Protective Effect of Expired Drug on Corrosion of Copper in Acidic Medium

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ABSTRACT
Researchers used weight loss methods to investigate how the influence of expired Augmentin had on the ability of copper alloy to resist corrosion when exposed to solutions of hydrochloric acid. According to the findings, Augmentin shown remarkable effectiveness as a copper alloy inhibiting agent in acidic environment. We investigated how temperature affected the effectiveness of the medicine against corrosion, and in the end, we calculated the activation and adsorption parameters based on thermodynamics. The findings of this investigation revealed a high level of congruence regardless of the methodology employed.
By using the Langmuir adsorption isotherm to match experimental data, we found that inhibitor molecules adsorb onto copper surfaces via physical adsorption, as evidenced by the levels and signs of the adsorption Gibb's free energy.

Keywords: Expired Augmentine, copper inhibition, weight loss, thermodynamic parameters, Langmuir.

Introduction

Corrosion, which is an inescapable problem that occurs on metals or alloys that are in an aqueous solution, can be thought of as one of the greatest technological challenges of our day and is considered to be one of the top five problems in this category. In addition to the immediate monetary expenditures it imposes, corrosion is an extremely problematic issue due to the fact that it unquestionably adds to the exhaustion of our natural resources. Because of its widespread industrial applicability and economic significance, corrosion studies of copper and its alloys have attracted a significant amount of interest from researchers. Copper is widely utilized in the production of electrical conductors, thermal exchangers, and electronics. Copper dissolution is a possibility in potentially aggressive conditions, regardless of the area of application. [1-3]

 Controlling and preventing corrosion can be accomplished in a variety of different ways. The most typical practice involves the application of corrosion inhibitors [4].

 The application of corrosion inhibitors is a method for the protection of metal surfaces that is efficient, cost-effective, and practicable. In corrosive environments, extremely trace amounts of chemical compounds known as corrosion inhibitors can slow the pace at which metals corrode [5]. Extremely diluted solutions of these substances are released into the environment. Many drugs have been used as corrosion inhibitors in recent years. In contrast to the use of some organic or inorganic inhibitors, the use of pharmaceuticals for the suppression of corrosion of metals has some advantages, as stated by Eddy and Odoemelam. [6] Pharmaceuticals offer these benefits because they can be employed in place of organic or inorganic inhibitors. Drugs were proposed as an alternative to the typically damaging corrosion inhibitors because they are non-toxic, cheap, and have a low environmental impact [7]. To

make the most of this opportunity, it is recommended that you use pharmaceuticals that have already passed their expiration date. This approach will result in the resolution of issues relating to both the economy and the environment. It is important to note that beyond the date of expiration, more than ninety percent of the active component of the medicine stays stable for a considerable amount of time [8]. A medicine that has beyond its expiration date may also be found in the environment if improper disposal practices are followed. [9-11] Household garbage and toilets are two common entry points for illicit substances into the environment. Degrading the medications that are not fit for continued consumption by humans should be done using the appropriate method. According to them, making use of medications that have passed their expiration date as viable corrosion inhibitors might limit the amount of pollutants that is released into the environment while also cutting expenditures associated with degradation. Recently, several authors looked into the inhibitory action of several medications, including those listed in Table 1:

Table 1. Some expired medications used as copper corrosion inhibitors in alkaline environments.

Inhibitor (drug)	medium	%IE	references
Losartan Potassium (LP)	H_2SO_4	91.2	[12]
Meropenem	HCl	87.6	[13]
Cefpirome	H_2SO_4	91.9	[14]
Streptoquin	HCl	83.1	[15]

In this study, researchers use the same techniques used to examine the effects of expired Augmentin-like corrosion inhibitors on coppers in hydrochloric acid solutions, but apply them to the new environmentally friendly inhibitors.

2. Experimental

2.1 Materials and methods

The 99 percent pure copper sheets utilized came from an Iraqi market. Samples (2cm in diameter and 0.5cm in height) were sliced off the sheet. Additionally, grade 220, 400, and 600 emery sheets are used to mechanically polish it. In addition, it is degreased thoroughly before being stored in a desiccator by being rinsed with distilled water, ethanol, and acetone.

