

Expired Domestic Drug - Paracetamol - as Corrosion Inhibitor for Carbon Steel in Acid Media

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Abstract. In this paper, the possibility to use expired drug paracetamol as corrosion inhibitor for carbon steel in acid solutions has been investigated. 0.5 mol L⁻¹ sulfuric acid and 1 mol L⁻¹ hydrochloric acid have been used as corrosive media in the experimental studies. Electrochemical behaviour of paracetamol and its stability in test solutions have been examined by cyclic voltammetry. Further, the inhibitory effect has been studied by several methods: linear polarization, electrochemical impedance spectroscopy and chronoamperometry. As well, Tafel plots method was used in order to determine kinetic parameters of the corrosion process.

1. Introduction

In recent years, the use of expired drugs as corrosion inhibitors for different metals and alloys represents a new challenge in terms of recovering the active compounds from pharmaceutical drugs existing in increased amounts, both in households and pharmacies, hospitals, etc. The properties that recommend the use of active substances from expired drugs in corrosion prevention are high molecular size and the presence of hetero atoms like nitrogen, sulphur, oxygen and π bonds in their structures [1]. Also, most of these compounds are high soluble in aqueous solutions and stable in different aggressive environments [2]. It is reported that after the expiration date, for more than 90% of the drugs, the active constituents do not degrade and maintain their stability for a long period [3,4]. Based on presented considerations, expired drugs are safe to be used and because of their non-toxic characteristics and negligible negative impact on the environment, these commercial pharmaceutical products seem to be potential candidates to replace traditional toxic chemical corrosion inhibitors [1]. Moreover, the expired drugs were included in *green corrosion inhibitors* family.

In the context of an increasing amount of expired drugs, their use as corrosion inhibitors can not only reduce environmental pollution, but can also lead to a reduction of disposal and degradation costs of these expired drugs.

The use of expired paracetamol as a corrosion inhibitor for metals and alloys in acidic media, was mentioned for the first time in 2012, but until now no complete experimental studies have been performed [5].

In this paper, the possibility to use paracetamol (PCTM) drug as corrosion inhibitor for carbon steel in acid solution was investigated. 0.5 mol L⁻¹ sulfuric acid and 1 mol L⁻¹ hydrochloric acid have been used as corrosive media in the experimental tests. The electrochemical behaviour of paracetamol and its stability in test solutions have been examined by cyclic voltammetry. Further, the inhibitory effect



has been studied by linear polarization, electrochemical impedance spectroscopy and chronoamperometry. Tafel plots method was used in order to determine kinetic parameters.

2. Experimental part

2.1. Materials

In order to study the corrosion behaviour of carbon steel in acid media (H_2SO_4 and HCl) and the inhibitory effect of commercial paracetamol expired drug, different concentrations of organic compound between 10^{-6} and 10^{-3} mol L^{-1} have been used. The corrosive media was prepared from sulfuric acid (Merck, p.a. 95-97%) and hydrochloric acid (Merck, p.a. 37%). Paracetamol ($\text{C}_8\text{H}_9\text{NO}_2$) IUPAC name is N-(4-hydroxyphenyl)acetamide and its chemical structure is presented in figure 1.

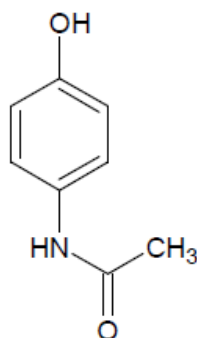


Figure 1. Paracetamol chemical structure.

The corrosion test electrode was a cylindrical disc cut from a carbon steel sample type OL52-3k with the elemental composition presented in table 1.

Table 1. Elemental composition of the carbon steel samples.

Element	Fe	C	Si	Mn	P	S	Al	Cu
wt%	98.58	0.196	0.034	0.896	0.013	0.037	0.023	0.125

2.2. Methods

Electrochemical behaviour of paracetamol expired drug in both acidic media has been studied by cyclic voltammetry (CV) on platinum electrode. Linear polarization (LV) (Tafel method), chronoamperometry and electrochemical impedance spectroscopy (EIS) were carried out in order to emphasize the inhibitive properties of paracetamol on carbon steel corrosion process. The experimental set-up consisted of a conventional three-electrode typical glass cell of 100 mL and a Biologic SP150 potentiostat/galvanostat. The potentiostat was connected with two graphite counter electrodes, a carbon steel working electrode with 0.8 cm^2 surface area and the saturated Ag/AgCl reference electrode. All potentials are referred to this electrode ($E_{\text{Ag}/\text{AgCl}} = 0.197 \text{ V/NHE}$). The working electrode surface was polished before each experiment with different grit abrasive paper, cleaned in ultrasonic bath and rinsed with distilled water. The electrode potential was stabilized for 60 minutes before each measurement.

Cyclic voltammograms (CVs) have been recorded at different scan rates, between 5 and 500 mV s^{-1} while linear polarization (LVs) only at low scan rate (1 mV s^{-1}) in order to ensure quasi-stationary conditions.

EIS studies were performed using the SP-150 impedance module, in frequency range 0.1 Hz - 100 kHz and alternative voltage amplitude of 10 mV . For each spectrum, 60 points were collected, with a logarithmic distribution of 10 points per decade. The experimental EIS data have been fitted to the electrical equivalent circuits (EEC) by CNLS Levenberg – Marquardt method using ZView – Scribner Associates Inc. software.

