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Investigation of Inhibition Performance of Epdantoin for Mild Steel Protection in HCl Solution: Electrochemical and Quantum Theoretical Approaches

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Corrosion, Density functional theory, Mild steel, Epdantoin

Abstract: In this study, the application potential of the expired "Epdantoin" drug which includes phenytoin (EP) as the corrosion inhibitor was investigated. For this purpose, the electrochemical impedance spectroscopy measurements and polarization curves were obtained for 168 hours immersion period in 0.5 M HCl in the absence and presence of various concentrations of EP. The experimental results were compared with quantum theoretical parameters in order to present adsorption behavior of EP. The adsorption equilibrium constant and Gibbs free energy were calculated as 5000 M^{-1} and -31,05 kj mol^{-1}, respectively. The detected HOMO and LUMO values were -6.67 eV and -0.72 eV, respectively. Results indicated that EP is a convenient candidate of corrosion inhibitor for mild steel (MS) in HCl medium.

Yumuşak Çeliğin HCl Çözeltisinde Korunması için Epdantoin'in İnhibisyon Performansının Araştırılması: Elektrokimyasal ve Kuantum Teorik Yaklaşımlar

Anahtar Kelimeler
Korozyon, Yoğunluk fonksiyonel teorisi, Yumuşak çelik, Epdantoin

Öz: Bu çalışmada, korozyon inhibitörü olarak fenitoin (EP) içeren son kullanma tarihi geçmiş "Epdantoin" ilacının uygulama potansiyeli araştırıldı. Bu amaçla, çeşitli konsantrasyonlarda EP'nin varlığında ve yokluğunda 0,5 M HCl'de 168 saatlik daldırma süresi boyunca elektrokimyasal empedans spektroskopi ölçümleri ve polarizasyon eğrileri elde edildi. EP'nin adsorpsiyon davranışını göstermek için deneysel sonuçlar kuantum teorik parametrelerle karşılaştırıldı. Adsorpsiyon denge sabiti ve Gibbs serbest enerjisi sırasıyla 5000 M^{-1} ve -31,05 kj mol^{-1} olarak hesaplandı. Tespit edilen HOMO ve LUMO değerleri sırasıyla -6,67 eV ve -0,72 eV dir. Sonuçlar, EP'nin HCl ortamındaki yumuşak çelik (MS) için uygun bir korozyon önleyici aday olduğunu gösterdi.

1. INTRODUCTION

Mild steel (MS) is a low-priced material with good machinability that is used in various industries [1]. Although it has a broad range of uses, corrosion is the main issue that restricts usage [2]. The sensitivity of MS to corrosion has been the subject of extensive research up to the present time. The storage of nutrients in a healthy environment, the pipe systems used in the transfer of fluids, construction equipment, vehicles, buildings made of steel construction, coastal structures, production lines, warehouses made of metal and controlling corrosion in many industrial areas are of great importance in terms of reducing operating costs [3]. At the same time, metal poles and transport systems, whose structure is deteriorated due to corrosion, also pose great risks in terms of occupational safety. The simplest method to minimize or slow down the exposure of metals to corrosion is to provide isolation between the metal and the corrosive environment, such as an acidic, basic, or salty environment, in which the metal is present. This is possible by forming a film layer on the metal or by coating the metal [4]. It is impossible to avoid rusting with perfect effectiveness. However, by using corrosion inhibitors, the rate of corrosion to which the steel is exposed can be reduced or the process can be slowed down. As a result, a high financial advantage can be achieved with a low-cost electrochemical process. For this purpose usage of inhibitor chemicals to prevent corrosion is a very efficient strategy [5-7].

Chemicals known as corrosion inhibitors lessen the interaction between the metallic surface and the corrosive environment, hence lowering the vulnerability of metals to corrosion. The inorganic salts such as Arsenic acid and arsenate acids, have been used as inhibitors in the past. Unfortunatelly, they caused environmental damage due to the ecological side effects. But in this century new high-efficiency non-toxic chemicals have been offered which strongly cover the surface, resulting in improved efficiency while also being environmentally safe. The researchers' interest has recently increased to green/non-toxic inhibitor molecules [8-12].

