J. Electrochem. Sci. Eng. **13(6)** (2023) 1005-1013; http://dx.doi.org/10.5599/jese.1867

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

Original scientific paper

Corrosion inhibition effect of expired ibuprofen drug on copper in sulfuric acid solution

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Received: May 2, 2023; Accepted: July 31, 2023; Published: August 7, 2023

Abstract

The application of copper as a material in various fields is widely recognized. However, in acidic environments, the electrical and mechanical properties of copper undergo negative alterations, resulting in its dissolution. To protect copper from degradation, the most effective approach is to employ inhibitors. Hence, in this paper, the expired ibuprofen drug has been investigated as a corrosion inhibitor for copper in 0.5 M H_2SO_4, employing weight loss and electrochemical tests. Compared with the pharmaceutical products used by other researchers in this field, the results showed that ibuprofen is highly effective in protecting copper from corrosion. It was noted that the inhibitory efficacy of ibuprofen increases with concentration. In addition, it was found that its adsorption follows Langmuir isotherm.

Keywords

Expired drugs; copper corrosion; inhibition efficiency; weight loss; electrochemical tests

Introduction

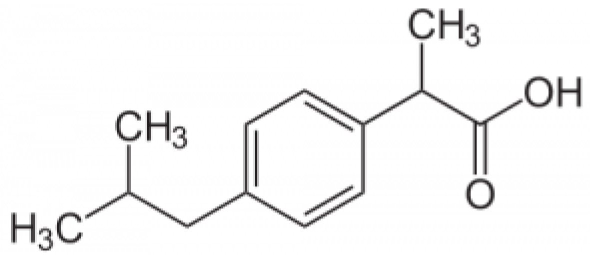
Copper is utilized as a conductor in the electronics sector because it is thermally and electrically conductive. Copper can dissolve under certain situations [1], which has detrimental effects on metal characteristics and may result in large financial losses [2]. Therefore, researchers have created a variety of corrosion inhibitors to protect metals and alloys against corroding by acids like sulphuric acid. These blockers are either organic or inorganic compounds [3,4]. In comparison to organic chemicals, particularly azole compounds, inorganic compounds have lower inhibitory effectiveness [5,6]. Many of these substances are poisonous to the environment and therefore, research has been focused on developing waste disposal methods and corrosion inhibitors that are acceptable to the environment. Pharmacological substances [7] are potentially environmentally friendly corrosion inhibitors for copper, according to numerous studies and investigations [8], and pharmaceuticals that are out-of-date or flawed could also be used as conventional inhibitors. Green corrosion inhibitors are natural substances that find application not only in pharmaceutical production [9] but also in plant extraction, which helps to mitigate costs while ensuring the continued availability of traditional medicines [10]. About 90 % of the medicine's active ingredient remains stable after expiration for a long time [11]. Drugs are released into the environment through household garbage [12] and utilizing outdated medications as potential corrosion inhibitors may help lessen environmental pollution. According to studies [13], the pharmaceutical industries are also in charge of getting rid of old medications [14]. Because of this, unused drugs should be carefully eliminated using techniques including photochemical and biodegradation [15,16]. Furthermore, the potential for reusing the medications in corrosion testing would lead to reduced environmental damage from their application. Ibuprofen $C_{13}H_{18}O_2$, (RS)-2-(4-(2-methylpropyl) phenyl) propanoic acid is an anti-inflammatory drug widely used in the treatment of muscle pain in rheumatic diseases. In this paper, the question of whether or not the expired ibuprofen could be used for the effective corrosion inhibition of copper in a sulfuric acid solution (H_2SO_4), should be clearly answered.

Experimental

Materials and solution preparation

The metal used in this study was copper, with 99 % purity. The metal was covered with epoxy resin to leave a contact surface of 0.5 cm^2. The sample was abraded with emery paper (600, 800, 1200, 1500 grad grit) and cleaned with distilled water before each experiment. 0.5 M H_2SO_4 was prepared using 97 % H_2SO_4 solution of Sigma-Aldrich.

