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Expired nizatidine drug as eco-friendly corrosion Inhibitor for α-brass alloy in aqueous solutions

ABSTRACT

Expired nizatidine drug (END) was studied as inhibitor for α-brass in 1M HCl utilizing weight loss (WL), and electrochemical methods namely, AC impedance (EIS), Potentiodynamic polarization (PP), and electrochemical frequency modulation (EFM) tests. The protection efficiency (%IE) was improved with raising in the dose of the expired nizatidine and decreases with raising the temperature. The (%IE) reaching maximum value 95 % at higher dose of expired nizatidine drug at 25^{o}C. PP data indicated that nizatidine drug behaves like a mixed kind drug. The protection of α-brass corrosion by nizatidine can fit to the adsorption ability of nizatidine drug molecules onto the reactive sites of the α-brass surface. The adsorption of the drug follows Langmuir adsorption isotherm. The surface morphology of α-brass was investigated. The results obtained from different methods are in excellent agreement.

***Keywords:** Acidic inhibition, α-brass, Nizatidine, EFM, EIS, AFM, FTIR*

1. INTRODUCTION

Brass is a combination of Cu and Zn in alloy which can be changed to variable mechanical and electrical properties [1]. It is a substitutional alloy: particles of the two constituents may replace each other inside the same crystal structure [2]; both brass and bronze may incorporate little extents of a range of different components containing lead, arsenic, phosphorus, silicon and manganese. The differentiation among the two alloys is to a great extent historical [3] and present-day practice in museums and archaeology studies progressively maintains a strategic distance from the two terms for historical objects in favor of the more general "copper alloy" [4]. The applicability of pharmaceutical compounds as Eco- friendly corrosion inhibitors for metals in acidic media has been recognize for a long time [5–19].

Organic composites that mainly contains oxygen, sulphur, nitrogen atoms, and multiple bonds in the molecule are mostly utilize in industry for preventing dissolution through which they are adsorbed on metal surface [20-27]. Also, the utilized of drugs as a corrosion hindrance has been described [28-31]. Depending on type of force adsorption can be physisorption, chemisorption or a combination of both [32].

The main impartial of this research was to examine expired nizatidine drug, as a green inhibitor for brass dissolution in acidic medium due to existence of oxygen and nitrogen in its structure as active centers, high molecular size, nontoxic, and inexpensive all the pervious mentioned properties indicate that expired nizatidine drug is "Eco friendly" corrosion inhibitor. The dissolution behavior of α-brass in acidic environment is a subject of pronounced practical importance considering its widespread applications

2. EXPERIMENTAL TESTS

2.1. Materials and Solutions

α-brass sample with the composition (weight%): 70% Cu and Zn 30%. Test materials

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were scratched with various emery papers equal to 1200 grade, clean with distilled water and properly dried prior to test. Analar grade 37% HCl and distilled water were utilized to solution preparation. Chemical structure of nizatidine drug is presented in Fig. 1. nizatidine ((E)-1-N'-[2-[[2-[(dimethylamino) methyl]-1,3-thiazol-4-yl] methylsulfanyl] ethyl]-1-N-methyl-2-nitroethene-1,1-diamine commonly used treatment of treatment of peptic ulcer disease. Nizatidine (molecular weight of 331.46) was utilized for the study.

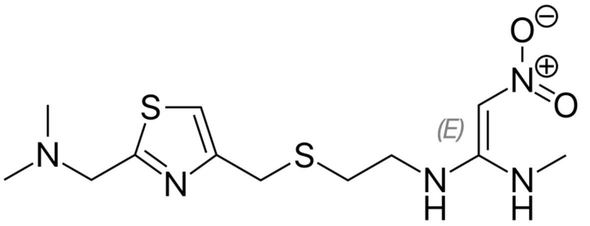


Figure 1. Chemical structures of the nizatidine drug

Slika 1. Hemijske strukture leka nizatidina

2.2. Weight Loss (WL) tests

(WL) is a method in which seven sample of brass with dimension of 2cm×2cm×1mm are abraded well by emery papers that started with 300 and ended with 1200 grit size, rinsed with bidistilled water, degreased in acetone and dried, then weighed accurately. The (% IE) is calculated by following equation [33].

$$IE\ \% = \theta \times 100 = [1 - (W / W°)] \times 100 \qquad (1)$$

Where W^o and W values are (WL) of blank and existence altered doses of nizatidine inhibitor, correspondingly

2.3. Electrochemical tests

2.3.1 Potentiodynamic Polarization (PP) method

In the present work, destructive (PP) and nondestructive methods (EIS, EFM) used to determine the dissolution of α-brass. Three glass cells were utilized in this test. Before each test, (brass) samples were in the open system cleaned at $_{250C}$ as in the (WL) method. (brass) probe washed, dried and placed in the test environment until it takes 1800 second to arrive the open circuit potential. The (PP) procedure is performed as before [33]. The potential was taking place from −800 to +800 mV vs (E_{ocp}). An electrochemical solution potential is produced and the corrosion potential (E_{corr}) and corrosion current (i^o_{corr}) from the Tafel curves were measured from the extrapolating both cathodic and anodic Tafel lines. %IE is determined by Eq. (2) as follows:

$$\%IE = \theta \times 100 = [1 - (i_{corr}/i°_{corr})] \times 100 \qquad (2)$$

Where i^o_{corr} and i_{corr} are the current with and without nizatidine *drug*, individually

2.3.2. Electrochemical Impedance Spectroscopy (EIS) tests

EIS used AC signal in a frequency range of 100 kHz to 0.1 Hz during a 10-mV peak-to-peak amplitude. All EIS data had fitted to suitable equivalent circuit utilizing the software version 6.03 for Gamry Echem calculation.

2.3.3. Electrochemical Frequency Modulation (EFM) Measurements

EFM can be utilize as a fast and good non-destructive method for (brass) independent Tafel slope corrosion. EFM Amplitudes 10 mV to 2 and 5Hz techniques [34-36]. High peak used for calculating current density (i_{corr}), Tafel slope (β_c & β_a) and causal factors (CF-2 & CF-3) [37].

Gamry Instruments Series (G750TM Potentiostat / Galvanostat / ZRA) implemented electrochemical methods with Gamry applications including software: DC 105, EIS300 for EIS and EFM140 for EFM. Echem analyst 6.03 software was utilized for drawing, graphing, and data fitting.

2.4. Analysis of surface morphology

2.4.1. Fourier transform infrared spectroscopy (FTIR) tests

FT.IR is carried out using Thermo Fisher Nicolet IS10, USA spectrophotometer in the region between 4500 and 500 cm^{-1}

2.4.2. Atomic Force Microscopy (AFM) analysis

Surface examination of brass sample was examining utilizing (AFM) (Park systems, XE-100 model). After engagement in corrosive environment in the attendance and lack of the expired nizatidine *drug* inhibitor for 24 h at 25^0C.