3. Results and discussion

3.1. Cyclic voltammetry

In order to notice the electrochemical behaviour of paracetamol and obtain preliminary information about how this drug can influence the corrosion process of carbon steel, CVs were recorded with different scan rates on platinum electrode in acid solutions without and with all paracetamol concentrations used in experimental studies.

In figure 2, the CVs recorded at 10 mV s^{-1} scan rate are depicted. The base curve obtained in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and $1 \text{ mol L}^{-1} \text{ HCl}$ solutions presents the characteristics of polarization curves drawn on platinum in acid solutions. On the CVs recorded in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution without paracetamol (Figure 2a) at anodic polarization starting from open circuit potential (OCP) only the curve corresponding to oxygen evolution reaction (OER) can be observed. On the backward scan, a cathodic peak appears at about $+0.50 \text{ V}$, which can be associated with the reduction of superficial platinum oxides formed on the electrode surface concomitant with the reduction of superficial remanent oxygen. At more negative potentials (-0.25 V) the hydrogen evolution reaction (HER) can be observed. Supplementary, on CVs recorded in $1 \text{ mol L}^{-1} \text{ HCl}$ solution (Figure 2b) on anodic branch at $+1.35 \text{ V}$ a pronounced peak corresponding to chlorine evolution reaction on platinum electrode can be distinguished.

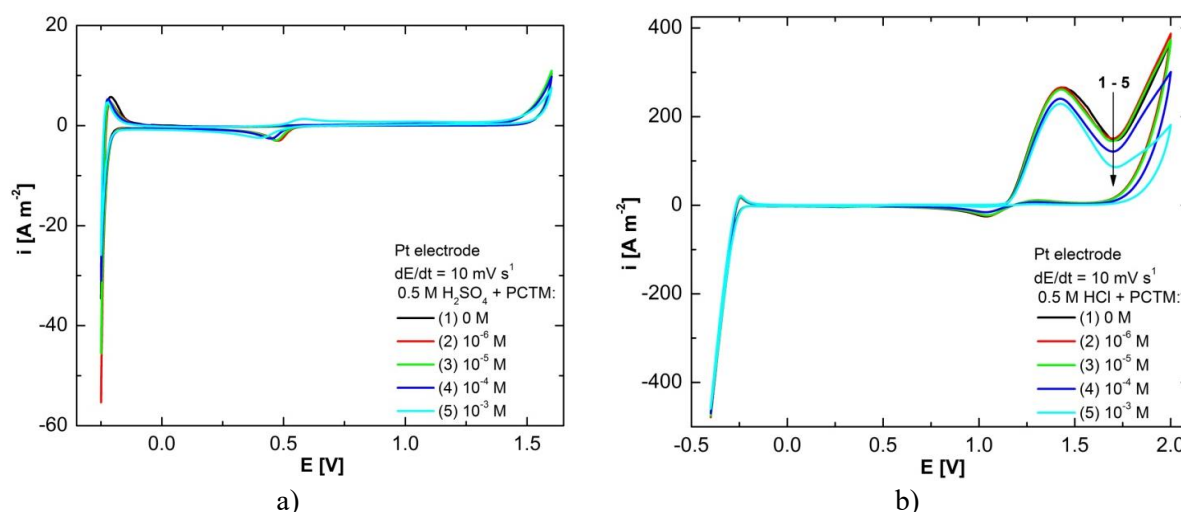


Figure 2. CVs recorded on Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ (a) and in 1 M HCl (b) in the absence/presence of paracetamol at 10 mV s^{-1} scan rate.

The effect of adding expired paracetamol in the $1 \text{ mol L}^{-1} \text{ HCl}$ electrolyte solution leads to a current decrease of chlorine evolution reaction and a shift of OER potential towards more positive values. No supplementary anodic or cathodic peaks characteristic for expired paracetamol oxidation or reduction processes was recorded on CVs. One can conclude this compound is stable for all added concentrations in $1 \text{ mol L}^{-1} \text{ HCl}$ solution.

On CVs plotted in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with paracetamol, on anodic branch at approximate $+0.6 \text{ V}$ a small intensity oxidation peak assigned with the organic compound oxidation can be seen. This is most pronounced for $10^{-3} \text{ mol L}^{-1}$ paracetamol (the higher concentration used in the corrosion tests) added in the solution. It can be assumed that paracetamol oxidation process is reversible because in the cathodic domain the reduction peak is enhanced.

In order to identify how paracetamol concentration influences the cathodic HER and anodic OER, polarization curves have been recorded separately in both acids at higher sensitivity (5 mV s^{-1}), in cathodic domain as well as in anodic one (Figures 3 and 4).