Solutions of ibuprofen inhibitor (Scheme 1) were prepared by dissolving the required amount of ibuprofen powder in H_2SO_4 solution. To create solutions with decreasing concentrations, the solution with the greatest concentration of 5 mM was diluted to 1, 0.5 and 0.1 mM. In our survey, the expired ibuprofen (stored at a local Moroccan pharmaceutical company's warehouse) was used in the form of drug powder made from ibuprofen tablets of 200 mg. It is known that ibuprofen tablets contain not only ibuprofen compound but also up to 15 % of non-active ingredients such as lactose, starch, microcrystalline cellulose, croscarmellose sodium, colloidal silicon dioxide, polyethylene glycol (PEG) and dyes. This ultimately means that “true” concentrations of ibuprofen were correspondingly lower than declared above.



***Scheme 1**: Chemical structure of ibuprofen $C_{13}H_{18}O_2$*

Electrochemical techniques

The three-electrode cell and a potentiostat device type PGZ 100, in conjunction with the required VOLTA Master software, were used to carry out electrochemical measurements. A copper electrode with an exposed surface of 0.031 cm^2 served as the working electrode, while a standard calomel electrode and a platinum wire as reference and auxiliary electrodes, respectively. The copper electrode was cleaned with distilled water and dried before each measurement.

The polarization measurements were recorded in the potential range between -600 mV and 600 mV with a sweep rate of 1 mV/s after a stabilization time of 40 minutes.

Electrochemical impedance measurements (EIS) were carried out at the constant OCP in the frequency range of 100 kHz to 10 mHz, under potentiostatic conditions using the alternating signal with the amplitude of 10 mV peak-to-peak. The values of electrochemical parameters were extracted using EC-LAB software.

Weight loss measurements

Copper samples of size 75×13×3 mm were used in the weight loss experiments. These samples were immersed in 0.5 M H_2SO_4 sulfuric acid solutions in the absence and presence of 5 mM ibuprofen for 10 days at room temperature. Each sample was washed with distilled water and then weighed on a PA214 analytical balance with a weighing accuracy of 0.0001 g.

Analysis of copper surfaces by scanning electron microscopy

In order to confirm the protective properties of ibuprofen, the surfaces of copper samples subjected previously to different acid solutions for 10 days were analyzed using a Hirox SH4000M scanning electron microscope. The copper samples were prepared for weight loss measurements.

Results and discussion

Polarization potentiometric measurements

The potentiodynamic polarization curves for copper in 0.5 M H_2SO_4 without and with the addition of an expired ibuprofen inhibitor are shown in Figure 1.

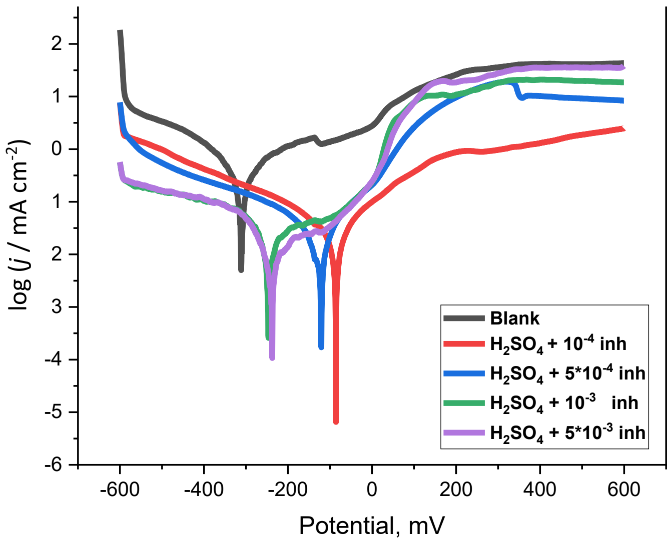


Figure 1. *Potentiodynamic polarization curves of copper in 0.5 M H_2SO_4 solution without and with the addition of ibuprofen*

It is evident that the corrosion current density (j_{corr}) decreased in the presence of the expired drug. The corrosion potential (E_{corr}) of the inhibited media is shifted in the positive direction compared to the E_{corr} of the blank solution. The change in E_{corr} in the inhibited solutions is more than 85 mV, compared to the value of E_{corr} in the blank solution, which suggests that ibuprofen can be classified as an anodic type inhibitor [17]. On the other side, parallel cathodic Tafel lines show that the presence of an ibuprofen inhibitor has little impact on the cathodic reaction [18].