2.2 Weight loss measurements.

Experiments on the effects of weight loss were conducted using preformatted copper specimens. These samples were submerged in 1M HCl solutions at temperatures between (298) and (328) K for three hours in the absence and presence of different doses of augmentin, and then reweighed. Every estimate of weight reduction was triangulated, and then the results were compared. Three hours were spent testing at varying temperatures and with new solutions in acid media .

Surface coverage values ($\boldsymbol{\theta}$), inhibition competence (%IE) and corrosion rates have measured as follows:

$$\%IE = [(CR_o-CR_i)/\ CR_o]\times 100\%\ (1)$$
$$\theta = (CR_o-CR_i)/\ CR_o (2)$$
$$CR(mdd) = (w_o-w_i)/\ A\times t(3)$$

The weight losses in milligrams of copper with and without inhibitors are denoted by w_o and w_i, respectively; θ is the inhibitor surface coverages; A is the inhibitor surface coverages of the copper specimens' outer layers.length of time (in days) spent underwater [16].

3-Consequences and Discussion:

3-1. Influence of Concentration and temperature

Table 2 displays the results of weight loss experiments conducted at different temperatures (298, 308, 318, and 328K) and varied inhibitor doses in 1 M HCl.

   The results showed that the IE% of inhibition increased with increasing inhibitor concentration and decreased with increasing temperature for a given inhibitor concentration, with the maximum efficiency being achieved at (298) K. The decrease in inhibition efficiency with increasing temperature is suggestive of a physical adsorption mechanism [17,18]. This may be due to the fact that when the inhibitor concentration rises, so do the inhibitor's adsorption quantity and surface coverage on the copper surface.

Table2. *Three-hour immersion times in 1M HCl at different temperatures, with and without expired augmentin, corrosion rates and inhibition efficiencies, respectively.*

Temp. (K)	$C_{inh.}$ (ppm)	CR mdd	θ	IE%
298	Blank	26.093	-	—
	100	6.947661	0.75349	75.349
	200	5.789717	0.82249	82.249
	300	4.631774	0.86686	86.686
	400	3.231	0.91124	91.124
	500	2.315887	0.93235	93.235
308	Blank	70.930	—	—
	100	22.00093	0.73358	73.358
	200	17.213	0.75733	75.733
	300	12.654	0.83066	83.066
	400	9.453	0.87169	87.169
	500	7.000	0.91559	91.559
318	Blank	130.069	—	—
	100	42.84391	0.70621	70.621
	200	34.232	0.74894	74.894
	300	27.321	0.81304	81.304
	400	21.021	0.84622	84.622

	500	17.001	0.89834	89.834
328	Blank	155.162	—	—
	100	55.58129	0.65070	65.070
	200	48.63363	0.71641	71.641
	300	40.754	0.77611	77.611
	400	33.58036	0.81343	81.343
	500	26.6327	0.83967	83.967

3.2 Copper corrosion activating energy: Using the Arrhenius equation [19,20], we determined the activation energy required for copper to corrode in HCl acid without and with expired augmentine, respectively.According to the formula:

$$\log i_{corr} = \frac{-Ea}{2.303RT} + \log A \ldots (4)$$

Where (Ea) denotes an activation energy, (R) denotes gas constant (8.314), and (A) denotes Arrhenius constant. Equation(4) envisages that $\log (i_{corr})$ plotting against $\frac{1}{T}$ must be linear as experimentally perceived. A slope for the line provides $\frac{-E^*}{RT}$, while the intercept of the extrapolated line to $\frac{1}{T} = o$ gives ln A.