Chemical drugs are increasingly being used as non-toxic organic inhibitors. The inhibitor prices are quite high, which has led researchers to investigate waste drugs applications that have recently expired. In this manner, the harm to the environment caused by disposing of expired medicine is avoided, and a low-cost organic inhibitor is acquired [13-16].

Despite the growing number of studies in the field of organic inhibitor corrosion prevention in scientific world, environmentally friendly corrosion prevention approaches have yet to gain general use in the industry. This demonstrates the need to improve studies on a practical basis [17-19].

In one of the studies [20], the drug with active ingredient Rosuvastatin used in the treatment of cholesterol, its behavior in 0.1 M HCl solution was examined. As a result, corrosion was prevented at 92% efficiency on MS. In another study, it was revealed that the effectiveness of the drug with irbesartan active ingredient in preventing corrosion formation in 1 M HCl solution is 94%. In the study by Zadeh et al. [5], the anti-corrosive activity of the drug with Bupropion active ingredient on carbon steel in HCl and H_2SO_4 solution was examined with the help of Fourier transform infrared (FTIR) Spectroscopy device, and the percent effectiveness was reached 88%. Weigh loss and electrochemical methods were used to investigate the inhibitory effect of an analyzed expired Ambroxol medicine on the corrosion of MS in acid media by Geethamani and Kasthuri. The highest IE observed was 94.03% with a amount of 9.0% inhibitor [21]. Singh et al. [22] modified expired Dapsone drug via chemical reaction with benzaldehyde; salicylaldehyde and they produced new Schiff bases. They researched the corrosion inhibiton performance of the Schiff bases for MS in sulphuric acid solution. Schiff base 1 (Dapsone-benzaldehyde) and Schiff base 2 (Dapsone salicylaldehyde) exhibited 95.67% and 94.23% inhibition efficiency at a concentration of 0.219 mM respectively. Addition of 0.602 mM KI further increased their efficiency up to 99.03% and 97.98% respectively. The corrosion inhibition behavior of carbon steel by three kinds of expired cephalosporins was investigated by Guo et al. [23]. The ceftriaxone sodium (Ceft), cefuroxime sodium (Cefu) and cefotaxime sodium (Cefo) were used for this purpose. The comparison of cephalosporins showed that Ceft was prefable than the others, according to EIS results, the highest inhibition efficiency was detected for 1mM Ceft as 84.4%.

In this study expired Epdantoin drug was investigated as inhibitor against MS corrosion in acidic media. It is a widely available, inexpensive drug made in Turkey and it is distributed with a white prescription. The aim of the study is to get rid of costly destruction processes and to offer an effective inhibitor alternative that does not harm the nature.

2. MATERIAL AND METHOD

The electrochemical measurements were carried out using a CHI 660b electrochemical analyzer. All of the electrochemical tests were carried out in an open atmosphere with three-electrode configuration. The counter electrode was a platinum sheet (2 cm^2), and the reference electrode was Ag/AgCl (3 M KCl). The working electrodes were made of MS alloy with almost 0.5 cm^2 surface area. The chemical composition (in weight percent) was: 0.09645 C, 0.22423 Si, 0.41797 Mn, 0.02095 P, 0.04229 S, 0.02533 Cu, 0.03594 Ni, 0.01396 Cr, 0.00271 Mo, 0.00591 V, 0.00216 Sn, and a Fe balance. Before each experiment, the surface of the MS was polished to 1200 degrees using sandpaper. Epdantoin drug includes 100 mg phenytoin per tablet and excipients are aerosil 200, citric acid, talc. The molecular structure of phenytoin is shown in Figure 1.