2.4.3 Scanning Electron Microscopy tests (SEM, EDX)

Scanning Microscope Electron – type JOEL 840, Japan earlier and later dipping in corrosive environment in the existence and nonattendance of the 300 ppm of the expired nizatidine drug at 25°C, for 1 day, studied the electrode surface of brass.

2.5. Quantum Chemical Calculations

Theoretical studies have utilized to decide the relation among the structure of expired nizatidine *drug* and the effectiveness of corrosion inhibition. Therefore, PM3 semi empirical method is a very powerful test to study barrier-surface interaction, and to investigate investigational value

3. RESULTS AND DISCUSSION

3.1. WL tests

The reduction in WL of α-brass alloy can be studied in the presence of expired nizatidine *drug* at 25°C. Figure (2) shows that expired nizatidine *drug* decreases the WL and therefore corrosion rate. The curves after 120 min. begin to go to constancy, due to the formation of corrosion products on alloy surface. The (%IE) and then θ, of the expired nizatidine *drug* for the α-brass were founded by eq. (1). The data of %IE are given in Tables 1,2. From these tables, it is indicated that the IE% was improved steadily with improving the dose of expired nizatidine *drug* and lowered with temperature rising from 25-45ºC.

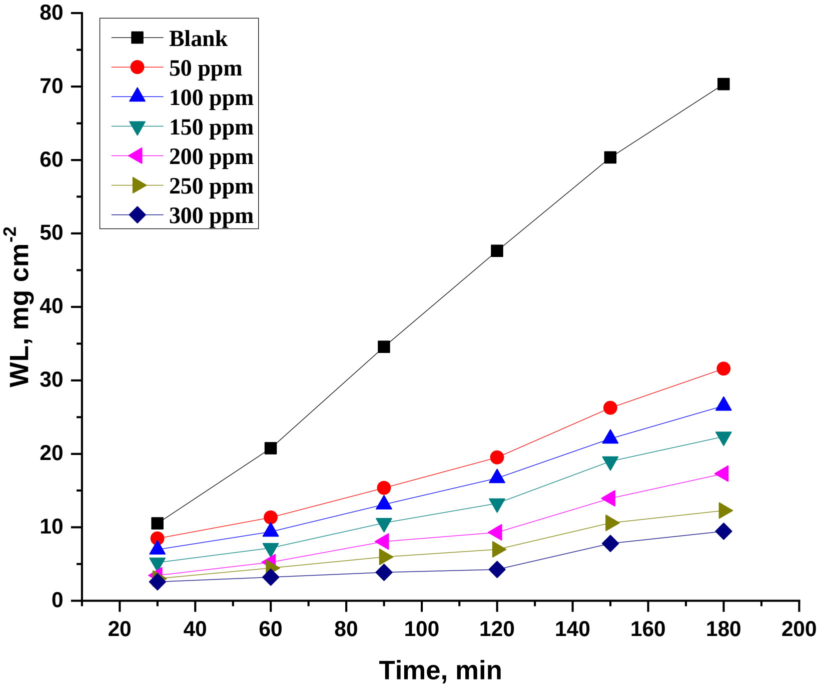


Figure 2. Time -WL curves for the dissolution of α-brass in 1M HCl with and without varied doses of expired nizatidine.

Slika 2. Kriva vreme-WL rastvaranja α -mesinga u 1M HCl sa i bez različitih doza isteklog nizatidina

Table 1. % IE and è of the used expired nizatidine in 1M HCl at 25°C, obtained from WL test

Tabela 1. % IE i è korišćenog isteklog leka nizatidina u 1M HCl na 25°C, dobijen WL testom

Conc., ppm	k_{corr} mg $cm^{-2}min^{-1}$	è	%IE
Blank	0.40	-----	-----
50	0.16	0.602	60.2
100	0.14	0.694	69.4
150	0.11	0.772	77.2
200	0.08	0.841	84.1
250	0.06	0.901	90.1
300	0.03	0.951	95.05

3.2 Effect of Temperature

It was discovered that the IE diminishes with raising temperature yet at lower rate than in unprotected medium with expanding the dose of the nizatidine, as record in Table 5. The noted protection activity of the expired nizatidine drug could ascribed to the adsorption of their expired nizatidine drug on α-brass interface. The coated film of the adsorbed atoms must have isolated the metal surface from the α-brass interface from the aggressive medium that limited the dissolution of the alloy by blocking of their corrosion sites and hence the corrosion rate decreases with raising efficiency as the doses were increased. % IE lowering with raising the temperature indication the physical adsorption.

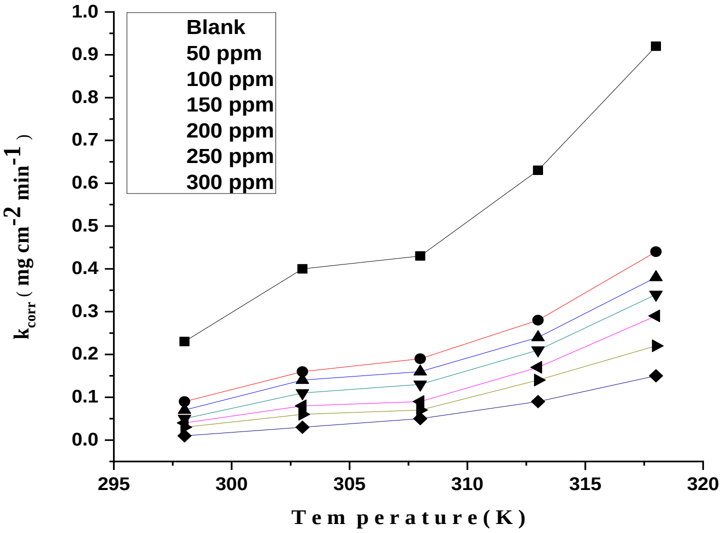


Figure 3. k_{corr} vs. temperature for varies doses of expired nizatidine drug

Slika 3. Odnos k_{corr} i temperature za različite doze isteklog leka nizatidina

Table 2. % IE and k_{corr} (in mg cm^{-2} min^{-1}) at various doses of expired nizatidine drug for the dissolution of α-brass from WL tests at 25 to 45˚C

Tabela 2. % IE i k_{cor} (u mg cm^{-2} min^{-1}) kod različitih doza isteklog leka nizatidina za rastvaranje α-mesinga iz WL testova na 25 do 45°C