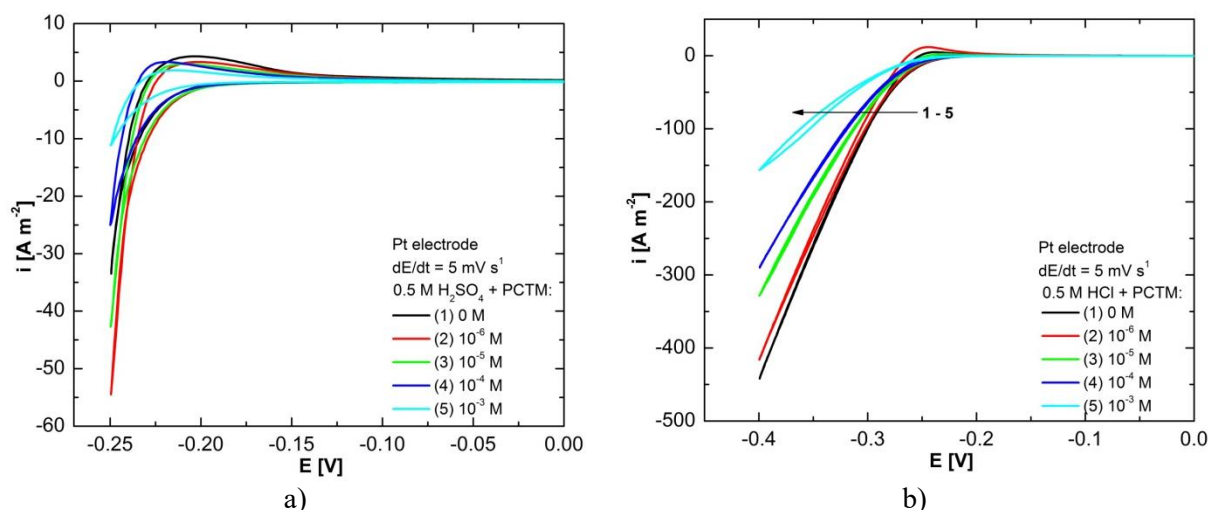


Figure 3. CVs for cathodic polarization recorded on Pt electrode in 0.5 M H_2SO_4 (a) and in 1 M HCl (b) in the absence/presence of paracetamol at 5 mV s^{-1} scan rate.

According to figure 3, HER is inhibited due to the adsorption on platinum electrode of paracetamol molecules; the effect is more evident when 1 mol L^{-1} HCl is used as a corrosive agent.

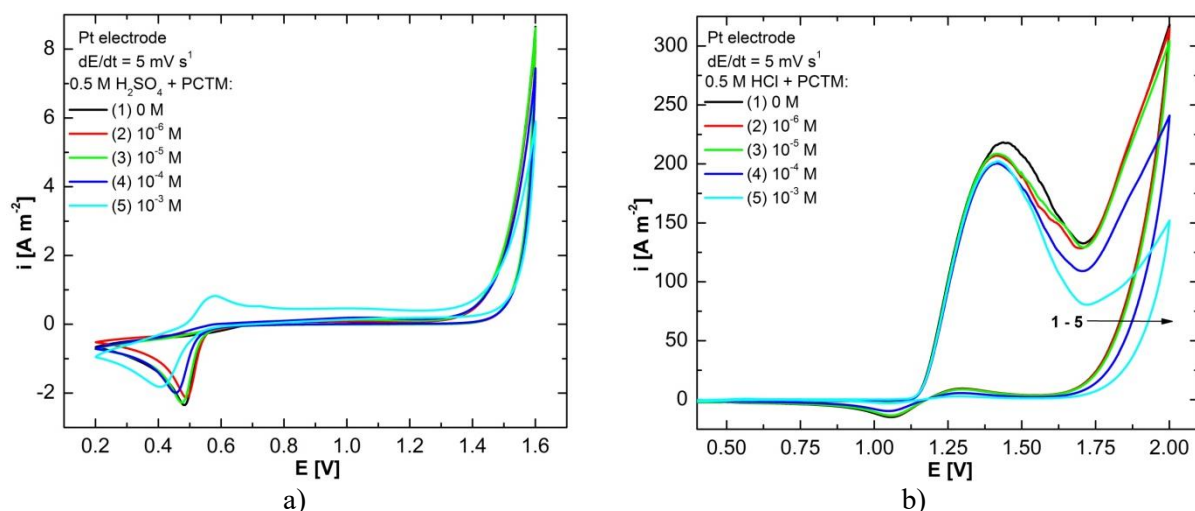


Figure 4. CVs for anodic polarization recorded on Pt electrode in 0.5 M H_2SO_4 (a) and in 1 M HCl (b) in the absence/presence of paracetamol at 5 mV s^{-1} scan rate.

The anodic CVs recorded on Pt electrode in 1 mol L^{-1} HCl solution (Figure 4b) highlight an inhibition of both anodic OER and chlorine evolution reaction processes, stronger effect is noticeable as paracetamol concentration increases in the electrolyte solution. OER process is not influenced by the presences of the expired drug in 0.5 mol L^{-1} H_2SO_4 solution (Figure 4a).

However, as previously noted, in 0.5 mol L^{-1} H_2SO_4 solution paracetamol is oxidized, the peak corresponding to this process being recorded on the CVs anodic plateau at $+0.55 \text{ V}$. Paracetamol electrochemical oxidation in acidic media proceeds in two steps according to the mechanism shown in figure 5 [6,7]. In first step, by releasing of two electrons and two protons paracetamol (N-(4-hydroxyphenyl)acetamide) is oxidized to N-acetyl-p-benzoquinone-imine and in the second step, this compound will hydrolyze. Although it was initially assumed that paracetamol oxidation process is

irreversible, the shape of the corresponding cathode peak recorded on CVs at +0.45 V and literature data shows that this process is cvasi-reversible [7].