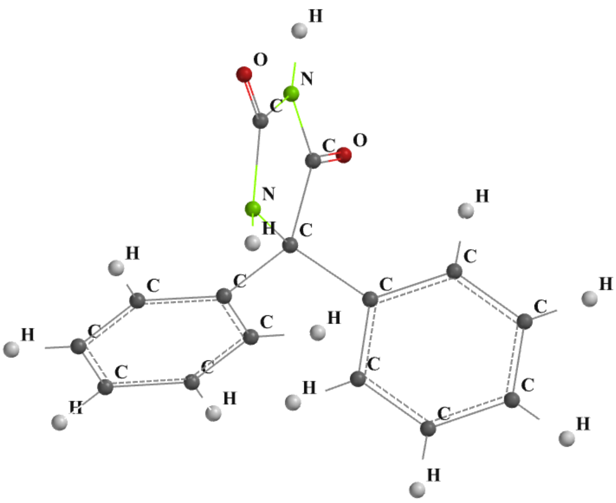


Figure 1. The phenytoin (EP) molecule

For the corrosion tests, MS electrodes were immersed in 0.5 M HCl solutions containing various concentrations (0.5; 1; 3; 5 mM) of EP, and EIS measurements were performed without stirring the electrolyte by applying 5 mV amplitude in the frequency range of 10^5 – $6x10^{-2}$ Hz. The current potential curves were acquired with a scanning speed of 1 mV/s. All of the experiments were conducted at a temperature of 293 K. The potential zero charge (pzc) measurements were done with the help of EIS and graphs were presented as applied potential vs charge transfer resistance. All EIS measurements were fitted via the ZView program. Theoretical calculations were carried out using density functional theory (DFT) with 6-311++G (d,p) basis set for all atoms with the Gaussian 03W program. Some electronic properties such as energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), dipole moment, and Mulliken charges were determined.

3. RESULTS

The Nyquist plots of MS were presented in Figures 2, 4 and 5. The equivalent circuits were presented in Figure 3. In Figure 2, the semi-elliptic curves could be seen in the Nyquist diagrams which were started in the high frequency region, continued in the mid-frequency region, and closed in the low-frequency region. It indicated that MS corrosion in 1.0 M HCl solution was under the control of activation [24, 25]. According to obtained results in Figure 2, the resistance of MS decreased with increasing immersion period. MS corroded due to the corrosive acidic environment and specific absorption ability of chloride ions [26, 27].

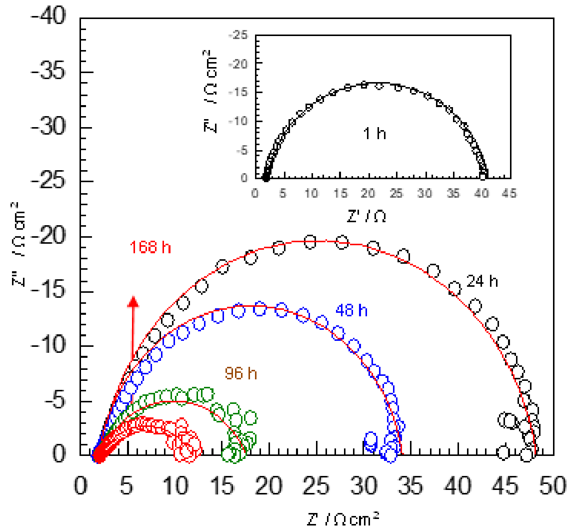


Figure 2. The Nyquist plots of MS in 0.5 M HCl for various exposure times

As seen in Table 1, polarization resistance values of MS were 39 and 9.8 ohm cm^{-2} for 1 and 168 hours immersion period, respectively. The constant phase element values were $690.1x10^{-6}$ and $9973.8x10^{-6}$ sn Ω^{-1} cm^{-2} respectively.

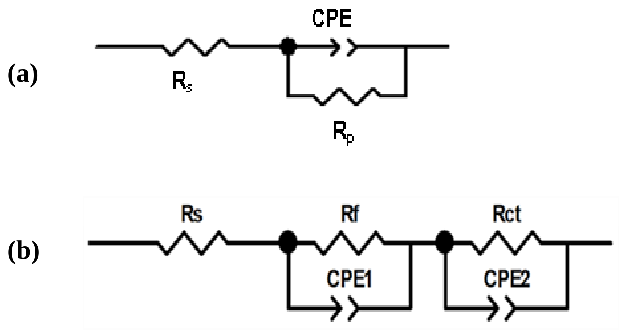


Figure 3. The equivalent circuit models for MSin HCl (a) and EP containing (b) media. The solution resistance R_s; the polarization resistance R_p (includes film resistance; R_f and charge transfer resistance; R_{ct}) and related constant phase elements; CPE1-2.