The data for corrosion potentials as well as corrosion current densities, anodic (b_a) and cathodic (b_c) Tafel slopes, and inhibition efficiencies (IE), are presented in Table 1.

Table 1 . *Electrochemical parameters of copper corrosion in 0.5M H_2SO_4 solution without and with addition of different concentrations of ibuprofen*

Inhibitor concentration, mM	E_{corr} / mV	j_{corr} /μA cm^{-2})	b_a / mV decade^{-1}	b_c / mV decade^{-1}	IE, %
0.0	-309	171.40	93.4	-83.9	---
0.1	-84	30.56	167.8	-241.9	82.17
0.5	-117	24.59	117.6	-219.4	85.65
1.0	-244.6	13.80	219.0	-89.2	91.95
5.0	-235.5	8.89	136.6	-81.4	94.81

According to Table 1, the addition of the inhibitor changed the values of b_a and b_c as a result of the inhibitor molecules adhering to the metal surface to form a protective layer [19]. Also, adding ibuprofen to sulphuric acid caused a drop in current density values, and this behavior continuously takes place as ibuprofen concentration rises. This demonstrates that under these circumstances, ibuprofen can shield copper surface. The inhibitor efficiency (IE, %) values of the expired ibuprofen were determined by Eq. (1) [20]:

$$IE = ((j_{corr}–j_{corr(inh)}) / j_{corr})\ 100 \qquad (1)$$

where j_{corr} and $j_{corr(inh)}$ are corrosion current densities in the absence and presence of the inhibitor, respectively.

It is clearly seen in Table 1 that the inhibitor concentration affects inhibitor efficiency, which is connected to the adsorption of inhibitor molecules on the copper surface. Furthermore, ibuprofen was found to be an efficient inhibitor for copper corrosion in the studied medium as the inhibition effectiveness reached even 94.81 % at 5 mM.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy experiments were carried out to further examine the impact of ibuprofen on copper corrosion behavior. The outcomes are displayed in Figure 2 in the form of Nyquist plots (-Z_i *vs.* Z_r). By analyzing the Nyquist diagrams in Figure 2, it is evident that when the inhibitor concentration rises, so does the diameter of an obtained semicircle, suggesting a decrease in the corrosion rate of the Cu sample [21]. Additionally, a small contribution of the Warburg impedance is seen at the lowest frequencies, indicating diffusion processes, such as diffusion of soluble copper species or dissolved oxygen on the copper surface [22].

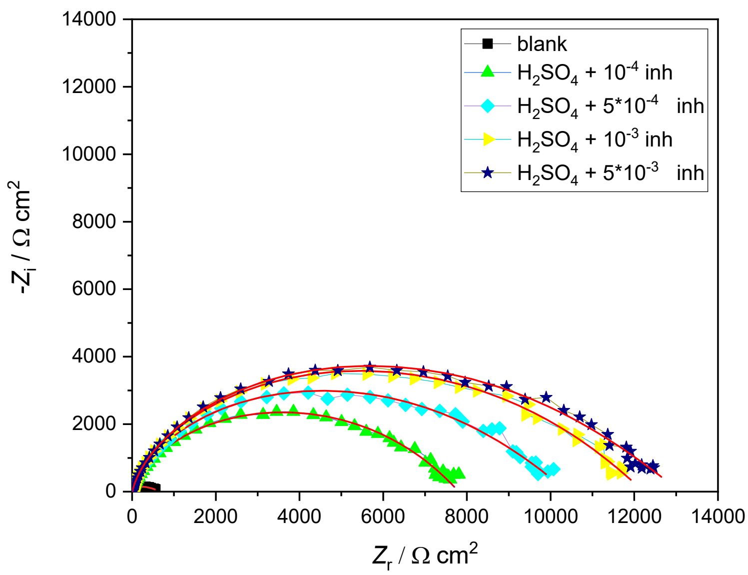


Figure 2: *Nyquist plots for copper in 0.5M H_2SO_4 in the absence and presence of different concentrations of ibuprofen*