[inh] ppm	25˚C		30˚C		35˚C		40˚C		45˚C	
	k_{corr}	% IE	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE
Blank	0.23	---	0.40	---	0.43	---	0.63	---	0.92	---
50	0.09	60.2	0.16	59.1	0.19	55.2	0.28	54.4	0.44	52.6
100	0.07	69.4	0.14	65.0	0.16	63.1	0.24	62.4	0.38	58.9
150	0.05	77.2	0.11	72.2	0.13	69.3	0.21	66.2	0.34	63.0
200	0.04	84.1	0.08	80.4	0.09	78.3	0.17	73.0	0.29	68.9
250	0.03	90.1	0.06	85.3	0.07	82.5	0.14	81.1	0.22	78.2
300	0.01	95.05	0.03	92.0	0.05	90.1	0.09	88.2	0.15	85.1

3.3. Adsorption Isotherms

Numerous isotherms equations were established by using adsorption isotherm regression analyses. It is evident that the Langmuir isotherm equation is the best fit equation to the results where the data of the regression coefficient (R^2) approaches to unity. This behavior showed that the monolayer of adsorbed inhibitors has been formed on α-brass interface according to the Langmuir equation (3) [38]

$$C/\Theta) = 1/K_{ads} + C \qquad (3)$$

Where the concentration of the nizatidine expressed as *C*, the adsorptive equilibrium constant expressed as *K* and can be computed from the intercept of the difference among the *C/ Ө* and C in Figure (4), the variation between *C/ Ө* and C where *Ө* is the surface coverage, = *IE/100*.

The $\Delta G°_{ads}$ and K_{ads} data are in Table (3). The ΔG^o_{ads} founded by:

$$\Delta G^o_{ads} = - RT \ln (55.5\, K_{ads}) \qquad (4)$$

The nizatidine adsorption is spontaneous and this is proven by the $\Delta G°_{ads}$ negative sign. From the data of ΔG^o_{ads} (less than -20 kJ mol^{-1}), proven that the nizatidine adsorption is physically adsorbed.

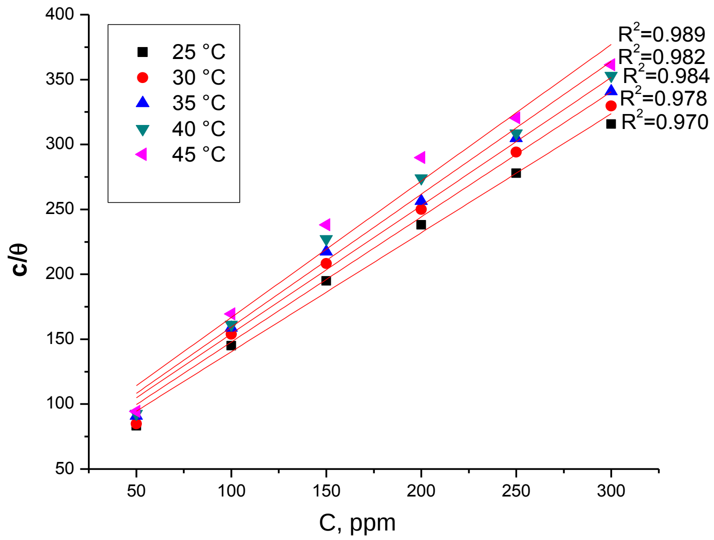


Figure 4. Langmuir diagrams for α-brass in 1M HCl at different temperatures

Slika 4. Lengmirove krive za α-mesinga u 1M HCl na razlicitim temperaturama

Table 3. Langmuir parameters of nizatidine drug at 25-45°C

Tabela 3. Lengmirovi parametri za lek nizatidin na 25 do 45°C

$-\Delta G°_{ads}$, kJ mol^{-1}	slope	K_{ads}, M^{-1}	Temp., °C
16.98	0.9866	20.5	25
17.58	0.9941	19.4	30
17.68	0.9871	18.0	35
17.89	1.0231	17.5	40
17.97	1.0116	16.2	45

The thermodynamic basic equation can be used to measure $\Delta H°_{ads}$ and $\Delta S°_{ads}$ [39] expressed by:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\,\Delta S^o_{ads} \qquad (5)$$

Table 4. Parameters for nizatidine adsorbed on α-brass interface in 1M HCl at varied temperature

Tabela 4. Parametri za lek nizatidin adsorbovan na povrsinu α-mesinga u 1M HCl pri različitim temperaturama

Temp., °C	$-\Delta G°_{ads}$ kJ mol^{-1}	$-\Delta H°_{ads}$ kJ mol^{-1}	$-\Delta S°_{ads}$ J mol^{-1} K^{-1}
25	16.98	51.6	156
30	17.58		
35	17.68		
40	17.89		
45	17.97		

Figure 5 shows the relation between ΔG^o_{ads} and T. A negative sign of ΔS^o_{ads} proved that the disorder of corrosion process is decreases by using nizatidine (Table 4)

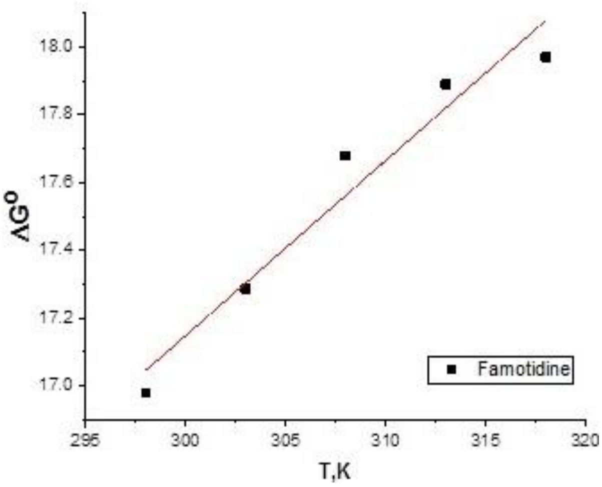


Figure 5. ΔG^o_{ads} vs. T for the adsorption of nizatidine drug at varied temperatures

Slika 5. Odnos ΔG^o_{ads} vs. T za adsorpciju leka nizatidina pri različitim temperaturama

3.4. Kinetic –thermodynamic corrosion parameters

The Arrhenius Eq. (6):

$$k_{corr} = A \exp(E^*a/RT) \qquad (6)$$

Where A is Arrhenius constant and E_a^* is the activation energy [40]. Figure 6 refers to the straight lines given by a plot [log k_{corr} vs.1/T], which can be calculate the E_a^* from their slopes which illustrated in Table 5.

$$k_{corr} = (RT/Nh)\ exp(\Delta S^*/R)\ exp(-\Delta H^*/RT) \quad (7$$

Where ΔS^* and ΔH^* are entropy and activation enthalpy [41]. Plot [log k_{corr} / T vs. 1/T] from their slopes ΔH^* and their intercepts ΔS^* can be measured and documented in Figure 7 and Table 5. The outcome data designate that E_a^* increase in the existence of expired nizatidine drug than in its nonattendance, representative physical adsorption, significance that the block of α-brass surface activities by from protected film and inhibiting. However, the value of (ΔS^*) lowered gradually with raising expired nizatidine drug dose in all the acidic solution