Table 1. Electrochemical parameters for MS in 0.5 M HCl solution

t (h)	R_p (Ω cm^2)	CPE (10^{-6} sn $\Omega^{-1}cm^{-2}$)
1	39.0	690.1
24	46.1	1084.4
48	32.2	2934.6
96	15.5	7940.3
168	9.8	9973.8

In the presence of inhibitor molecules, the corrosion resistance of MS increased with increasing EP concentration. As seen in Figure 4 and Table 2, polarization resistance values of MS were 928.9 and 1220 Ω cm^{-2} for 3 and 5 mM EP containing HCl, respectively. The constant phase element values were $65.3x10^{-6}$ and $58.3x10^{-6}$ sn Ω^{-1} cm^{-2} respectively. The corrosion protection was noticed almost 97% in the presence of 5 mM EP. This is the comparable value for inhibition efficiency according to literature. The expired Abacavir Sulfate drug was investigated for MS protection against corrosion in 3 M HCl, according to obtained EIS results almost 72.7% inhibition efficiency was detected [28]. The expired salbutamol drug molecule as an emerging anticorrosion additive for MS corrosion in oilfield acidizing fluid was investigated [29]. The maximum inhibition efficiencies of 80 %, 89 % and 84 % were determined from weight loss, potentiodynamics study and EIS at concentration of 0.4 g L^{-1} respectively. Using electrochemical methods and the weight loss method, the antipsychotic drug thioridazine hydrochloride (TH) was assessed for its ability to effectively inhibit corrosion on MS in 1 M HCl [30]. To understand the long-term effect of TH, MS was tested for 7 days in 100 ppm TH containing electrolyte. EIS results showed that the R_p did not change significantly after 24 h exposure as compared to 2 h exposure; whereas the R_p increased by 28% after 7 days exposure. After a 7 days exposure, weight loss assessments showed that TH's remarkable high (98.8%) inhibitory efficiency.

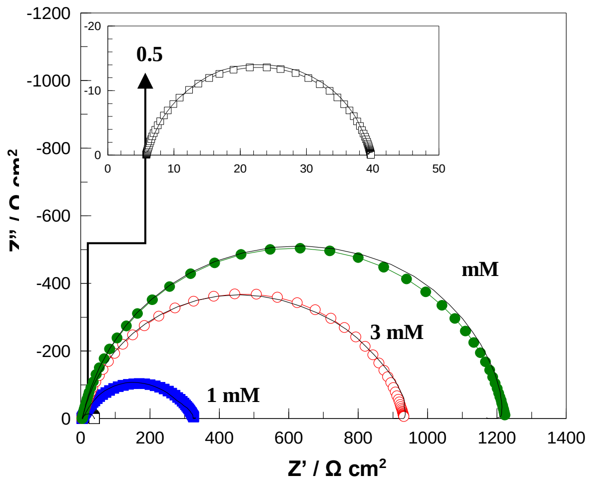


Figure 4. The Nyquist plots of MS in various EP containing 0.5 M HCl for 1h immersion time

Table 2. Electrochemical parameters for MS in various EP containing 0.5 M HCl for 1h immersion time

C *(mM)*	R_p *(Ω cm^2)*	CPE *(10^{-6} sn Ω^{-1}cm^{-2})*	$\%\eta$
0.5	33.9	242.7	-
1	324.3	306.0	88
3	928.9	65.3	95.8
5	1220	58.3	96.8