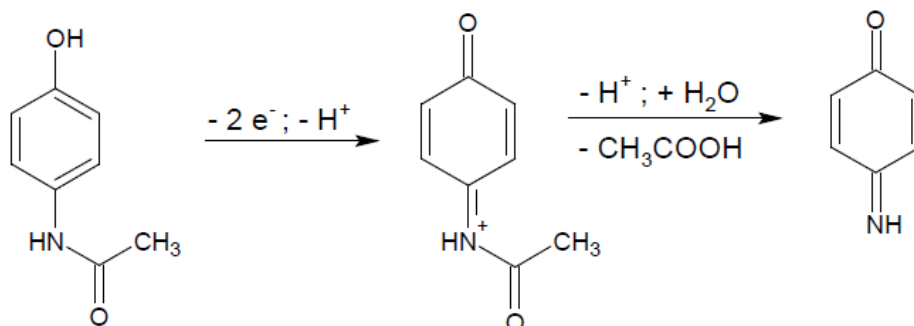


Figure 5. Paracetamol electrooxidation mechanism in 0.5 M H₂SO₄.

3.2. Linear voltammetry

LVs shown in figure 6 were recorded at low scan rate, (1 mV s⁻¹) in the range ± 250 mV/OCP, at 25°C on OL52-3k electrodes in aggressive solutions (0.5 mol L⁻¹ H₂SO₄ and in 1 mol L⁻¹ HCl) in the absence and presence of paracetamol different concentrations (10⁻⁶-10⁻³ mol L⁻¹). LVs were plotted after removing dissolved oxygen from the acid solutions to avoid secondary reactions that may occur on the electrode surface and after 60 minutes conditioning at OCP in order to reach a quasi-equilibrium state at the interface metal/electrolyte solution.

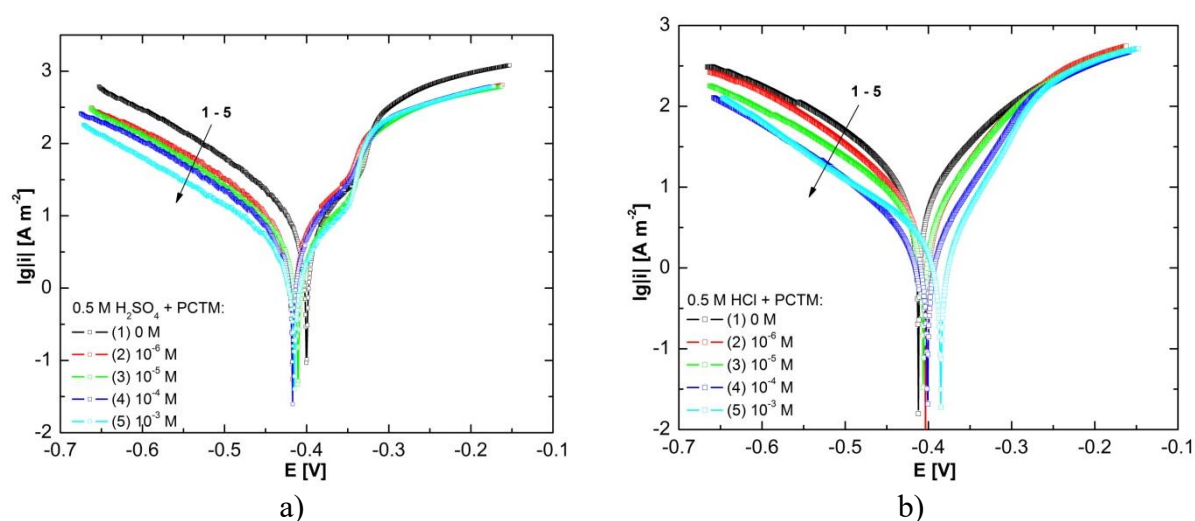


Figure 6. Tafel curves on OL52-3k electrodes in 0.5 M H₂SO₄ (a) and in 1 M HCl (b) in the absence/presence of paracetamol expired drug, scan rate: 1 mV s⁻¹.

Polarization parameters for OL52-3k corrosion in both acid media, 0.5 mol L⁻¹ H₂SO₄ and 1 mol L⁻¹ HCl, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (b_c and b_a), polarization resistance (R_p) and corrosion rate (v_{corr}) were determined extrapolating the potentiodynamic curves. The inhibition efficiency (IE) (Equation 1) and surface coverage degree (θ) with the paracetamol molecules have been calculated and the results are gathered in table 1.

$$IE(\%) = \left(\frac{i_{\text{corr}}^o - i_{\text{corr}}^{\text{inh}}}{i_{\text{corr}}^o} \right) \cdot 100 \quad (1)$$

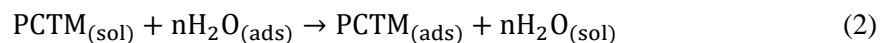
where i_{corr}^o and $i_{\text{corr}}^{\text{inh}}$ are the uninhibited, respectively inhibited corrosion current densities.

Table 2. Polarization parameters for OL52-3k corrosion process in acid solutions.