By adopting other form for Arrhenius relationship (ΔH) and (ΔS) can be obtained where:

$$\ln\left(\frac{i_{corr}}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{act}}{R}\right) - \left(\frac{\Delta H_{act}}{RT}\right) \ldots (5)$$

Here, (h) is "planks constant"($6.626*10^{-34}$ J.S), (N) is "Avogadro's number" ($6.022*10^{23}$ mol^{-1}), it is potential to plot $(\ln \frac{i_{corr}}{T})$ vs. $(\frac{1}{T})$, where a slope for a straight line displays its magnitude $(-\frac{\Delta H_{act}}{R})$ and the intersection displays its magnitude $(ln\frac{R}{Nh} + \frac{\Delta S_{act}}{R})$. As presented in the figures (1).The consequences are explained in Table 3:
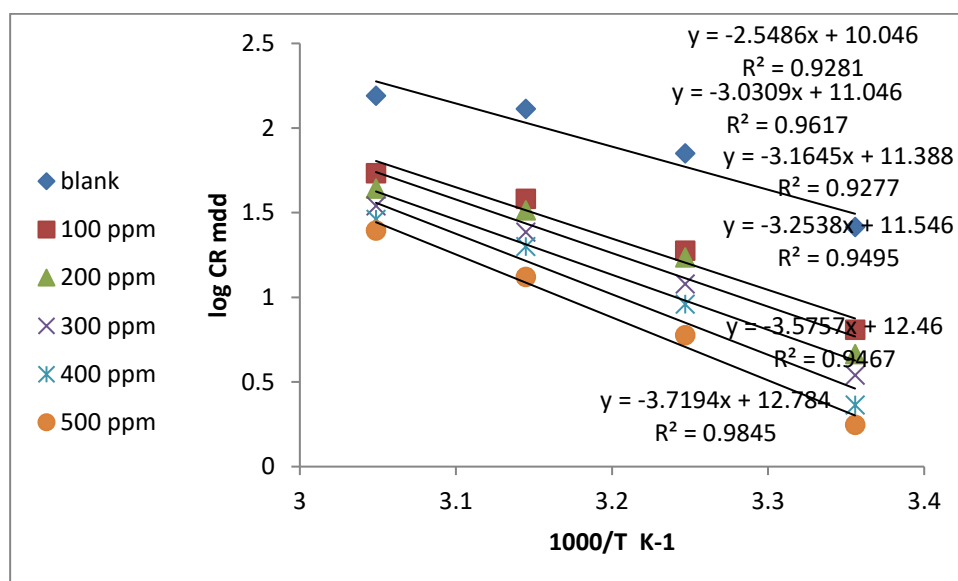
Figure (1) log CR. Arrhenius plots vs. 1/T for the corrosions of Cu in 1 M HCl with and without dissimilar dosage of expired augmentine .
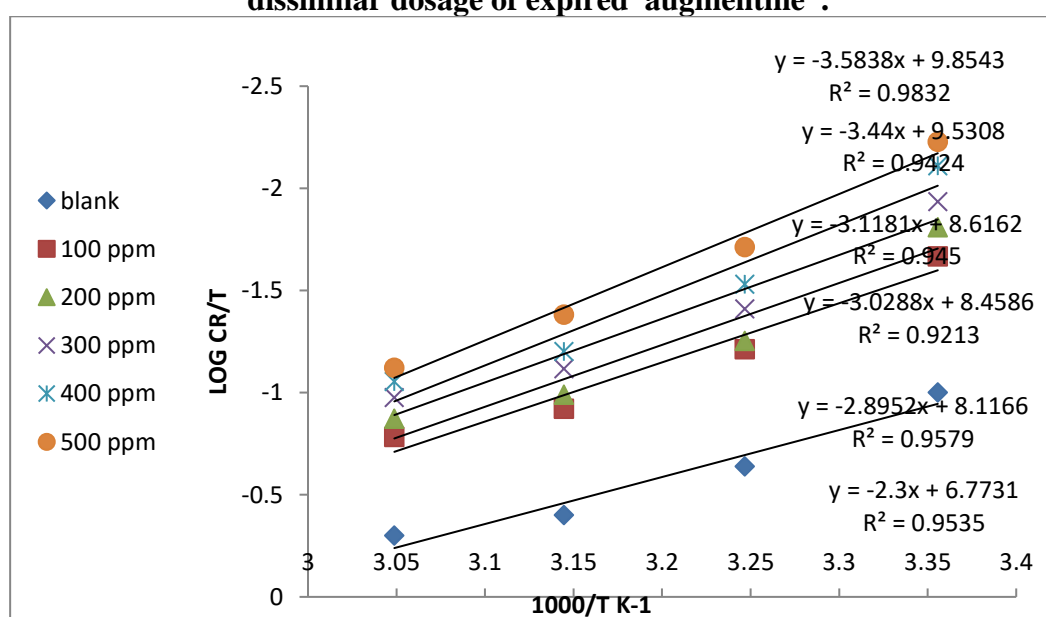

