Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

USING EXPIRED DRUGS AS ENVIRONMENTALLY FRIENDLY CORROSION INHIBITORS

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Abstract

Hazardous waste management is one of the problems our society is facing today. Expired drugs are a type of waste that is not reused in any way, but rather incinerated to be disposed of. These drugs have been proven to act as corrosion inhibitors for different metals and in different corrosive solutions. They are a good alternative to the synthetic inhibitors the industry uses today, due to their environmental friendliness, good corrosion inhibitor efficiency and economic advantages. The present research focuses on expired drugs as corrosion inhibitors for mild steel in concentrated sulfuric acid solution and characterize their inhibitive performance through weight loss measurements, Electrochemical Impedance Spectroscopy (EIS) spectra, and cyclic voltammetry (CV). The drug proved to be effective environmentally friendly corrosion inhibitor for mild steel, being a possible way of recycling expired drugs.

***Key words**: expired drugs, hazardous waste, green corrosion inhibitor, industrial pickling.*

INTRODUCTION

One of the most important steps in mild steel (MS) manufacturing is the surface cleaning process, often done by acid pickling. This process generates an important quantity of industrial waste, exhausted pickling solutions (ESP) that contain high concentrations of metal ions (Gao et al., 2021). The two main solutions used for pickling are hydrochloric and sulfuric acid dilutes with water in a 1:1 ratio (Zaferani et al., 2013). This work focuses on using hydrochloric acid as a pickling liquor.

Literature reports show that the EU generates 0.38 million m^3/year compared to the USA's 1.89 million m^3/year (Agrawal & Sahu, 2009), managing EPS being a significant environmental concern that the metal manufacturing sector is currently facing. The higher metal concentration within the ESP is caused by the corrosion phenomena that occurs throughout the pickling process. The most common strategy used to manage this phenomenon is to add corrosion inhibitors to the acid solution (Deflorian et al., 2019; Predko et al., 2021).

Due to environmental awareness and stricter guidelines, green corrosion inhibitors have been explored as an alternative to the synthetic chemicals that have been and are presently used for corrosion inhibition. These synthetic compounds are more expensive and damaging to the environment, while being as effective if not less effective than their eco-friendly counterparts (Chaubey et al., 2021).

Several substances, including plant extracts (Verma et al., 2023), carbohydrates (Seddik et al., 2024), natural polymers (Timothy et al., 2023), ionic liquids (Souza et al., 2023), amino acids (Seddik et al., 2024), and medicinal substances (drugs) (Verma et al., 2021), have been designated as "*green corrosion inhibitors*". Research shows that adsorption is the main mechanism by which these compounds protect the metal surface, the existence of double bonds, phenyl rings, heteroatoms (N, S, and O) (Quraishi et al., 2021), and other functional groups facilitate their ability to adsorb on the metal substrate effectively inhibiting the corrosion phenomenon, thus lowering the metal ion concentration found the resulted pickling sludge.

There is extended research on expired drugs used as corrosion inhibitors for multiple experimental conditions (e.g. hydrochloric acid, sulfuric acid aluminium, mild steel, copper etc.) (Tanwer & Shukla, 2022). However, the subject is far from being exhausted due to the complexity of the inhibition mechanism of drug

molecules and the limitation of their solubility in polar solvents. Drug molecules prevent corrosion by creating a protective coating by adsorption, however this process is extremely complicated and highly dependent on the characteristics of the metals and electrolyte (Iroha & James, 2019).
In addition, the absence of defined recycling guidelines and procedures has made it difficult to recycle old medications. There are standards for disposing of outdated medications in homes but incinerating them is the only safe way to remove these chemicals which poses concerns to the environment as well (Luo et al., 2021).
There have been reports of metamizole sodium being used as a corrosion inhibitor for carbons steel in 1M hydrochloric acid solution (Salem et al., 2022) and of caffein being successfully used as a green corrosion inhibitor for copper in 0.1M aerated sulfuric acid solution medium (Souza et al., 2012). However, there have been no reports on the possible synergistic relation between these two substances. The aim of this work is to evaluate the inhibition efficiency of the expired Quarelin drug, which contains metamizole sodium, caffein and drotaverine hydrochloride (Figure 1) as active substances. The presence of multiple double bonds, sulphur oxygen, nitrogen as well as multiple aromatic cycles shows the multiple adsorption sites through both chemisorption and physisorption. Expired drugs are considered eco-friendly, nontoxic, and non-bioaccumulative which makes Quarelin a good potential green corrosion inhibitor.