Solution	PCTM conc (M)	E_{corr} (mV)	i_{corr} (mA cm ⁻²)	$-b_c$ (mV)	b_a (mV)	R_p (Ω)	v_{corr} (mm/year)	IE (%)	θ
H ₂ SO ₄	0	-398	3.31	197	126	6.72	51.0	-	-
	10 ⁻⁶	-419	1.91	181	114	16.9	29.4	42.3	0.42
	10 ⁻⁵	-413	0.72	164	102	19.4	11.5	78.3	0.78
	10 ⁻⁴	-417	0.30	154	89	21.9	4.76	90.9	0.91
	10 ⁻³	-414	0.21	146	77	28.2	6.38	93.7	0.94
HCl	0	-410	1.30	216	165	21.7	27.1	-	-
	10 ⁻⁶	-404	0.84	190	130	29.8	17.1	35.4	0.35
	10 ⁻⁵	405	0.43	182	112	33.0	9.43	67.1	0.67
	10 ⁻⁴	-400	0.31	148	77	50.8	3.16	76.5	0.77
	10 ⁻³	-384	0.19	138	63	54.6	2.10	85.8	0.86

From the results presented in table 2, one can see that OL52-3k corrosion rate is diminished by increasing the paracetamol concentration added in aggressive solution, maximum inhibition efficiency values of 86% in HCl and 94% in H₂SO₄ solutions were obtained for 10⁻³ mol L⁻¹ expired drug added in acid solution. The presence of paracetamol and its oxidation products cause significant changes of the anodic and cathodic Tafel slopes. This suggest paracetamol can be classified as a mixed-type inhibitor.

OL52-3k corrosion process mitigation in the presence of paracetamol can be attributed to its adsorption on the metal surface blocking thus the active sites. In the acid aqueous solutions, the adsorption of expired drug molecules can be considered as a quasi-substitution process between the paracetamol from the aqueous phase and water molecules at the metal surface, according to equation 2 [8,9]:



where PCTM_(sol) and PCTM_(ads) are paracetamol molecules in the acid aqueous solutions, respectively in adsorbed state and n is the water molecules number replaced by PCTM.

3.3. Electrochemical impedance spectroscopy.

Figures 7 and 8 illustrate EIS spectra expressed as Nyquist and Bode plots recorded for OL52-3k corrosion in 0.5 mol L⁻¹ H₂SO₄ and 1 mol L⁻¹ HCl solutions in the absence and presence of paracetamol different concentrations used in experimental studies.

On Nyquist diagrams, OL52-3k corrosion process is described by a single semi-circle corresponding to a single charge transfer process during carbon steel dissolution in acid media. As can be seen, each paracetamol concentration added in aggressive solutions has a distinctive semicircular graph in Nyquist spectra. The semicircle diameter can be associated with charge transfer resistance and also, with the corrosion rate. The semicircle diameter increases substantially with increase the paracetamol concentration added in test solutions, which means that the OL52-3k corrosion rate decreases. In other words, the inhibition efficiency of paracetamol is increasing in the same way [10,11].

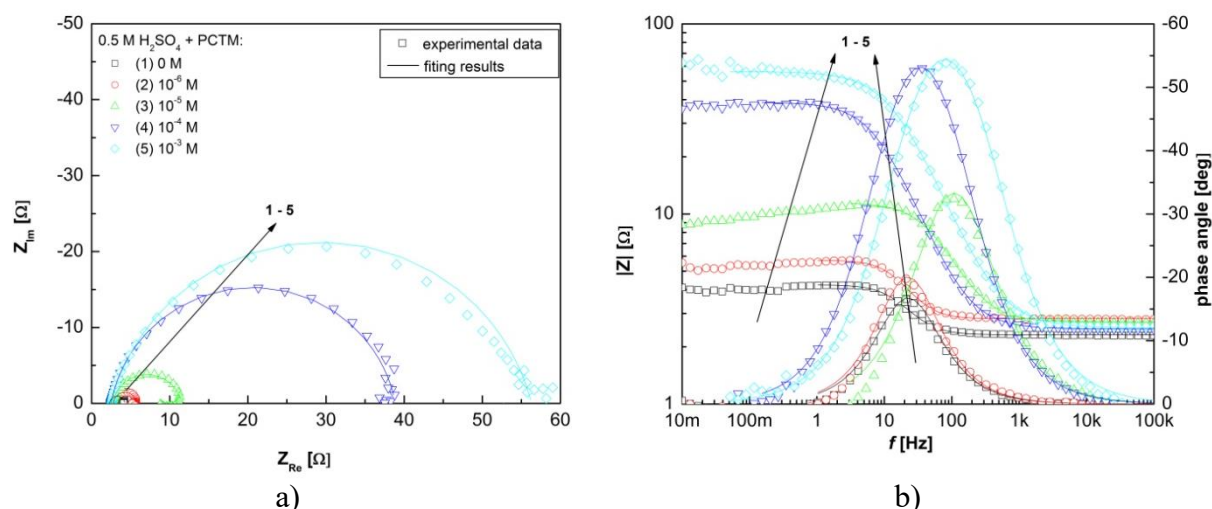


Figure 7. Nyquist (a) and Bode (b) plots on OL 52-3k in 0.5 M H₂SO₄ without and with different concentrations of paracetamol expired drug.