Table 5. Activation data for α-brass corrosion without and with altered doses of expired nizatidine drug in 1M HCl

Tabela 5. Podaci o aktivaciji korozije α-mesinga bez i sa izmenjenim dozama isteklog leka nizatidina u 1M HCl

[inh] ppm	E_a^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}
Blank	50.9	48.3	94.5
50	64.7	61.2	85.4
100	69.2	66.1	80.5
150	72.2	69.5	78.6
200	74.5	72.3	70.5
250	81.2	79.3	68.1
300	85.6	81.2	65.4

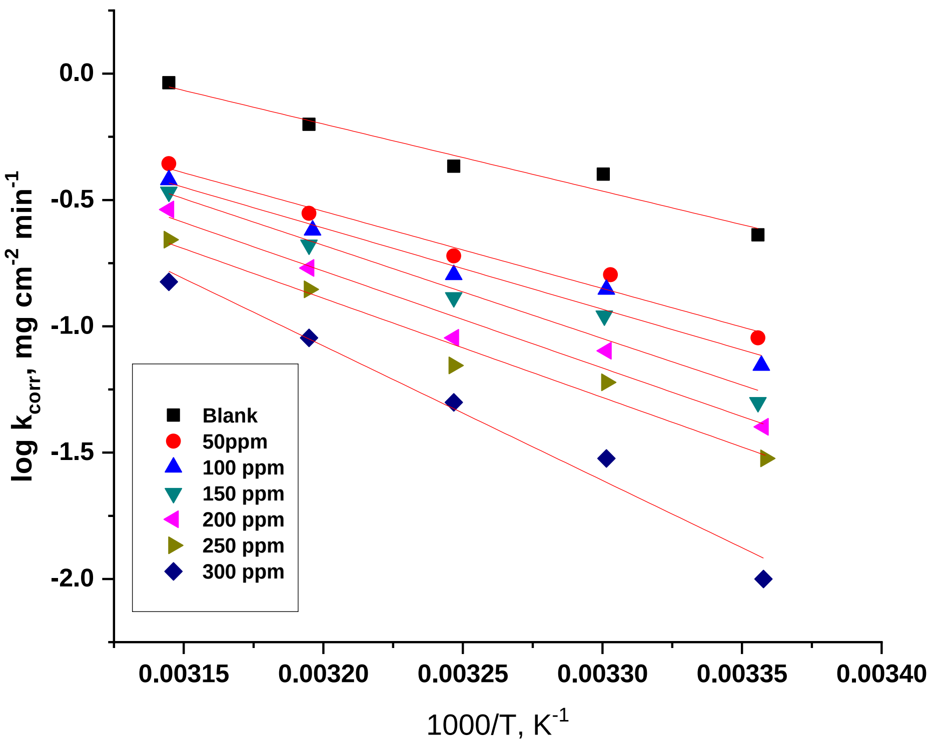


Figure 6. Plotting the Arrhenius of Log (k_{corr}) vs. (1/ T) for dissolution of α-brass in 1M HCl solution with and without various doses of expired nizatidine drug at altered temperatures.

Slika 6. Arrheniusove krive o Log kcorr vs (1 / T) za rastvaranje α-mesinga u rastvoru 1M HCl sa i bez različitih doza isteklog leka nizatidina na razlicitim temperaturama.

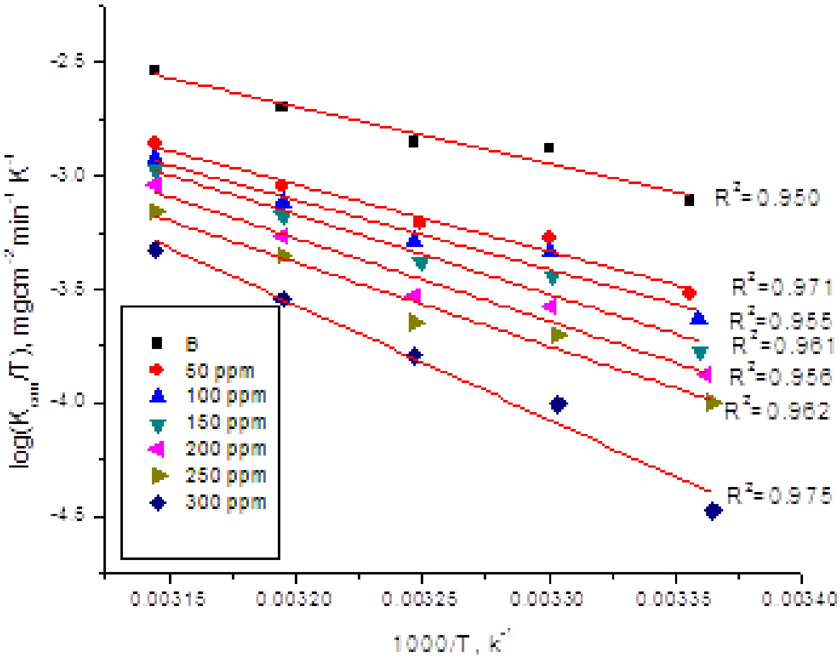


Figure 7. Plotting Log (k_{corr} / T) vs. (1/ T) for dissolution of α-brass in 1M HCl solution in without and with of various doses of expired nizatidine drug at altered temperatures.

Slika 7. Krive Log (kcorr / T) vs. (1 / T) za rastvaranje α-mesinga u rastvoru 1M HCl bez i sa raznim dozama isteklog leka nizatidina na razlicitim temperaturama

3.5. Polarization (PP) measurements

Figure 8 demonstrations PP bends registered for brass in 1M HCl attendance and lack of altered dose of expired nizatidine at 25ºC. With the rise of the dose of nizatidine the curves move both anodic and cathodic sections to the lesser data of current densities which chief lowering in the k_{corr}. The PP result in Table 6. Variation of the data of (log i_{corr}) with (E_{corr}), (β_a, β_c), the rate of corrosion (k_{corr}), (θ) and (%IE). This means that both reactions of α-brass are retarded by expired nizatidine drug in acidic environment. β_a and β_c, were smaller different with the increasing the dose of expired nizatidine. This indicates that expired nizatidine drug signifies as mixed kind [42] The both anodic and cathodic constants didn't exchange essentially with increment in expired nizatidine drug dose, recommending that the existence of the expired nizatidine drug doesn't modify the reaction mechanism.