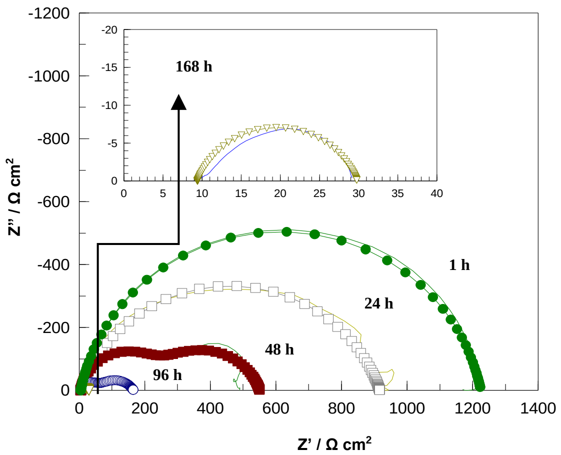


Figure 5. The Nyquist plots of MS in 5mM EP containing 0.5 M HCl for various exposure times

Table 3. Electrochemical parameters for MS in 5mM EP containing 0.5 M HCl for various exposure times

<table>
<tr><th>t</th><th colspan="2">R_p</th><th colspan="2">CPE</th><th>%η</th></tr>
<tr><td>1</td><td colspan="2">1220</td><td colspan="2">58.3</td><td>96.8</td></tr>
<tr><td>24</td><td colspan="2">912.5</td><td colspan="2">78.6</td><td>94.9</td></tr>
<tr><td rowspan="2">48</td><td>R_f</td><td>R_{ct}</td><td>CPE₁</td><td>CPE₂</td><td rowspan="2">94.1</td></tr>
<tr><td>225</td><td>320</td><td>56.3</td><td>1000</td></tr>
<tr><td>96</td><td>56</td><td>102</td><td>52</td><td>220</td><td>90.2</td></tr>
<tr><td>168</td><td colspan="2">20.4</td><td colspan="2">1500</td><td>52</td></tr>
</table>

The corrosion resistance of MS expanded considerably in the presence of EP molecules. As seen in Figure 5 and Table 3, the polarization resistance values of MS were 912.5 and 20.4 Ω cm^{-2} for 24 and 168 hours immersion periods, respectively. The constant phase element values were 78.6×10^{-6} and 1.5×10^{-3} sn Ω^{-1} cm^{-2} respectively. Despite the fact that resistance values decreased with increasing immersion time, the presence of EP provided improved corrosion prevention.

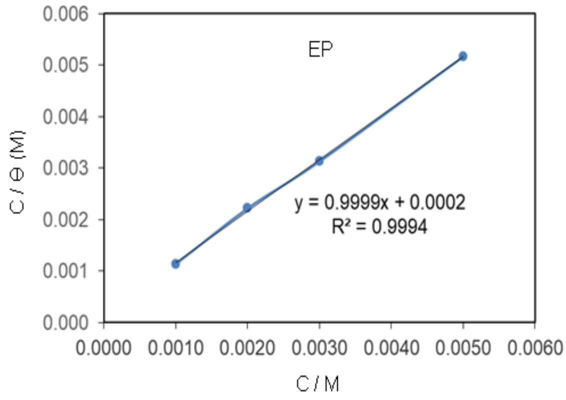


Figure 6. Langmuir adsorption plot for the MS

In order to clarify the adsorption mechanism, several isotherm models were operated but the Langmuir was most convenient for experimental results. In Figure 6, the Langmuir adsorption isotherm was presented and the following equation was used [31];

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

where C_{inh} was the concentration of inhibitor, Θ was the degree of surface coverage values for various concentrations of the inhibitors in acidic solution. The Kads was the adsorption equilibrium constant, which was 5×10^3 M^{-1}, and for EP that signed the adherent adsorption ability of inhibitor molecules on the MS surface. The standard free energy of adsorption ΔGºads value was calculated according to the following equation [32];

$$\Delta G^{o}_{ads} = -RT \ln\left(55.5 K_{ads}\right) \qquad (2)$$

where R was universal gas constant and T was the absolute temperature, the calculated value was -31.05 kJ mol^{-1} for EP. The fact that the value of ΔGºads for EP was less than 40 kJ mol^{-1} indicated both physical and chemical interactions.