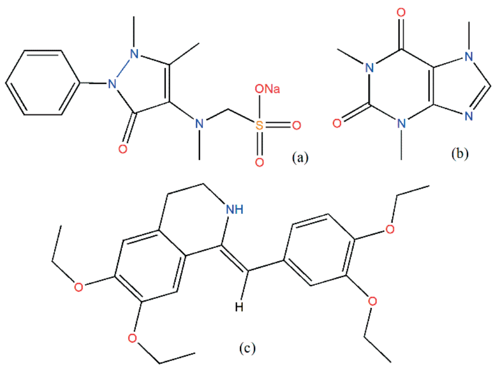

Figure 1. Chemical structure of metamizole sodium (a), caffeine (b), drotaverine hydrochloride (c)

MATERIALS AND METHODS

Expired Quareline since 2021 has been used in this study. It is a pain medication often used in the case of headaches. According to the drug insert one Quarelin tablet contains 400 mg metamizole sodium (an analgesic substance), 40 mg drotaverine hydrochloride (a spasmolytic substance) and 60 mg caffein as active substances. The drug also contains several excipients such as cornstarch, polyvidone, microcrystalline cellulose, magnesium stearate and talc. In this study three concentrations of expired Quarelin were used and the active substance quantities are presented in Table 1.

Table 1. Active substance quantities

Quarelin conc. (ppm)	Metamizole sodium (mg)	Drotaverine hydrochloride (mg)	Caffeine (mg)
200	8	0.8	1.2
250	10	1	1.5
300	12	1.2	1.8

For the experiments coupon of mild steel were used with the dimension of 25 mm x 25 mm x 0.01 mm. Before the coupons were immersed in the acidic media ($HCl:H_2O$ 1:1, 5.6M) the surface was cleaned, polished with emery sheets, washed with ethanol and dried.
The easiest and cost-efficient method of calculating inhibitor efficiency is the weight loss method, in which the samples are initially weighted, immersed in the acidic media containing different inhibitor concentration for a predetermined time, taken out washed dried and weighted again. For this study, concentrations of 200, 250, 300 ppm of expired Quarelin were used and the immersion time was 8h. Every 2h the coupons were removed from the pickling solution, rinsed with water to remove the corrosion products, dried with hot air and weighted in order to observe the evolution of mass. With the help of this experimental data corrosion rate and inhibitor efficiency calculation were carried out by using Eq. (1) and Eq. (2):

$$CR = \frac{\Delta m}{tS} \quad (1)$$

$$IE_{WL} = \frac{CR_B - CR_I}{CR_B} \, x \, 100 \quad (2)$$

where:
- Δm is the mass loss difference (g),
- t is the time of immersion (h),
- S the surface of the coupon (cm^2),
- CR_B/CR_I the corrosion rate in the absence/presence of the inhibitor (g/cm^{2}h).

The electrochemical system used was a three-cell electrode in which 100 mL of electrolyte solution was used. Working MS electrodes were prepared prior to each experiment by abrading with 1200 emery paper, introduced in an ultrasonic bath in ethanol and dried. As an auxiliary electrode platinum was used and the reference electrode was Ag/AgCl.

Electrochemical impedance spectroscopy (EIS) was carried out with a OrigaFlex 500 potentiostat interfaced with a computer using the OrigaMaster5 software for data acquisition and analysis. The EIS spectra were drawn at a frequency range of 10 kHz to 10 mHz, 5 per decade with an AC amplitude of ± 10 mV. The inhibition efficiency (IE_{eis}) was calculated using Eq. (3) from the polarization resistance determined from the Nyquist plots.

$$IE_{EIS} = \frac{R_p - R_p^B}{R_p} \ x\ 100 \quad (3)$$

where:
- R_p and R_p^B are the polarization resistance with and without the inhibitor present.

Potentiodynamic polarization (PDP) curves were drawn from -500 mV to +500mV vs the corrosion potential. In this case the inhibitor efficiency was calculate with Eq. (4).

$$IE_{Taf} = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \ x\ 100 \quad (4)$$

where:
- I_{corr} and $I_{corr(inh)}$ are the corrosion currents in the absence/presence of the inhibitor.

RESULTS AND DISCUSSIONS

The wight loss methos can be used for any metal or alloy that is readily available for purchase, and it is an extremely flexible method of corrosion monitoring. Table 2 shows the change in weight loss between each measurement while Figure 2 shows the corrosion rate evolution.