Table 6. Parameters obtained from PP tests of α-brass for expired nizatidine drug

Tabela 6. Parametri dobijeni iz PP testova za α-mesinga za istekli lek nizatidin

[inh] ppm	i_{corr} µA/cm^2	$-E_{corr}$ mV	â$_a$ mV/decade	â$_c$ mV/decade	k_{corr}	IE (%)
blank	411	539	89	128	187.1	----
100	108	510	106	146	44.1	73.7
150	84	518	110	148	37.9	79.6
200	63	515	103	121	30.5	84.7
250	39	508	98	128	22.3	90.5
300	22	470	83	118	15.5	94.6

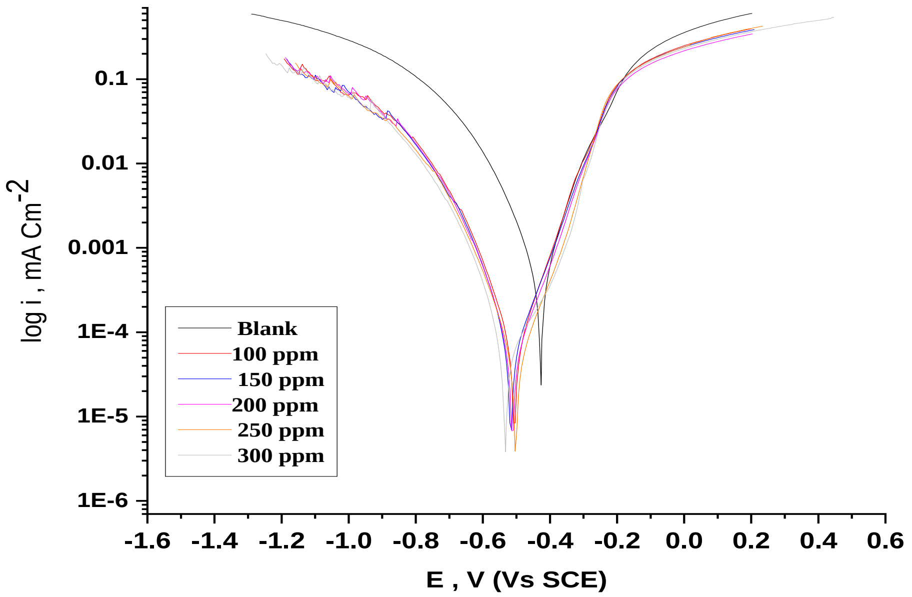


Figure 8. PP bends for dissolution of α-brass in attendance and nonattendance of altered concentration of expired nizatidine at 25^{0}C

Slika 8. PP krive za rastvaranje α-mesinga u prisustvu i odsustvo izmenjene koncentracije isteklog leka nizatidina na 25^{0}C

3.6. Electrochemical impedance spectroscopy (EIS) tests

The EIS parameters were analyze by fitting the equivalent circuit model displayed in Figure 9, which fits well with the experimental data. Figure 10(a, b) demonstration EIS (Nyquist and bode) in 1 M HCl solutions with and without nizatidine drug at 25°C. The values of R_{ct}, C_{dl} and the IE% were gotten and recorded in Table 7. The decrease in C_{dl} is a consequence of a lower in local dielectric constant and/or improve in the double layer thickness. The corresponding Rct was also used to calculate IE and CPE which is utilized to describe the double layer [43]:

$$C_{dl} = Y_0(\omega_{max})^{n-1} \quad (8)$$

Where $\omega_{max} = 2\pi f_{max}$, f_{max} is the frequency of the highest imaginary value. The impedance, Z, associated with CPE is described as follows [44]:

$$Z_{CPE} = Q^{-1}(j\omega)^{-} \quad (9)$$

Where Q stand for the CPE constant and exponent, respectively. The factor n (exponent) is an adjustable parameter that usually lies among 0.50 and 1.0 [45].

For n=0, Z_{CPE} represents a resistance with R= Q^{-1}, for n = 1, a capacitance with C = Q for n = 0.5, a Warburg element with W = Q and for n =-1, an inductance with L = Q^{-1}

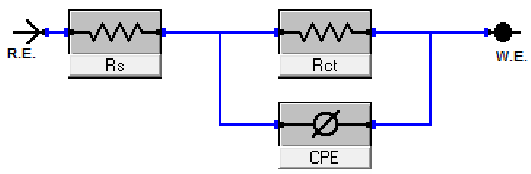


Figure 9. Equivalent electrochemical circuit model

Slika 9. Ekvivalentni elektrohemijski model kruga

The value gotten from the equivalent circuit are display in Table 7. The data display that R_{ct} data were improve by appending the nizatidine drug. Because the creation of an insulating coating film at the surface brass/solution. Alternatively, C_{dl} data lowered, signifying that the nizatidine drug are adsorbed at the interface between brass/solution [46]. Nizatidine drug adsorbed on the bras surface lowered the electrical capacity for the reason they displace the water molecules by nizatidine drug adsorbed on the brass interface. The % IE was measured from eq. 10 [47]:

$$\% IE_{EIS} = [1 - (R^\circ_{ct}/ R_{ct})] \times 100 \quad (10)$$

where R^o_{ct} and R_{ct} are the resistance data attendance and lack of expired nizatidine drug individual.

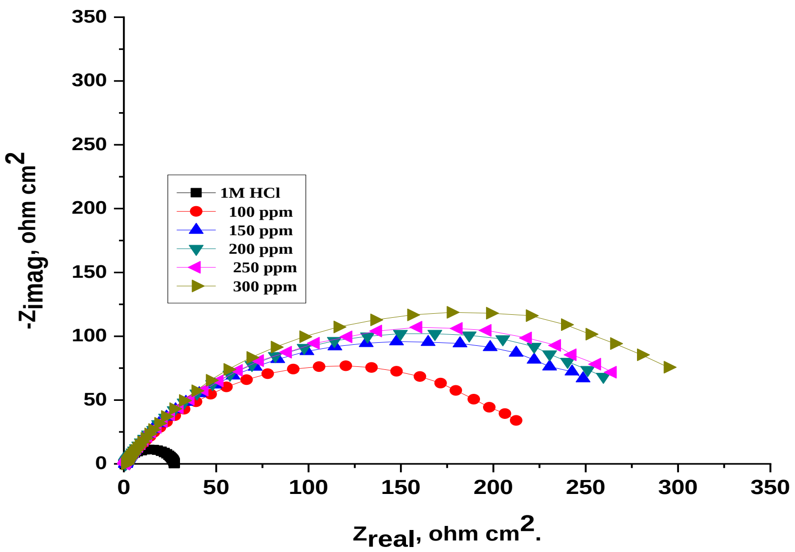


Figure 10 a. The Nyquist bends for dissolution of α-brass existence and nonexistence various doses of the expired nizatidine drug

Slika 10 a. Nyquist krive rastvaranja α-mesinga sa i bez različitih doza isteklog leka nizatidina