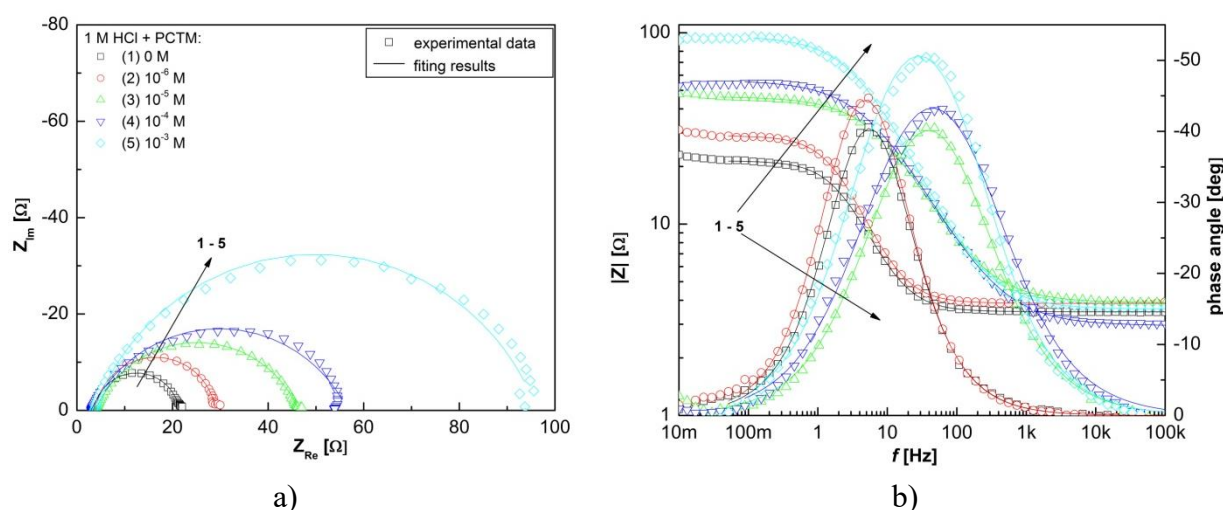


Figure 8. Nyquist (a) and Bode (b) plots on OL 52-3k in 1 M HCl without and with different concentrations of paracetamol expired drug.

For a precise corrosion process description, the experimental EIS data were fitted using the electrical equivalent circuit (EEC) shown in figure 9, characteristic for carbon steel corrosion in acid media, using a complex non-linear least squares (CNLS) procedure [10-12].

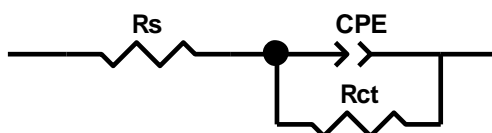


Figure 9. EEC for modeling OL52-3k corrosion in acid solution.

The EEC consists of a solution resistance R_s in series with a parallel connection of a constant phase element (CPE) accounting for the double layer capacity and a charge transfer resistance R_{ct} . The resistance R_s represents the uncompensated solution resistance. In EEC used for modelling OL52-3k corrosion process the ideal capacitor characterized by double layer capacity (C_{dl}) is replaced by a constant phase element (CPE) because it represents more precisely the real electrochemical systems

behaviour (depressed loops in EIS diagrams). The impedance of *CPE* element is described by the Equation 3 [13]:

$$Z_{CPE} = 1/T(j\omega)^n \quad (3)$$

where T is a parameter proportional with double layer capacity, n is an exponent ranged between 0 and 1 which describes CPE angle.

The fitting results are depicted as continuous line in EIS spectra from figures 7 and 8 and the obtained values of the EEC elements are presented in table 3 for OL52-3k samples corrosion in both acid media. Also, double layer capacity values (C_{dl}) were calculated using Equation 4 [13]:

$$C_{dl} = T^{1/n} \left(\frac{1}{R_s} - \frac{1}{R_{ct}} \right)^{\frac{n-1}{n}} \quad (4)$$

Expired paracetamol inhibition efficiency values were calculated from the charge transfer resistance values (R_{ct}) from table 3 according to the Equation 5 [11,14]:

$$IE(\%) = \frac{(1/R_{ct}^0) - (1/R_{ct}^i)}{(1/R_{ct}^0)} \cdot 100 \quad (5)$$

where R_{ct}^0 and R_{ct}^i are the charge transfer resistance in acid solutions without respectively with different paracetamol concentrations.

Table 3. Calculated values of the EEC elements for OL52-3k corrosion in acid solutions.