Table 2. Weight loss experimental data for MS immersed in HCl with different concentrations of expired Quarelin

Time [h]	Expired Quarelin concentration [ppm]			
	Blank	200	250	300
0	4.9574	4.9345	5.0687	5.0489
2	4.9250	4.9136	5.0506	5.0372
4	4.8898	4.8915	5.0332	5.0246
6	4.8607	4.8747	5.0206	5.0124
8	4.8404	4.8664	5.0181	5.0069
IE_{WL} %	-	**38.83**	**51.18**	**63.81**

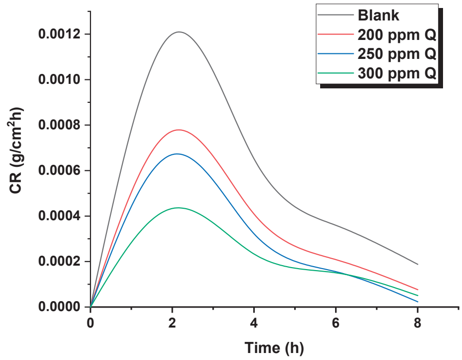

Figure 2. Corrosion rate evolution

The highest inhibitor efficiency was obtained at 300 ppm inhibitor concentration. The reason for this could be that the inhibitor molecules have adhered to the surface of the MS, delaying the metal's breakdown in the corrosive solution. Moreover, the heteroatoms in the molecule enhanced corrosion resistance and facilitated adsorption to the metal surface as other studies have mentioned (Salem et al., 2022).

After the inhibitor has been consumed due to the electrochemical reactions that take place at the metal surface and the repeated batched pickled during and industrial process, the corrosion rate starts to increase. Such increase cannot be seen in the case of this experiment. Further investigations should be carried out with bigger time frames in mind.

The Nyquist diagrams for MS in hydrochloric acid 5.6M with different concentration of expired Quarelin drug are shown in Figure 3 and the equivalent circuit obtained by fitting the EIS data is presented in Figure 4.

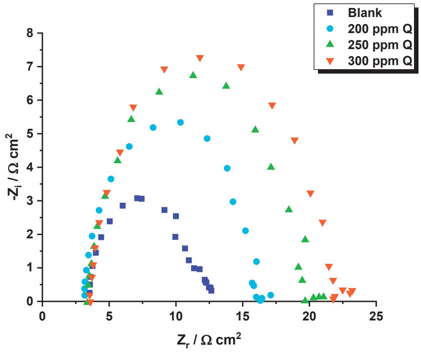

Figure 3. Nyquist plots for MS immersed in HCl solution with different expired Quarelin concentrations

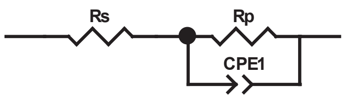

Figure 4. Equivalent circuit used for fitting EIS data

This circuit is composed of a resistance representing the solution (R_s), the polarization resistance (R_p) and a constant phase element (CPE) used instead of a capacitor (C_{dl}) for a better fitting with the help of ZView 3.0 software. The values for the double layer capacitor (C_{dl}) are derived from CPE parameters and were calculated with Eq. (5) and Eq. (6) as previously described by Brug et al. (1984).

$$Z_{CPE} = [Y(j\omega)^n]^{-1} \quad (5)$$

where: ω = 2πf the angular frequency, j = √(-1) the imaginary unit, Y is the magnitude of the CPE and n is a fitting parameter with values between 0 and 1, which measures the element deviation from the ideal capacitive behavior (in the case of n = 1)

$$C_{dl} = (R^{1-n}Y)^{1/n} \quad (6)$$

Using the potentiodynamic polarization (PDP) method, additional electrochemical evaluation of the corrosion of the MS surface in 5.6M HCl with and without expired Quarelin dosage was performed, as illustrated in Figure 5.

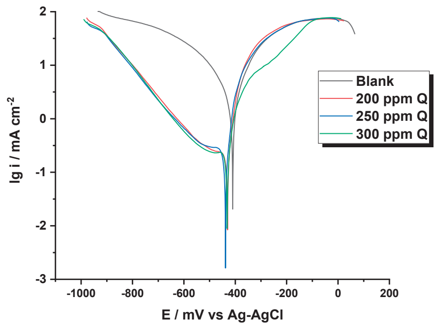

Figure 5. PDP curves for MS in HCl solution with different expired Quarelin concentrations

Table 3 displays the electrochemical parameters for MS immersed in HCl solution when expired Quarelin is added as a green corrosion inhibitor. Calculating the inhibitor efficiency, it is clear that this parameter rises as the concentration of the inhibitor rises, matching the general pattern of most green corrosion inhibitors.