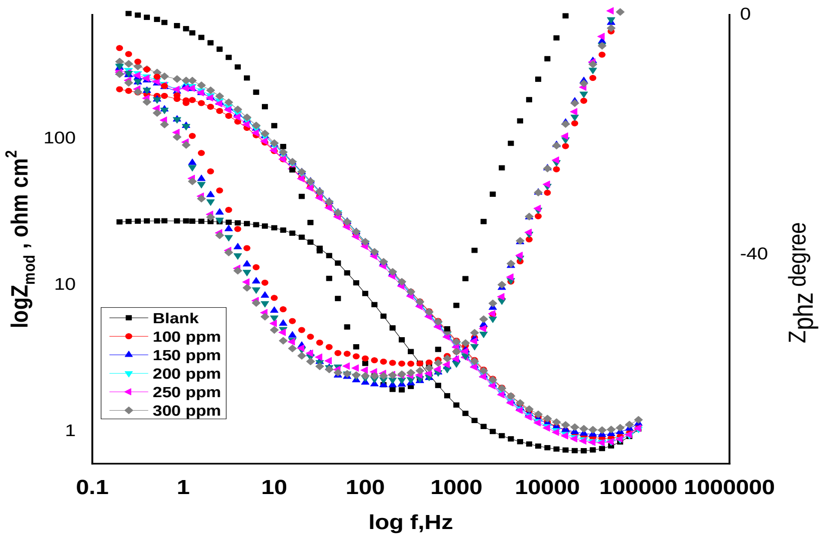


Figure 10 b. Bode diagram plots for dissolution of α-brass in 1M HCl without and with various doses of the expired nizatidine drug at 25^{0}C

Slika 10 b. Sheme Bode dijagrama za rastvaranje α-mesinga u 1M HCl bez i sa različitim dozama isteklog leka nizatidina na 25^{0}C

Table 7: EIS data for α-brass in 1M HCl with and without various doses of the expired nizatidine drug at 25^{o}C

Tabela 7. Podaci EIS-a za α-mesing u 1M HCl sa i bez različitih doza isteklog leka nizatidina pri 25^{0}C

% IE	θ	n	C_{dl}, μF cm^{-2}	R_{ct}, Ω cm^2	Conc., M
---	---	0.741	300	30.5	B
75.4	0.754	0.885	201	119.2	100
80.4	0.804	0.891	177	178.3	150
85.8	0.858	0.944	120	212.2	200
91.2	0.918	0.976	100	333.1	250
93.0	0.930	0.940	80	440.1	300

3.7. Electrochemical frequency modulation (EFM) tests

The EFM curves for expired nizatidine drug in 1M HCl solution at 25 ˚C attendance and nonattendance altered dose of (100 – 300 ppm) expired nizatidine drug had listed and presented in Figure 11. (EFM) can used to measure the corrosion current directly in which two waves (at different frequencies) have meanwhile been bound to the cell [48]. The data in Table 8 are derived from Figure 11, which indicates that the current of liquefaction lowered with an increment in the doses of expired nizatidine drug, and thus (IE%) increases. The largest peaks were utilized to measure the (i_{corr}), (β_c and β_a) and the causality factors (CF-2 and CF-3). CF-2 and CF-3 are utilized to checkered on the validity of EFM methods and are determine from the EFM are equal nearly to the theoretical value (2 and 3) representative that the value is verified and of excellent quality [49].

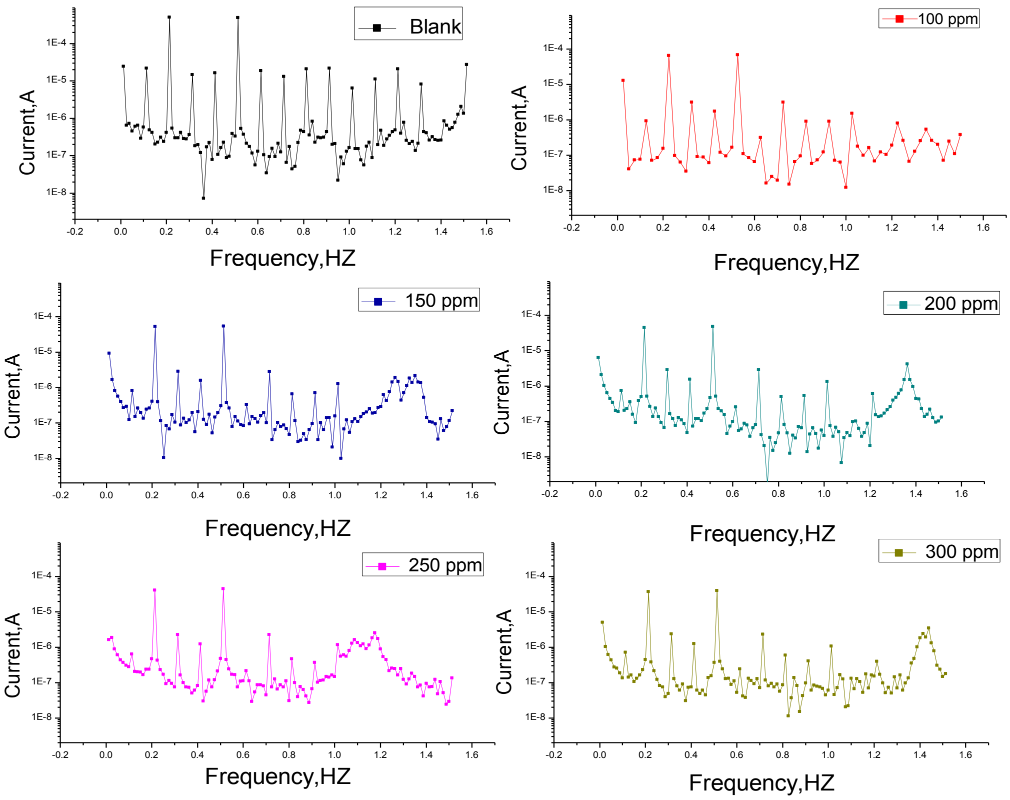


Figure 11 (a-f). EFM spectra for the dissolution of α-brass with and without various doses of expired nizatidine drug

Slika 11 a-f. EFM spektri za rastvaranje α-mesinga sa i bez različitih doza isteklog leka nizatidina

Table 8. Parameters gotten from EFM technique for various doses of nizatidine drug at 25°C

Tabela 8. Parametri dobijeni iz EFM tehnike za različite doze leka nizatidina na 25°C