Figure (2) log (CR/T) vs. 1/T for the Cu corrosion in 1 M HCl with several concentrations for expired augmentine .

Table 3 Ea, activating enthalpies (ΔHa), besides activation entropies (ΔSa) for Cu corrosions in 1 M with and without inhibitor

Conc. (ppm)	E_a (KJ.	ΔH_a (KJ.	$-\Delta S_a$ $(J.K^{-1}.mol^{-1})$

	mol^{-1})	mol^{-1})	
Blank	48.798	44.045	67.540
100	58.042	55.439	41.823
200	60.600	57.986	35.274
300	62.310	59.709	32.249
400	68.475	65.876	14.745
500	71.227	68.614	8.541

In addition to showing that the adsorption of augmentin molecules on Cu surface is physical, the rise in activation energy E*a with increasing concentrations of expired augmentin is indicative of a corresponding rise in the energy barrier for the corrosion reaction.

The Arhinius coefficient and the activation energies are not directly proportional to one another, and corrosion reactions tend to initiate at low-energy sites and propagate to higher-energy sites [21].

In other words, copper corrosion in a solution containing chlorine ions will still proceed, but the inhibitors will delay the process by raising the energy barrier associated with it. Additionally, an increase in temperature accelerates the corrosion process, which in turn reduces the effectiveness of inhibition, when the inhibitor concentration is raised, the electron density in the adsorption sites of the inhibitor molecules rises, leading to more effective inhibition [22].

The adsorption isotherm:

When discussing adsorption properties using isotherm adsorption, surface coverage data is helpful because it describes additions of molecules of inhibitor that are on the surface of the metal and interact with them.

Adsorption isotherms are used to analyze the inhibitors' (expired augmentin) effect on the working electrode (copper) surface coverage (θ) and the concentrations of inhibitors solutions ($Cinh$). The following equation describes the optimal Langmuir isotherm[23,24].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{adc}} + C_{inh} \ldots\ldots (6)$$

Here, K_{ads} is adsorption and desorption equilibrium constants imply that inhibitor molecules are getting close to surface adsorption sites.

Then measured K$_{ads}$ is for calculating Gibbs free energies for adsorption through **[25]**

$$\Delta G°_{ads} = -RTln (55.5K_{ads}) \ldots\ldots\ldots (7)$$

Here R represents gas constants, T represents absolute temperatures, while (55.5) value represent molar water concentrations in mol/L; the van t Hoff formula is used to determine the standard enthalpies of adsorption.

$$\ln K_{ads} = -\frac{\Delta H_{ads}}{RT} + constant......(8)$$

Schemes of in K_{ads} values vs. 1/T magnitudes display straight lines the straight lines slope equal $\frac{-\Delta H_{ads}}{R}$. The negative $\Delta H°$ values display an adsorption for expired augmentin molecules as exothermic .The $\Delta G°_{ads}$ negative values with the inhibitor are followed by exothermic adsorption processes. $\Delta S°_{ads}$ of inhibitions have been taken from [26] as in (4):