The EC-Lab software program and the equivalent circuit shown in Figure 3 were used to fit the experimental data, where R_s is the solution resistance, R_f is the resistance of the protective inhibitor film formed on the copper surface, R_{ct} is the charge transfer resistance of corrosion, while Q_f and Q_{dl} represent constant phase elements (CPE). CPEs are put instead of pure capacitors, C_f, for the film capacitance and C_{dl} for the capacitance of the double layer. W is the Warburg (diffusion) impedance and n is the deflection parameter.

The parameters C_f and C_{dl} were calculated according to the equations (2) and (3):

$$C_f = (Q_f R_f^{1-n_1})^{1/n_1} \tag{2}$$

$$C_{dl} = (Q_{dl} R_{ct}^{1-n_2})^{1/n_2} \tag{3}$$

The calculated capacitance values and other impedance parameter values obtained by curve fitting of the electric equivalent circuit (EEC) in Figure 3 to impedance plots in Figure 2 are listed in Table 2 for different concentrations of ibuprofen.

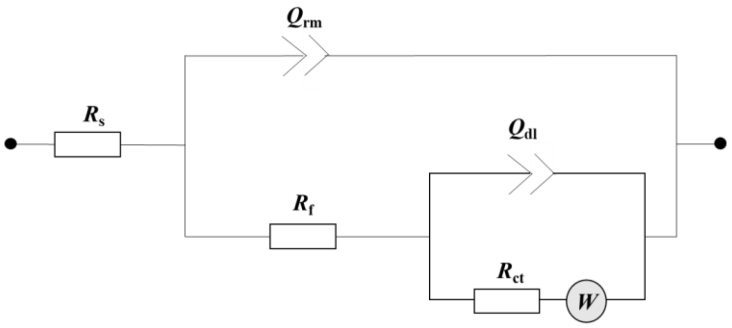


***Figure 3:** Equivalent electrical circuit for copper in sulphuric acid solution in the absence and presence of different concentrations of ibuprofen*

***Table 2.** Electrochemical impedance parameters for copper in 0.5 M H_2SO_4 solution without and with ibuprofen added*

Inhibitor concentration, M	R_s / Ω cm^2	C_f / F cm^{-2}	n_1	R_f / Ω cm^2	C_{dl} / F cm^{-2}	n_2	R_{ct} / Ω cm^2	W_0 / Ω^{-1} cm^{-2} s$^{0.5}$	$R_p = R_s + R_{ct}$ / Ω cm^2	IE, %
Blank	1.192	0.52×10^{-3}	0.72	399.6	7.21×10^{-3}	0.53	221.4	0.38	621	---
10^{-4}	7.522	1.49×10^{-6}	0.97	241.1	13.98×10^{-6}	0.57	7 561	/	7 802	92.04
5×10^{-4}	9.475	2.64V10^{-6}	0.93	733.7	16.85×10^{-6}	0.49	9 675	/	10 409	94.03
10^{-3}	7.260	1.97×10^{-6}	0.96	256.6	13.75×10^{-6}	0.53	11 965	/	12 222	94.91
5×10^{-3}	9.772	2.78×10^{-6}	0.93	989	16.16×10^{-6}	0.48	12 107	/	13 096	95.25