Conc, ppm	i_{corr}, μA	β_a mV dec^{-1}	β_c mV dec^{-1}	$k_{corr.}$ mpy	CF-2	CF-3	θ	%IE
Blank	256.3	36.8	64.9	124.4	1.65	2.84		
100	55.4	90.7	109.9	27.1	1.50	3.25	0.787	78.7
150	35.7	99.1	105.0	18.2	2.45	3.04	0.852	85.2
200	32.7	100.9	118.2	16.2	2.11	3.11	0.875	87.5
250	28.1	110.6	116.3	14.1	2.44	3.77	0.893	89.3
300	26.8	122.3	103.6	9.5	2.35	3.20	0.933	93.3

3.8. (FTIR) analysis

Figure 12 demonstrations the FTIR of the pure expired nizatidine drug and metal surface. Figure 12 (a) show the band at 3332 cm^{-1} demonstrations OH frequency. The FTIR spectra of the protective film found on the α-brass interface after rinsing in solution including 300 ppm of expired nizatidine drug is display in Figure 12(b) the OH seemed at 3356 cm^{-1}. This exchange is instigating by the density of electron cloud from the O atom to α-brass. This recommends that the O atom of the expired nizatidine drug is coordinated to α-brass. The band at 1651 cm^{-1} is C–C stretching of alkene non-conjugated on the interface of α-brass film that raised from 1622 cm^{-1} of pure nizatidine drug.

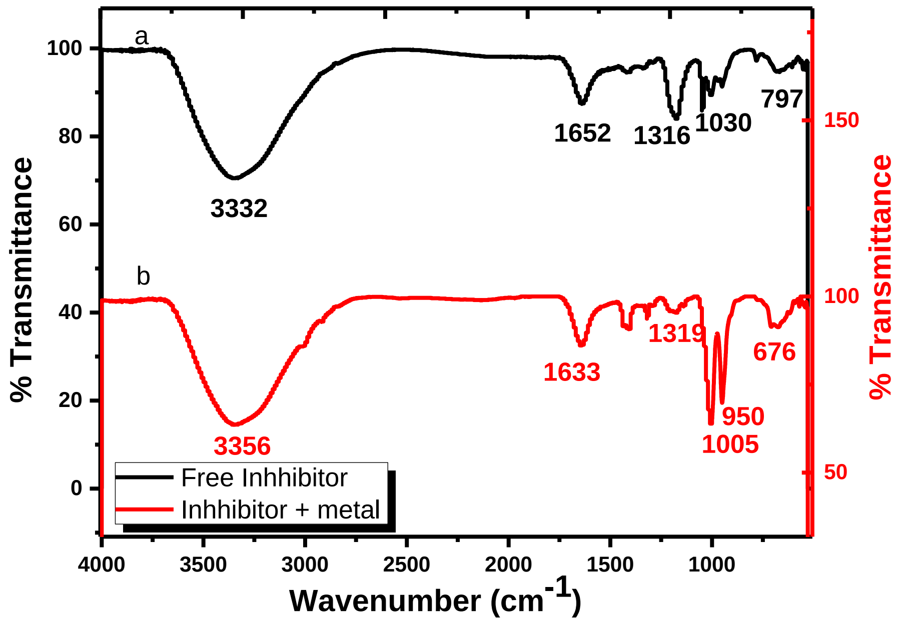


Figure 12. FT-IR spectra of expired nizatidine drug (a) black spectrum line and formed film of expired nizatidine drug on α-brass surface (b) the red spectrum line

Slika 12. FT-IR spectri isteklog nizatidinskog leka (a) crna linija spektra i formiran film isteklog leka nizatidina na površini α -mesinga (b) crvena linija spectra

3.9. AFM analysis

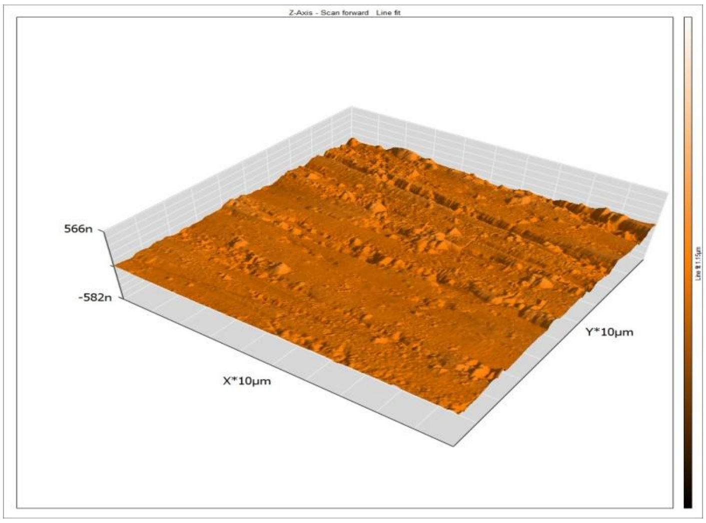
This method gives a map about the α-brass interface where roughness is indicating with an excessive resolve [50]. The 3D images of AFM shown in Figure 13.

The roughness calculated from the AFM image have summarized in Table 9. From the table, the surface of the alpha brass is smoother than in the existence of the expired nizatidine drug due to the expired nizatidine drug adsorption therefore the acid attack is reduced

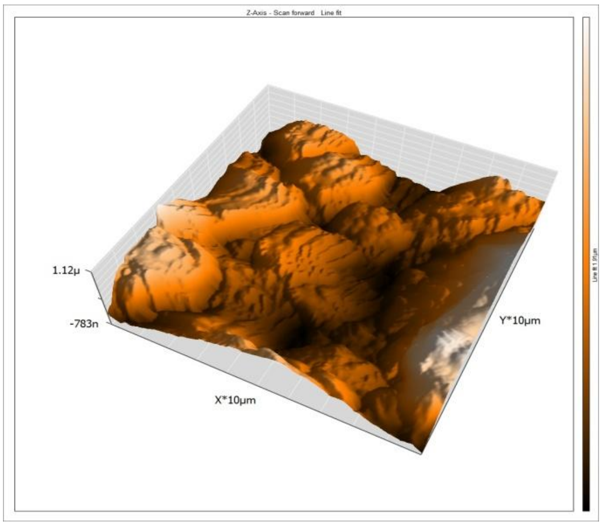
Table 9. AFM data for α-brass interface attendance and lack expired nizatidine.

Tabela 9. AFM podaci za prisustvo a-mesinga i nedostatak isteklog nizatidina.

