15 demonstrating the rationality of the used techniques.
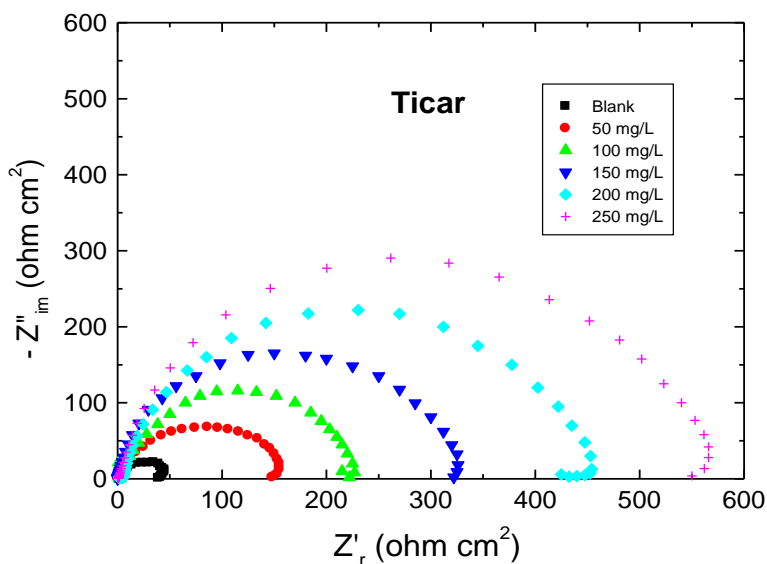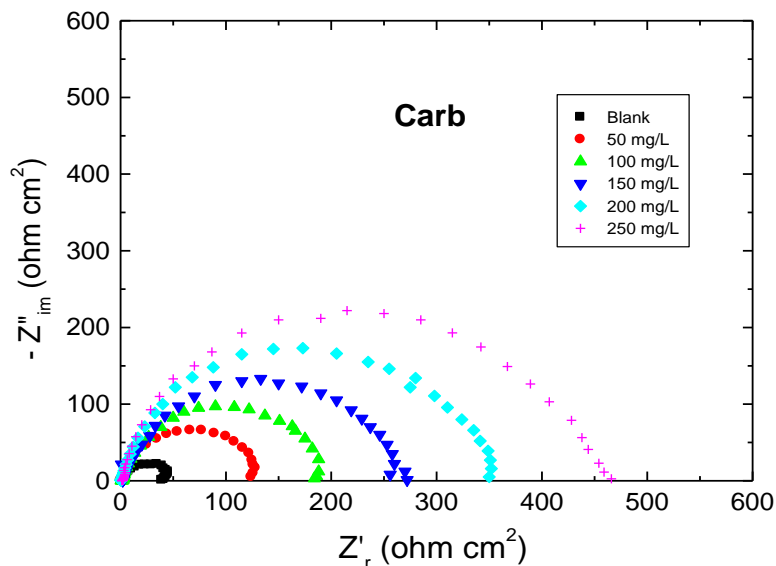
Figure 13. Nyquist plots for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.
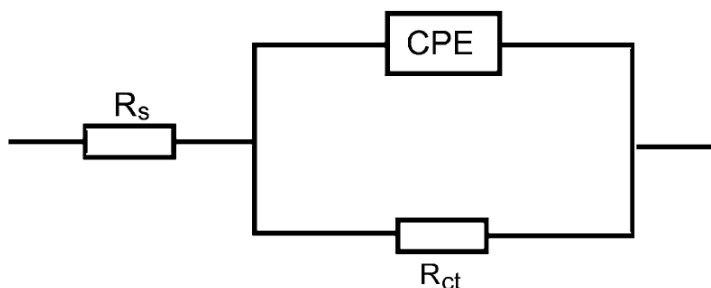

Figure 14. Electrochemical equivalent circuit utilized to analyze the EIS results for the corrosion of Al in 1.0 M HCl solution and with adding the examined drugs.

Table 6. EIS results for the corrosion of Al in 1.0 M HCl solution and with adding Ticarcillin (Ticar) and Carbenicillin (Carb) at 298 K.