According to the results presented in Table 2, the increased values of R_{ct} in the presence of the ibuprofen inhibitor indicate slower rates of copper corrosion, probably due to the increase in surface homogeneity due to inhibitor adsorption. Furthermore, as the inhibitor concentration increased, the values of C_f and C_{dl} decreased. This is related to the adsorption of inhibitor molecules on the copper surface, which reduces the surface area of copper exposed to aggressive ions. According to the obtained results, it is assumed that the copper surface is uniformly coated. The following equation was used to compute the inhibitory efficiency:

$$\text{IE} = [(R_p - R_{p0}) / R_p]\ 100 \tag{4}$$

where R_{p0} is the polarization resistance of the copper electrode in the blank solution and R_p is the polarization resistance of the studied medium in the presence of the inhibitor. Note that polarization resistance R_p is defined as $R_p = R_f + R_{ct}$. R_p values are also listed in Table 2. It can be seen that the computed IE values from EIS shown in Table 2 and from potentiodynamic polarization shown in Table 1 are in relatively good agreement.

More about the interactions at the adsorbate/substrate interface may be obtained by the analysis of adsorption isotherms [23]. Various adsorption isotherms were tested, and it was shown that the Langmuir adsorption isotherm, with a linear regression coefficient (R^2) equal to unity and a slope approaching unity, is the best representative for the inhibitor adsorption (Figure 4).

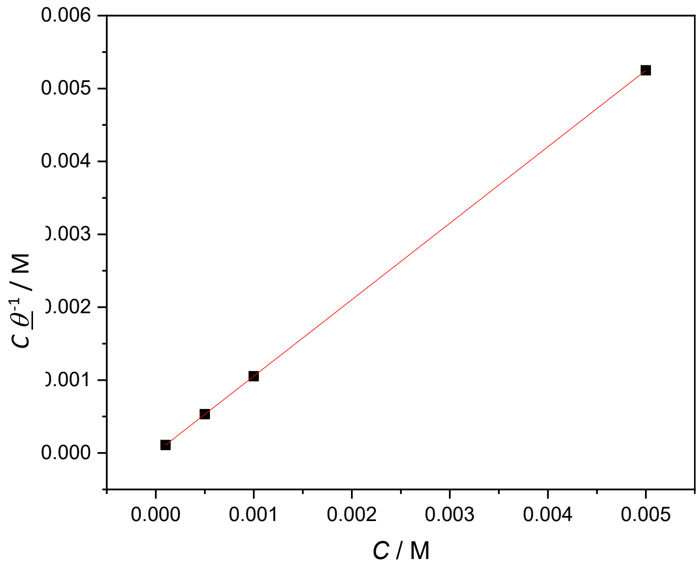


Figure 4. *Langmuir adsorption isotherm for the adsorption of ibuprofen on copper surface*

Equation (5) yields the Langmuir isotherm formula:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \tag{5}$$

where θ is the surface fraction covered by adsorbed species, and K_{ads} is the equilibrium adsorption constant (M^{-1}).

By using Figure 5 and eq. (5), the adsorption equilibrium constant was determined as K_{ads} = 1.897 mM^{-1}. Adsorption free energy change (ΔG^0_{ads}) value was calculated using equation (6):

$$\Delta G^0_{\text{ads}} = -RT \ln (55.4\, K_{\text{ads}}) \tag{6}$$

Herein, R is the universal gas constant, and T is the absolute temperature. The computed adsorption free energy value is ΔG^0_{ads}= -40 kJ mol^{-1}, which means the process is spontaneous. Since the value of ΔG is -40 kJ mol^{-1}, we can say that the adsorption of ibuprofen on the copper surface takes place *via* physicochemical adsorption [24].