$$\Delta S°_{ads} = \frac{\Delta H°_{ads} - \Delta G°_{ads}}{T} ....(9)$$
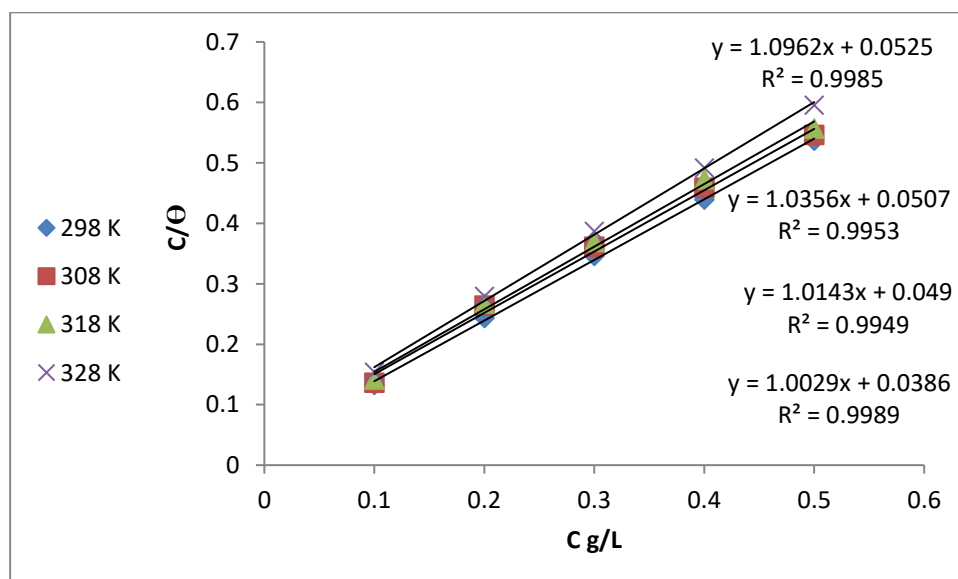

Figure (3) Langmuir Isotherm plots to expired augmentin adsorptions on Cu in 1M HCl.

The above results shown in table (4):

Table 4   Parameters of Thermodynamic for the adsorptions of expired augmentin adsorptions on coppers in 1M HCl.

T K	K_{ads} (g^{-1}.L)	-$\Delta G°_{ads}$ (kJ.mol^{-1})	$^-\Delta S°_{ads}$ (J.K-1.mol^{-1})	-$\Delta H°_{ads}$ (kJ.mol^{-1})
298	25.9			
		17.9	88	8.4
308	21.7			
		18.17	86	

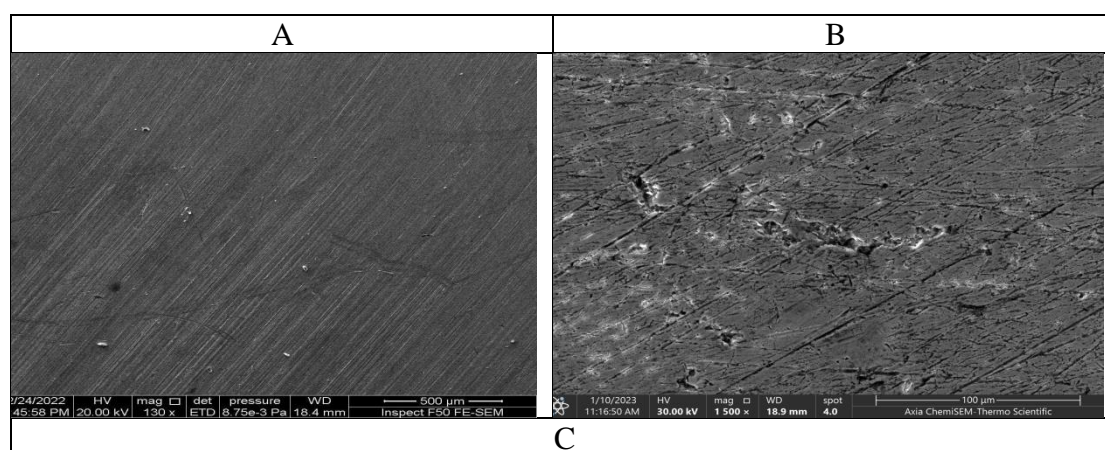| 318	19.7			
		18.5	84	
328	19			
		18.9	83	