In the literature, the study that defined the pharmaceutical thiazofurin as a novel, non-toxic corrosion inhibitor for MS in HCl solution revealed that adsorption corresponded with the Langmuir isotherm [33]. The obtained value of ΔGºads was almost –29.14 kJ/mol. Pour-Ali and Hejazi declared that tiazofurin adsorbs on the surface of MS in 0.5 M HCl by physiochemisorption mode. Electrochemical behavior for corrosion protection of MS in 1M HCl medium by using lidocaine drug was investigated by Adel et. al [34]. The adsorption of the Lidocaine on MS surface was found to obey Langmuir adsorption isotherm. The calculated ΔGºads values were –20.6 kJ/mol –20.7 kJ/mol at 298 K and 318 K, respectively. They declared that ΔG^oads values indicated both physical and chemical interactions between MS and Lidocaine.

Further, the potentiodynamic polarization measurements were achieved in the absence and presence of EP and related results were presented in Figure 7.

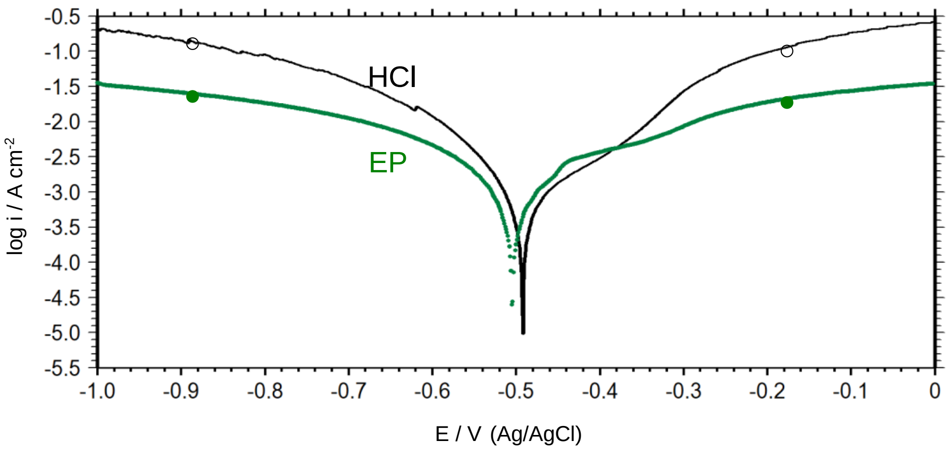


Figure 7. The potentiodynamic polarization curves for the MS electrode in 0.5 M HCl containing 5 mM EP for 168 h exposure time

In the presence of EP, the cathodic and anodic current density values decreased, as shown in Figure 7. The corrosion potential values were almost the same in the presence of EP and they both affected the anodic and cathodic reactions; therefore EP could be identified as the mixed type inhibitor [35, 36].