Solution	PCTM conc (M)	R_s ($\Omega \text{ cm}^2$)	$T \cdot 10^4$ ($\text{F cm}^{-2} \text{ s}^{n-1}$)	n	R_{ct} ($\Omega \text{ cm}^2$)	$C_{dl} \cdot 10^5$ (F cm^{-2})	Chi^2 $\cdot 10^3$	IE (%)	θ
H_2SO_4	0	2.32	5.23	0.94	1.93	33.1	2.4	-	-
	10^{-6}	2.82	3.37	0.91	3.30	17.2	1.5	41.6	0.42
	10^{-5}	2.69	1.64	0.91	8.80	8.27	4.2	78.1	0.78
	10^{-4}	2.48	0.91	0.89	35.4	4.45	1.4	94.6	0.95
	10^{-3}	2.52	0.45	0.86	53.8	1.70	3.9	96.4	0.96
HCl	0	3.48	5.51	0.92	14.6	35.7	2.3	-	-
	10^{-6}	3.85	4.72	0.88	23.2	25.9	1.9	37.1	0.37
	10^{-5}	3.88	2.34	0.85	44.5	10.2	0.5	67.3	0.67
	10^{-4}	2.94	1.44	0.80	55.7	4.20	2.2	73.9	0.74
	10^{-3}	3.59	0.99	0.78	95.6	2.59	2.6	84.8	0.85

For a one time constant process, described by EEC from figure 9, R_{ct} value is directly proportional to the corrosion resistance of OL52-3k samples in acid solution. The fitting data from table 3 clearly shows that R_{ct} value increases when increased paracetamol drug amounts in acid solutions, confirming the results obtained in linear polarization experiments. Consecutively with increase of R_{ct} values the C_{dl} values are reduces. The decrease of C_{dl} values is according to the Helmholtz model in which the double layer capacitance is inversely proportional to the surface charges and can result from a decrease in local dielectric constant or an increase in the electric double layer thickness, suggesting that paracetamol molecules are adsorbed at the carbon steel electrode/acid solution interface [11,14]. This means that the paracetamol molecules were adsorbed by the gradual replacement of water on the electrode surface and form an adherent protective film on OL52-3k samples, decreasing the electrochemical dissolution rate for carbon steel in acid media [11,12]. The order of 10^{-3} for chi-square values indicate an excellent correlation between the experimental EIS data and the chosen EEC model values. Also, the inhibition efficiency (IE) increases with the increasing of expired drug concentration added in acid solutions. The inhibitory efficiency values calculated from EIS data (Table 3) are comparable to those obtained in linear polarization studies (Table 2).

3.4. Chronoamperometric studies

Chronoamperometric measurements were carried out in order to further elucidate the comparative corrosion behaviour of the OL52-3k samples in acid solutions without and with different concentrations of paracetamol drug at anodic polarization [15,16]. Current-time (i - t) curves have been recorded for a period of 15 minutes in the case of two different values applied anodic potential, +25 and +250 mV/ E_{corr} for carbon steel samples in all test solution. Figure 10 shows the i - t curves recorded on OL52-3k electrode in 1 mol L⁻¹ HCl solution in the absence and presence of paracetamol.

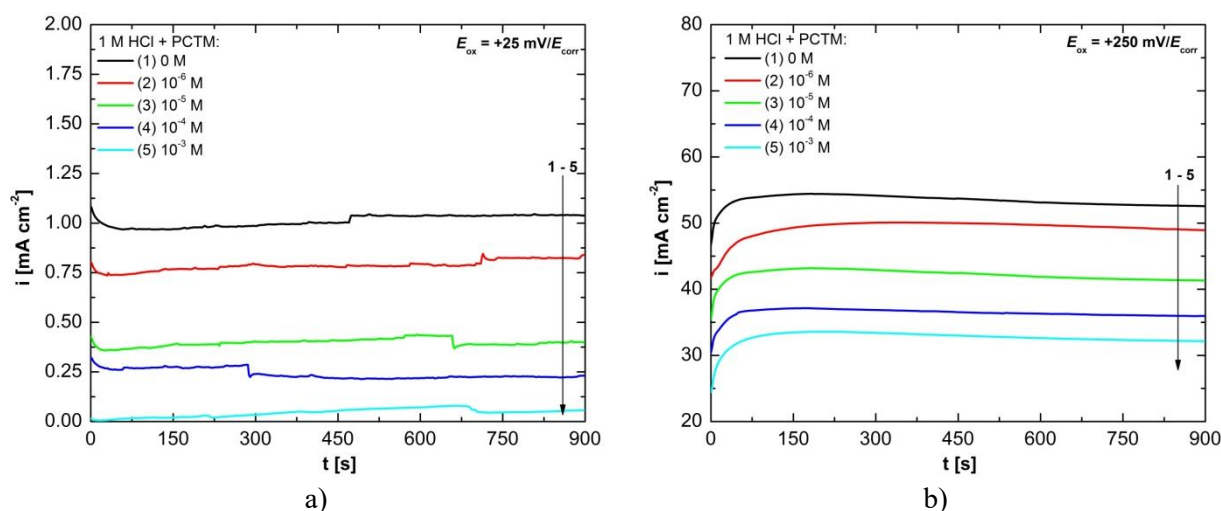


Figure 10. Chronoamperometric measurements recorded at +25 mV/ E_{corr} (a) and +250 mV/ E_{corr} (b) for the anodic oxidation of OL52-3k electrodes in 0.5 M HCl without and with different paracetamol concentrations for 15 min.

Analyzing the graphical i - t results, a common feature of carbon steel electrooxidation at two potential values is the rapid stabilization of current density after about 5 minutes, probably due to the formation and growth of a passive oxide film uniformly distributed on the metal surface [15]. The shape of presented curves indicates a continuous carbon steel oxidation and the current density characteristic of this process is depending on the paracetamol concentration. The current density values recorded after 15 minutes for all chronoamperometric measurements are shown in table 4.

Table 4. Chronoamperometric data for OL52-3k oxidation in test solutions.