Drugs	Drug conc. (mg/L)	R_s (ohm cm^2)	R_{ct} (ohm cm^2)	CPE (µF/cm^2)	% IE	θ
	0	1.1	46	313	--	--
Ticar	50	0.9	159	104	71	0.71
	100	2.1	230	87	80	0.80
	150	2.0	329	61	86	0.86
	200	4.6	460	41	90	0.90
	250	1.8	575	27	92	0.92

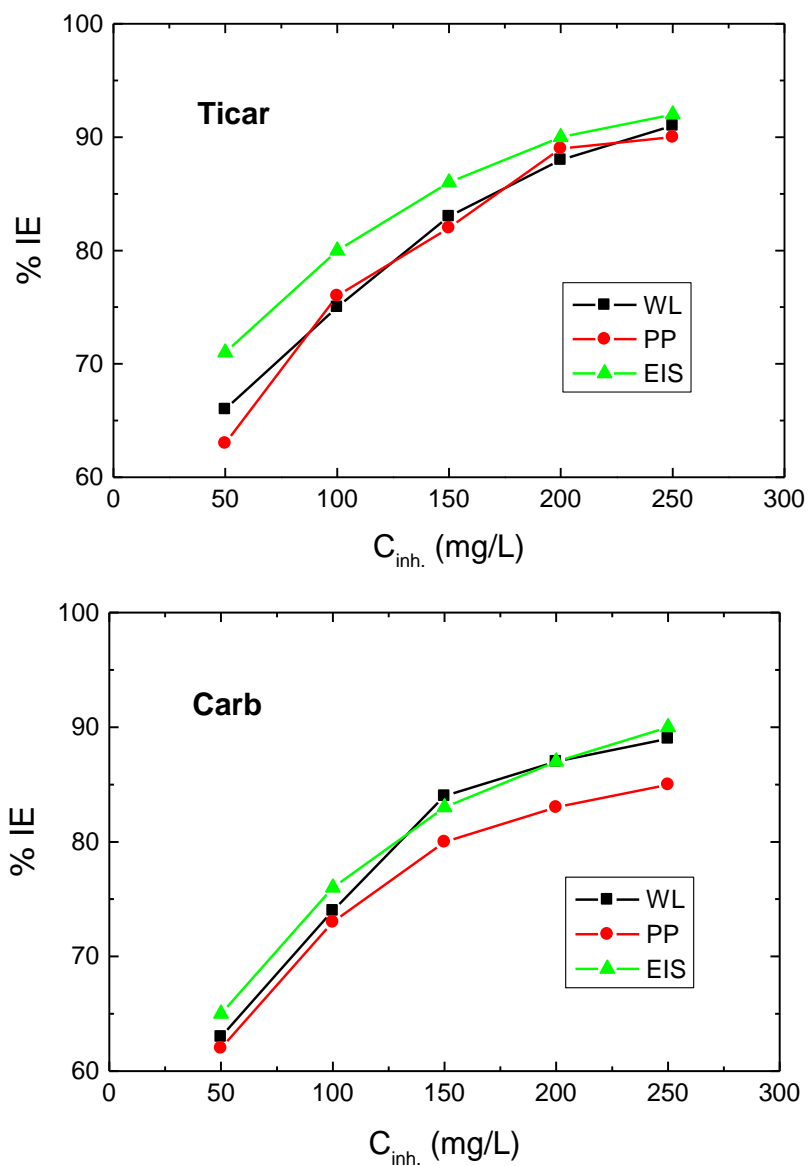|	50	1.2	131	109	65	0.65
	100	1.7	192	94	76	0.76
Carb	**150**	2.2	270	76	83	0.83
	200	1.4	354	55	87	0.87
	250	1.1	460	40	90	0.90

Figure 15. Comparison between the three employed techniques: WL, PDP and EIS regarding to the obtained values of % IEs of Ticarcillin (Ticar) and Carbenicillin (Carb) with their concentrations for the corrosion of Al in 1.0 M HCl solution at 298 K.