ΔG_{ads} values reach -20kJ/mol measured as an electrostatic for charged molecules interrelating with outer metal layers (physisorption). Yet, the ΔG_{ads} magnitudes are in higher negative level than -40kJ/mol as charges moving from the inhibitor molecules to the metal surfaces or creating coordinate covalent bonds (chemisorption). ΔG_{ads} magnitudes ranged (17.9 – 18.9) kJ.mole^{-1}, indicating an inhibitor adsorption onto copper alloy surfaces occur through physical adsorption [27].

Adsorption of the inhibitor molecules is exothermic, as indicated by the negative values of ($\Delta H°$). Although an adsorption can be physical or chemical, an endothermic nature of the positive value suggests that it is chemical. This article uses the term "physisorption" to describe the adsorption of augmentin molecules onto copper surfaces [28,29].

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) analysis of copper surfaces Copper surfaces were studied by SEM to confirm that the extracted molecules were adsorbed on Cu alloy surfaces, rather than simply peeled off. Figure 4 shows a SEM micrograph of copper alloy surfaces before and after being immersed in 1M hydrochloric acid with and without the optimal concentrations of augmentin. Figure (a) depicts refined Cu alloys, (b) Cu alloys immersed in 1M hydrochloric, and (c) copper alloys dipped in 1M hydrochloric with 500 ppm of augmentin.
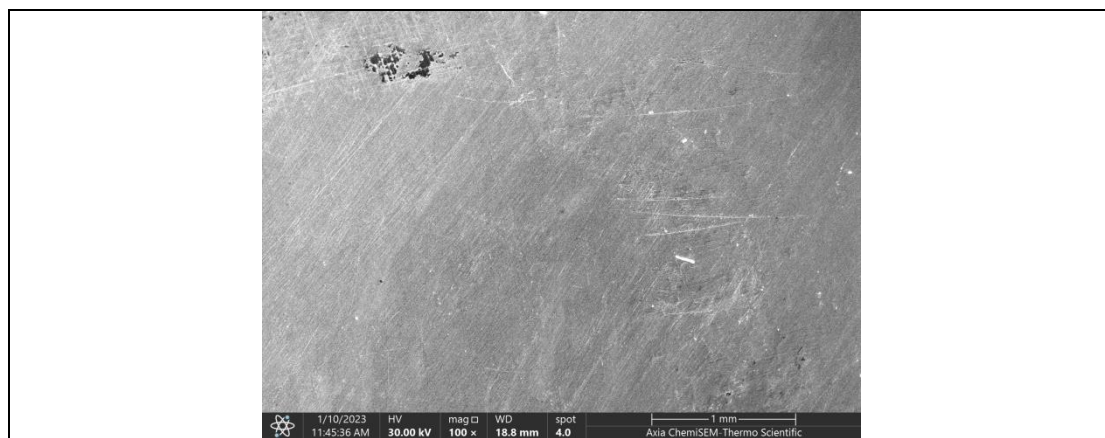
Figure (4)   Scanned micrographs for electron (a) polished copper alloys, (b) Cu alloys dipped in (HCl), and (c) Cu alloys in(1) M(HCl) solutions with a 500 ppm of expired augmentin.

Conclusions

According to the study's findings, expierd augmentin is an effective weight-loss-technique-based inhibitor for copper in 1M (HCl) solutions. The inhibitors adsorb on the metal surface spontaneously, as shown by negative values of G. This finding is corroborated by the observed Ea and ΔH values for the corrosion process. Inhibited and blank solutions are all negative because the activation complex in the rate-determining stage represents an association rather than a dissociation for $\Delta S*ads$. Adsorption data for augmentin on a metal surface were modeled using the Langmuir adsorption isotherm, and the data were found to be in good agreement with this model. As the concentration of the inhibitor rose, so did the effectiveness of the protection it provided. At 500 ppm of stale augnentin, the maximum value reaches 93%.

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