The parameters determined by the Tafel method such as i_{corr}, E_{corr}, β_a, β_c and IE_{Taf} are included in Table 4. The values show that the presence of the inhibitor reduces the corrosion current from 8.86 mA, solution with no inhibitor, to 0.62 mA for the best inhibitor concentration (300 ppm). This further confirms that the inhibitor efficiency of this expired drug is dependent on the concentration used.

Table 3. Electrochemical parameters for MS in HCl solution using expired Quarelin as corrosion inhibitor at different concentrations

C (ppm)	R_s (Ωcm^2)	R_p (Ωcm^2)	CPE ($\mu F s^{n-1} cm^{-2}$)	n	C_{dl} ($\mu F cm^{-2}$)	IE_{EIS} (%)
Blank	2.975	8.119	875.22	0.7403	1964.626	-
200	3.037	13.46	273.44	0.8623	101.461	39.680
250	3.302	16.44	266.98	0.8417	129.273	50.614
300	3.506	21.81	242.62	0.8454	116.377	62.774

Table 4. Electrochemical parameters determined by Tafel method for MS in HCl solution with different expired Quarelin concentrations

C (ppm)	E_{corr} (mV vs. Ag/AgCl)	i_{corr} (mA/cm^2)	$\lvert\beta_C\rvert$ (mV/dec)	β_a (mV/dec)	IE_{Taf} (%)
Blank	-409.85	8.868	328.8	244.6	-
200	-430.13	4.983	319.7	28.2	43.815
250	-436.71	3.768	171.2	18.3	57.514
300	-431.17	2.667	174.1	15.5	69.929

In acidic liquids, there are two different kinds of electrochemical processes: cathodic and anodic. In the former, metal ions in the electrolyte undergo a transition, whereas in the latter, hydrogen ions are released to produce hydrogen gas or decrease oxygen. As a result, the inhibitor is classified as either a mixed type of inhibitor since it affects both processes and as anodic/cathodic type inhibitor because it affects just one of these two processes (Lavanya & Machado, 2024). The Tafel slopes (β_a and β_c) change with the change in inhibitor concentration, both currents decreasing with the increase in inhibitor concentration. This means that expired Quarelin is acting as a mixed type of inhibitor in this case, fact also supported by the change of the corrosion potential (E_{corr}). When the change in value of this parameter is greater than 85 mV it can be classified as a cathodic or anodic type inhibitor (Musa et al., 2012). The largest displacement of corrosion potential presented in this research is approximately 27 mV, showing that expired Quarelin affects both reactions.

The optimal inhibitor concentration for MS immersion in 5.6 M hydrochloric acid, according to all research techniques, the maximum concentration tested, 300 ppm. Even though there is a difference up to 10 percentage points when it comes the different ways of calculating the inhibitor efficiency, the interpretation of the physical phenomena is the same, increasing the inhibitor concentration means increasing its efficiency.

Comparing these results with the already existing research of the inhibition efficiency of metamizole sodium (Salem et al., 2022) and caffein (Souza et al., 2012), it can be said they are comparable in terms of inhibitor efficiency. Combining these active substances did not increase the inhibitor efficiency in a significant way as reported in cases of other synergistic relations between compounds (Wang et al., 2023). However this research has focused on the industrial conditions of acid pickling using a more concentrated acidic solution and the results are promising from an industry perspective.

CONCLUSIONS

Hazardous materials such as used pickling solutions and expired pharmaceuticals must be managed and recycled in today's society. One solution for this problem can be expired medications such as Quarelin which was effectively used in this work as a corrosion inhibitor for mild steel immersed in highly concentrated hydrochloric acid. Results have shown that the best inhibition was obtained at 300 ppm concentration.

Electrochemical tests revealed that the efficiency of corrosion inhibition increases with an increase in inhibitor concentration and PDP results demonstrated that expired Quarelin acts as a mixed type of inhibitor. Because the three active ingredients of expired Quarelin are constituted of polar groups, their adsorption on the metal surface serves as the primary mechanism by which the expired medicine inhibits corrosion.

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