PCTM conc (M)	0.5 M H ₂ SO ₄		1 M HCl	
	$E_{\text{ox}} = +25 \text{ mV}/E_{\text{corr}}$	$E_{\text{ox}} = +250 \text{ mV}/E_{\text{corr}}$	$E_{\text{ox}} = +25 \text{ mV}/E_{\text{corr}}$	$E_{\text{ox}} = +250 \text{ mV}/E_{\text{corr}}$
	i (mA cm ²)			
0	6.47	78.2	1.04	52.6
10 ⁻⁶	5.41	69.1	0.82	48.8
10 ⁻⁵	3.62	50.3	0.41	41.4
10 ⁻⁴	2.95	47.7	0.22	36.1
10 ⁻³	2.07	43.7	0.06	31.9

In acid solution without expired drug, on the electrode surface, a protective layer based on corrosion products is formed, which provides a partial anticorrosive protection [17]. The current density lower values recorded for the oxidized samples in the acid media with paracetamol are due to the formation of a protective film of organic molecules on the OL52-3k active surface, according to the mechanism described by equation 2 and explained based on EIS data, which prevents or decreases the rate of the carbon steel corrosion.

The current densities values specific for the OL52-3k samples anodic oxidation in 0.5 mol L⁻¹ H₂SO₄ in the absence, respectively presence of paracetamol expired drug, are higher than those recorded in 1 mol L⁻¹ HCl, indicating that the corrosion rate of this carbon steel type is higher in sulfuric acid according to the experimental results obtained in linear polarization method and EIS studies.

4. Conclusions

The presented studies shows excellent inhibition properties of paracetamol expired drug for the corrosion of carbon steel type OL52-3k in 0.5 mol L⁻¹ H₂SO₄ and 1 mol L⁻¹ HCl. The paracetamol concentration added in acid media influences significantly the inhibition efficiency, calculated from Tafel polarization method and confirmed by EIS data. The maximum inhibition efficiency values of 94% in 0.5 mol L⁻¹ H₂SO₄ and 86% in 1 mol L⁻¹ HCl were obtained for 10⁻³ mol L⁻¹ paracetamol concentration added in both acid solutions. Based on the linear polarization results, the expired drug acts predominantly as a mixed-type inhibitor (anodic and cathodic). Cyclic voltammetry studies concluded that the expired paracetamol are electrochemical stable in HCl solution. In H₂SO₄ solution it is oxidized in two steps mechanism according to a quasi-reversible process, the oxidation products formed being adsorbed on the active surface of the samples, contributing to the increase of the inhibitory efficiency. The results show that paracetamol molecules or its oxidation products form a barrier layer on the OL52-3k samples surface by adsorption, thus inhibiting the corrosion process.

5. References

- [1] Singh P, Chauhan DS, Srivastava K, Srivastava V and Quraishi MA 2017 *Int. J. Ind. Chem.* **8** 363-72
- [2] Karthikeyan S, 2016 *Int. J. Chemtech. Res.* **9** 251-9
- [3] Stark G, Fawcett JP and Tucker IG *Pharm. J.* **258** 637-40
- [4] Lyon RC, Taylor JS, Porter DA, Prasanna HR and Hussain AS 2006 *J. Pharm. Sci.* **95** 1549-60
- [5] Vaszilcsin N, Ordodi V and Borza A 2012 *Int. J. Pharm.* **15** 241-4.
- [6] Zidan M, Tee TW, Abdullah AH, Zainal Z and Kheng GJ 2011 *Int. J. Electrochem. Sci.* **6** 279-88
- [7] Nematollahi D, Shayani-Jam H, Alimoradi M and Niroomand S 2009 *Electrochim. Acta* **54** 7407-15
- [8] Dan ML, Vaszilcsin N, Labosel MA and Pancan B, 2014 *Chem. Bull. "POLITEHNICA" Univ. Timisoara* **73** 13-18
- [9] Andreani S, Znini M, Paolini J, Majidi L, Hammouti B, Costa J and Muselli A 2016 *J. Mater. Environ. Sci.* **7** 187-95
- [10] Al-Amiery AA, Kadhum AAH, Kadhum A, Mohamad AB, How CK and Junaedi S 2014 *Materials* **7** 787-804
- [11] Galai M, El Gouri M, Dagdag, El Kacimi Y, Elharfi A and Ebn Touhami M 2016 *J. Mater. Environ. Sci.* **7** 1562-75
- [12] Kadhum AAH, Mohamad AB, Hammed LA, Al-Amiery AA, San NH and Musa AY 2014 *Materials* **7** 4335-48
- [13] Savencu CE, Costea LV, Dan ML and Porojan L 2018 *Int. J. Electrochem. Sci.* **13** 3588-600
- [14] El-Taib Heakal F, Fouda AS and Zahran SS 2015 *Int. J. Electrochem. Sci.* **10** 1595-615
- [15] Porojan L, Savencu CE, Costea LV, Dan ML and Porojan SD 2018 *Int. J. Electrochem. Sci.* **13** 410-23
- [16] Sherif E-SM, Abdo HS and El Abedin SZ 2017 *Int. J. Electrochem. Sci.* **12** 1600-11
- [17] Sherif E-SM 2012 *Int. J. Electrochem. Sci.* **7** 1482-95

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