3.4. Surface Investigation

SEM micrographs of the surfaces of aluminum sheets in the investigated corrosive solution and with adding a 250 mg/L of the examined expired drugs are appeared in Figure 16(A-D). Figure 16 (A) shows a cleaned and degreased aluminum sheet before immersion in the corrosive solution, while Figure 16 (B) shows aluminum sheet after the immersion which manifests a clear damage in its surface comprising large and deep holes or pits. Figure 16 (C) and (D) illustrate the micrographs after adding a 250 mg/L of Ticarcillin and Carbenicillin, correspondingly, to the tested corrosive solution. It can be manifest that, the damage observed in the Al surface was vanished and the surfaces were generally covered with the drugs' molecules. This situation can be explained on the basis of strong adsorption of drugs' molecules on the Al surface, resulting in the protection of such surface.
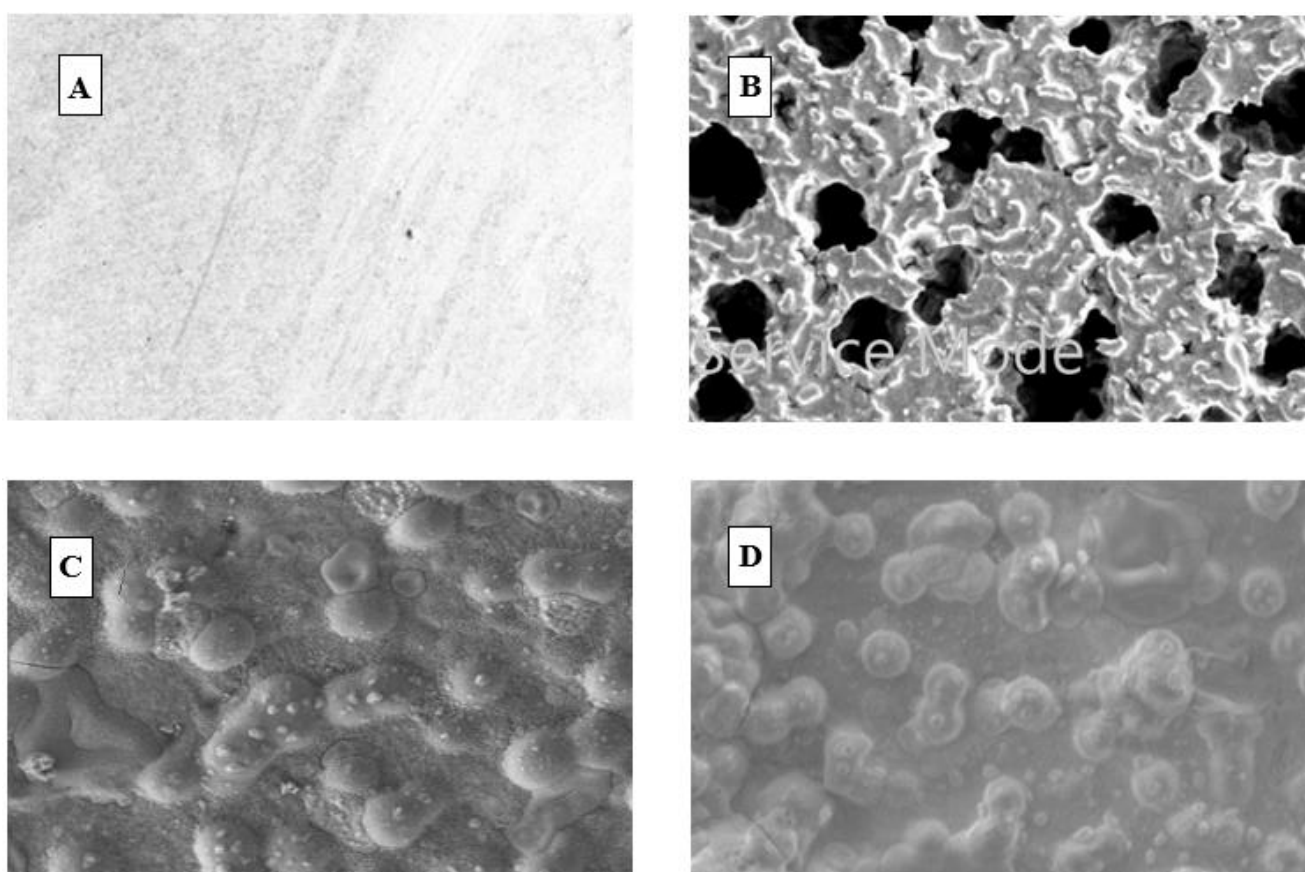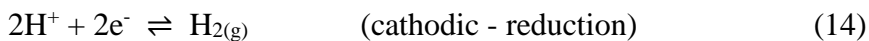

Figure 16. SEM micrographs (x 2500) of the surfaces of Al; (a) before immersion, (b) after immersion in 1.0 M HCl solution for 12 h, (c, d) after 12 h immersion in 1.0 M HCl with adding 250 mg/L of Ticarcillin and Carbenicillin, respectively.