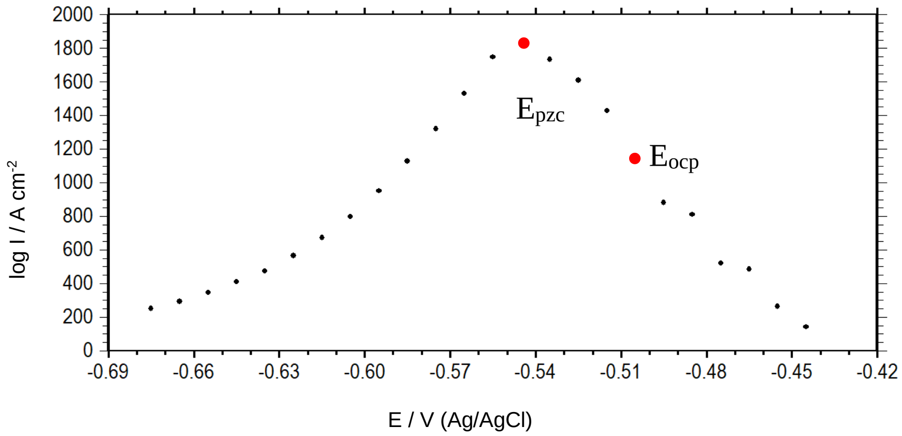
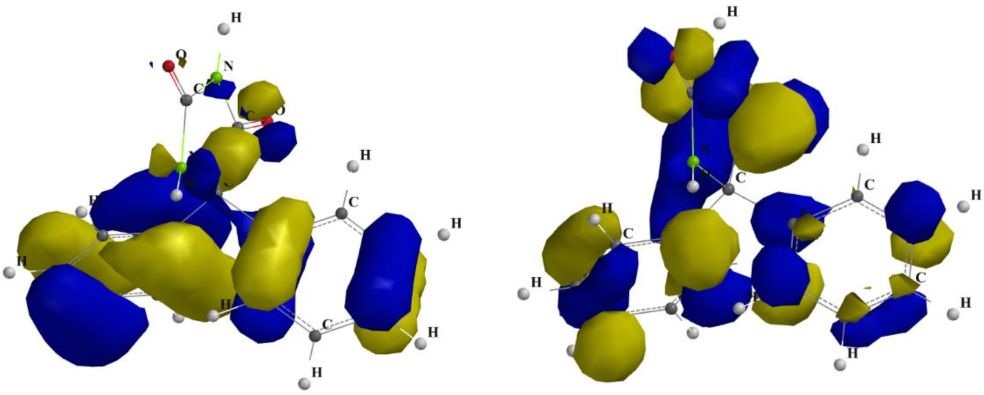


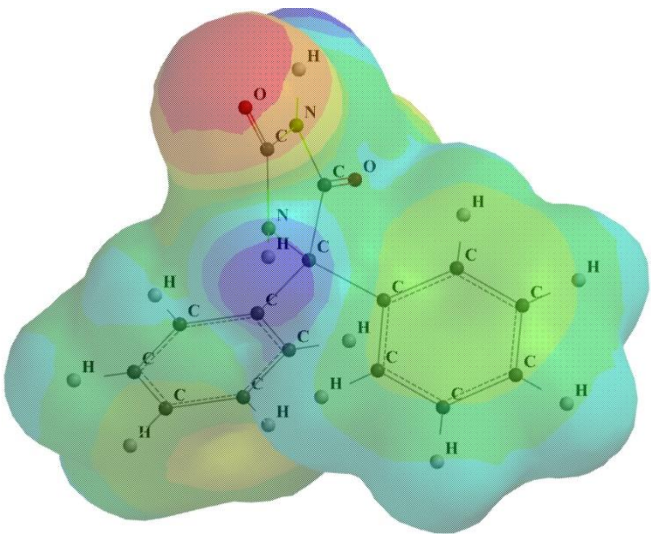
Figure 8. The pzc curve of MS electrode in 0.5 M HCl containing 5 mM EP

As seen in Figure 8, the highest polarization resistance (R_p) was detected at -0.545 V (vs Ag/AgCl; 3 M KCl) as 1824 ohm cm^{-2}. The open circuit potential of MS in this condition was -0.505 V and R_p was 1220 ohm cm^{-2}. According to obtained results, surface charge was positive. As a result, in the acidic solution, negatively charged chloride ions are deposited on the positively charged metal surface and negatively charge it. Following that, protonated (positively charged) EP molecules bond to the metal surface over chloride ions in the acidic environment to form a protective barrier. The obtained all experimental results were compared with quantum chemical methods. For this purpose, the structural analysis of EP was achieved. The highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between LUMO and HOMO and Mulliken charges on the backbone atoms were determined and presented in Figure 9.