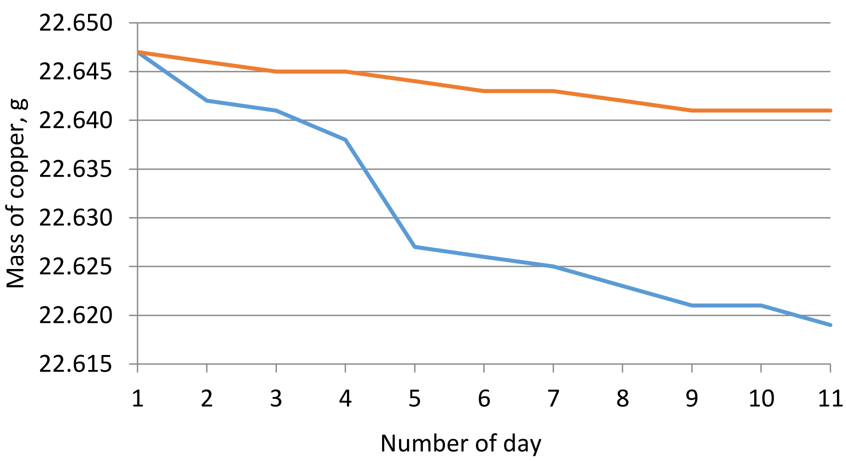


Figure 5. *Weight loss curves for copper in 0.5 M H_2SO_4 solution without and with addition of ibuprofen;* *copper in H_2SO_4,* *copper in H_2SO_4 with 5 mM of inhibitor*

Weight loss measurements

Figure 5 shows a decrease of the copper mass during immersion in 0.5 M H_2SO_4 without and with 0.5 mM of ibuprofen inhibitor. It is obvious, that the mass of the copper is less decreased once the inhibitor is added to the sulfuric acid [25].

In the absence of the inhibitor, the gravimetric test of copper immersed in sulfuric acid reveals a significant weight loss due to the aggression of the acid, but with the addition of 5 mM ibuprofen, the metal undergoes a much slower attack.

Surface characterization by SEM

SEM was used to characterize the surfaces of copper coupons subjected to 0.5 M H_2SO_4 in the presence and absence of the highest concentration of ibuprofen (5 mM). The coupons were submerged in solutions for 10 days at room temperature, as for weight loss measurements in Figure 5, and the resulting SEM micrographs are shown in Figure 6. In contrast to the pitting and cracking that were found in the solution without the inhibitor, it has been noticed that the copper surface is smoother in the presence of the inhibitor. This can be the effect of ibuprofen forming a thick film on the metal surface.

(a) (b) (c)

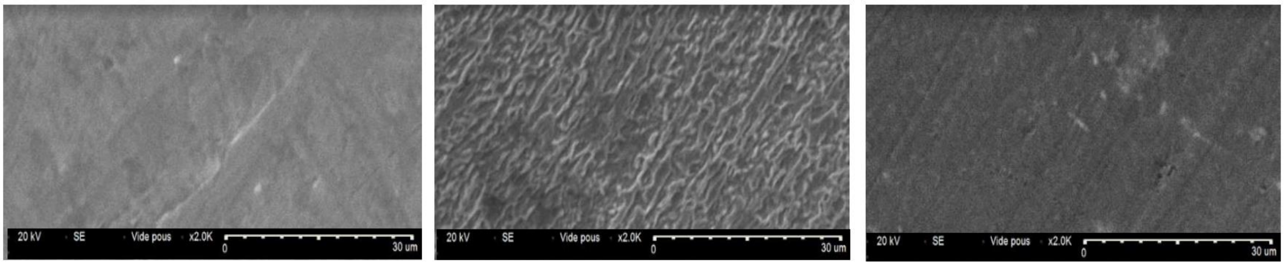


Figure 6. *SEM images of the copper surface in the initial state (a), and after 10 days of immersion in 0.5 M H_2SO_4 solution without inhibitor (b) and with 5 mM ibuprofen (c)*

Conclusions

The expired ibuprofen drug was tested as a possible corrosion inhibitor of copper in the sulfuric acid solution, showing that the ibuprofen product can efficiently protect copper surfaces.

The data showed that as the inhibitor concentration rises, the effectiveness of inhibition also rises, attaining about 95 % at the highest ibuprofen concentration of 5 mM. Ibuprofen is classified as an anodic type of corrosion inhibitor, which acts by forming a protective film on the copper surface. The development of a protective film was supported by SEM analysis of copper surfaces after immersion in sulfuric acid containing ibuprofen.

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