3.5. Mechanisms of Al Corrosion in HCl and Its Inhibition

The mechanism of Al corrosion in HCl solutions was elucidated [68] by the anodic and cathodic reactions, which are defined by Eqs. (13) and (14), respectively,

$$Al_{(s)} \rightleftharpoons Al^{3+} + 3e^{-} \qquad \text{(anodic - oxidation)} \qquad (13)$$

$2H^+ + 2e^- \rightleftharpoons H_{2(g)}$ (cathodic - reduction)   (14)

The overall reaction is:

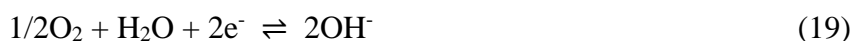$2Al + 6H^+ \rightleftharpoons 2Al^{3+} + 3H_{2(g)}$ (15)

Aluminum corrosion in aqueous solutions was found to depend on the solution pH [11] where in acidic or alkaline solutions, the solubility of the produced passive oxide layer was increased and Al corrodes more rapidly [10,11].

It was stated [8] that existence of Cl^- ions causes pitting corrosion where Cl^- ions enable anodic dissolution of Al as characterized by Eq. (16),

$Al^{3+} + 3Cl^- \rightarrow AlCl_3$ (16)

The plausible reactions at the cathodic sites:

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$ (17)

$3H^+ + 3e^- \rightleftharpoons 3/2H_2$ (18)

$1/2O_2 + H_2O + 2e^- \rightleftharpoons 2OH^-$ (19)

Regarding to Eq. (19), the corrosion products are formed on the pits due to precipitation of $Al(OH)_3$ [2].

In acidic solutions aluminum surface is suggested to be positively charged [69], in addition to the liberation of electrons from Al surface in the anodic reaction [68]. The obtained higher % IEs values of the tested drugs can be ascribed to strong adsorption of the drugs' molecules on the Al surface. This strong adsorption occurs due to such compounds contain lone pairs of electrons on the heteroatoms (O, N and S) and the π-bonds of the aromatic or heterocyclic rings that can form coordinate bonds with the vacant orbitals on the Al surface leading to formation of defensive layer. Also, in acidic media, the examined drugs which contain electron-donating polar atoms could be protonated forming positively charged ions as represented by the equation:

$Drug + xH^+ \rightleftharpoons [Drug - H_x]^{x+}$ (20)
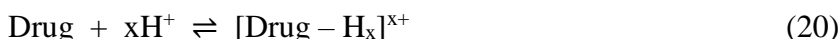
Therefore, the adsorption on the anodic sites could be occurred through the heteroatoms in the drugs' structures resulting in retardation of the aluminum dissolution process. Also, adsorption on the cathodic sites could be occurred via the protonated drugs' molecules (formed through the reaction (20)) leading to hindrance of the H_2 evolution reaction [70,71].

4. CONCLUSIONS

1. Corrosion inhibition of Al in 1.0 M HCl solution by the expired Ticarcillin and Carbenicillin drugs were investigated using different techniques.

2. The tested drugs were discovered to efficient inhibitors for the corrosion of Al in HCl.

3. The inhibition efficiencies (% IE) of the tested drugs enhanced with their concentrations and decreased with rising HCl concentration and temperature.

4. Thermodynamic and kinetic parameters were computed which confirm the mechanism of physical adsorption of the examined drugs.

5. The noticed greater % IE of the tested drugs was related to the strong adsorption of the drugs' molecules on the Al surface and such adsorption was agreed with Langmuir adsorption isotherm.

6. The examined drugs were found to act as mixed-type inhibitors with anodic majority.

7. The kinetics of Al corrosion and its inhibition indicated the gained greater % IE.

8. The gained values of % IE showed a good agreement amongst all used techniques.

9. The mechanisms of Al corrosion in HCl and its inhibition by the tested drugs were elucidated.

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