(a)



(b)



(c)

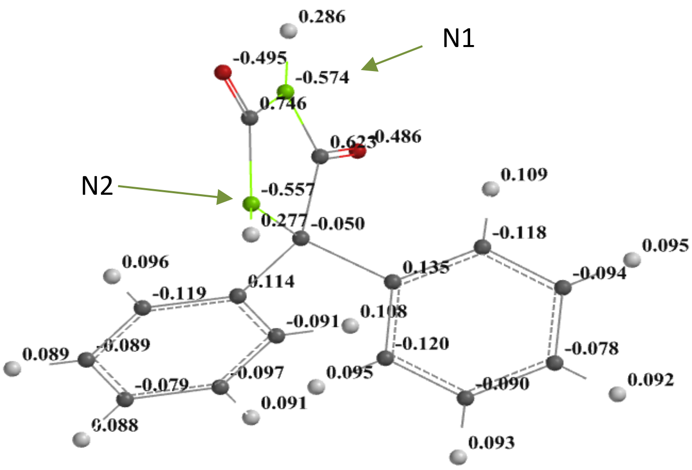


Figure 9. The HOMO and LUMO surfaces of EP **(a)**, electrostatic potential map of EP **(b)** and Mulliken charges of atoms on EP molecule **(c)**

As seen in Figure 9, wide HOMO and LUMO surfaces provide adherent adsorption ability of molecules. The determined HOMO value was -6.67 eV; LUMO value was -0.72 eV. The dipole moment was 2.66 Debye (Table 4). The Mulliken charges of oxygen atoms were -0.495 and -0.486 au and nitrogen atoms were -0.574 au and -0.557 au. In an acidic media, EP could protonate from the N1 and N2 atoms which were assigned in Figure 9c. EP in the protonated forms may adsorb predominantly through electrostatic interactions between such regions and the metal surface. For this purpose the protonated molecular structures (EP-N1 and EP-N2) were analyzed via quantum chemical calculation with the same basis sets and conditions, all data were presented in Table 4.

Tablo 4. The theoretical parameters of EP and protonated EP molecules

Molecules	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (E_{LUMO}-E_{HOMO}) (eV)	Dipole Moment (Debye)
EP	-6.67	-0.72	5.95	2.66
EP-N1	-10.01	-6.80	3.21	4.10
EP-N2	-10.25	-5.64	4.61	3.19

As seen in Table 4 the more favorable protonated structure was EP-N1. The obtained HOMO, LUMO and dipole moment values were -10.01 eV, - 6.80 eV and 4.10 Debye, respectively. When compared to all molecular forms, EP-N1 had the lowest band gap. The higher dipole moment of EP-N1 may accelerate the adsorption of molecules and may increase the inhibition efficiency, due to dipole–dipole interactions between molecules and electrode surface [35].

4. DISCUSSION AND CONCLUSION

The expired drug that was "Epdantoin" with phenytoin ingredient was investigated as the corrosion inhibitor for MS in HCl medium. The findings of electrochemical methods and quantum chemical computations lead to the following recommendations:

1.According to EIS parameters the inhibition efficiency of EP increased with increasing concentration. During long term immersion, EP could effectively protect MS against corrosion in HCl solution.

2.The adsorption of EP obeyed the Langmuir isotherm. The Kads was $5x10^3$ M^{-1} and the ΔG°ads indicated physical adsorption with 31.05 kJ mol^{-1} value.

3.The polarization curves proved that EP was a mixed type inhibitor via suppressed cathodic and anodic polarization reactions.

4.According to pzc results the surface charge was positive in presence of EP. Thus we offered that EP should be in the protonated forms in HCl.

5.The calculated quantum parameters revealed that EP-N1 inhibited more effectively than the other forms due to lower band gap and larger dipole moment values.

All results show that Epdantoin as an expired drug has potential application in the area of corrosion studies, especially MS protection in HCl medium during long term. We offer the usage of expired eco-friendly drugs not only to decrease the corrosion rate of technical metals but also re-gain these drugs for diminishing the carbon footprint all around the world. Because the expired drugs exhibit several advantages such as;

a.protective against corrosion,
b.economic benefits and eliminates the costs of disposal, transportation and storage,
c.lower carbon foot-print etc.

We should emphasize the potential applications.

Acknowledgement

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Conflict of Interest

There are no conflicts of interest declared by any of the writers.

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