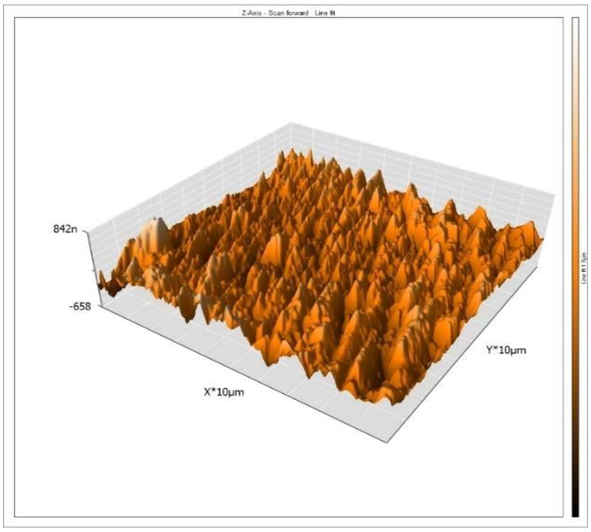
Sample	Average roughness (Sa) nm
Free	15
Blank	302
Expired nizatidine	37



a) Free



b) Blank



c) 300 ppm expired nizatidine drug

Figure 13. (3D) AFM images of α-brass without acid a) (free), α-brass in 1M HCl b) (blank), and c) α- brass in 1M HCl + 300 ppm of expired nizatidine drug for 24 hours at 25^{o}C

Slika 13. (3D) AFM slike α-mesinga bez kiseline a) (slobodan), α-mesing u 1M HCl b) (prazan) i c) α-mesing u 1M HCl + 300 ppm isteklog leka nizatidina tokom 24 sata na 25^{0}C

3.10. Energy Dispersion Spectroscopy (EDX) Studies

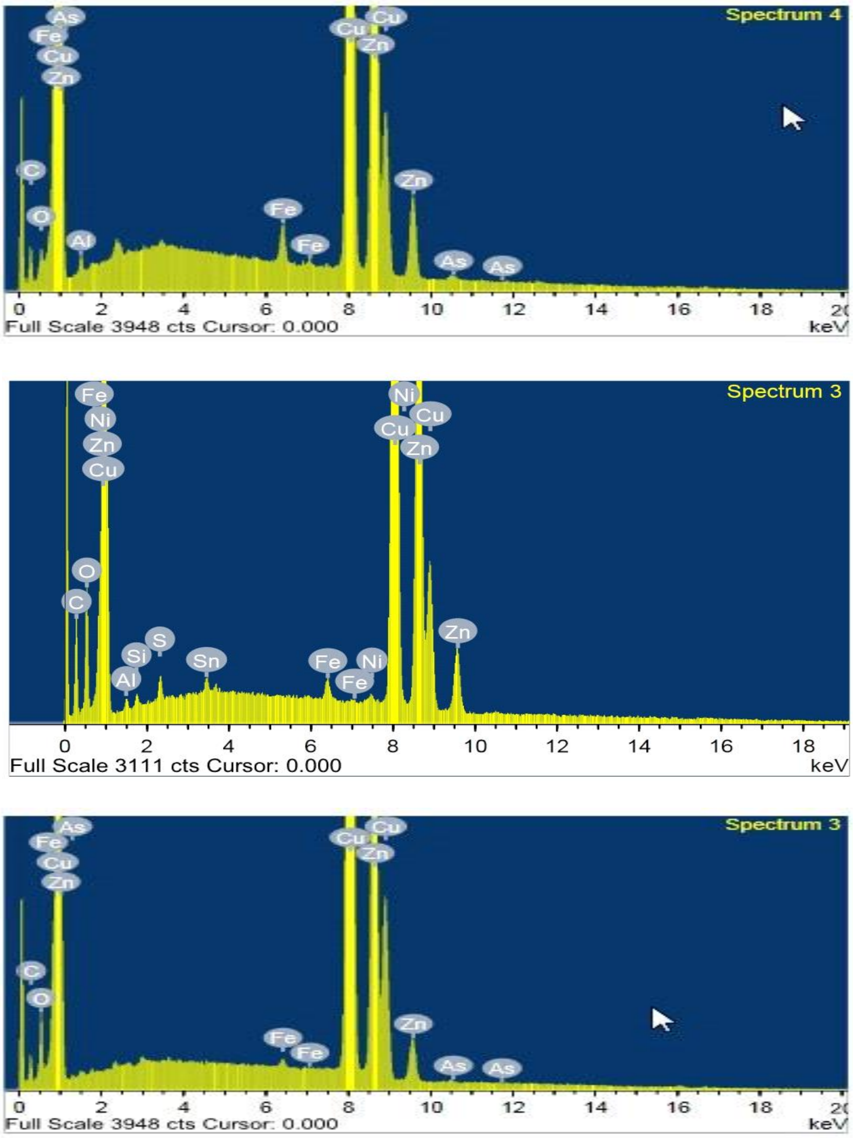
Fig. (14.a) shows the EDX examination result on the composition of α-brass with and without expired nizatidine drug. The EDX examination titles that only Fe and O were identified, which indicate that the passive film includes only Fe_2O_3. Fig. (14.b) EDX examination of α-brass in 1M HCl only and Fig. (14.c) displays the EDX of α-brass in 1M HCl in the presence of 300 ppm of expired nizatidine drug. The spectrum shows attached lines, indicating the presence of Cu (owing to the copper atoms of expired nizatidine). These result shows that the Cu and Zn metals covered the α-brass.

Table 10 shows weight % composition of α-brass after dipping in 24 hours in HCl with and without drug nizatidine.

Table 10. Weight % of α-brass after 24 h of dipping in 1M HCl with and without 300 ppm of the nizatidine drug

Tabela 10. Težina% α-mesinga nakon 24 sata uranja-nja u 1M HCl sa i bez 300 ppm nizatidin leka

Mass (%)	Cu	Zn	Fe	C	O
Free	60.78	32.72	0.79	3.48	1.13
Blank	54.57	25.78	0.78	10.41	7.85
Nizatidine	42.5	22.3	--	30.2	13.1



(a)

(b)

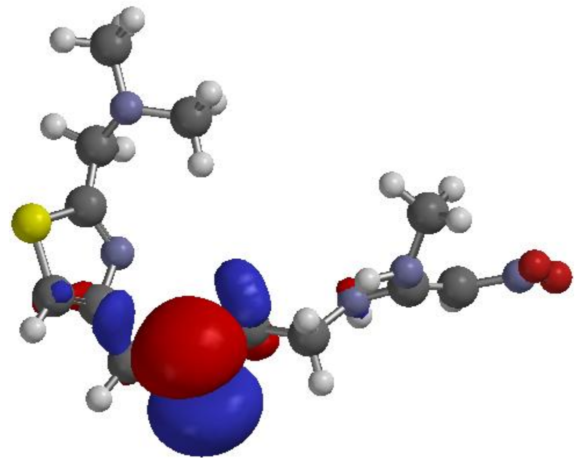
(c)

Figure (14) (a) EDX on α-brass (free) (b) α-brass in1M HCl (blank) (c) α-brass in 1M HCl with the presence of 300 ppm of expired nizatidine drug

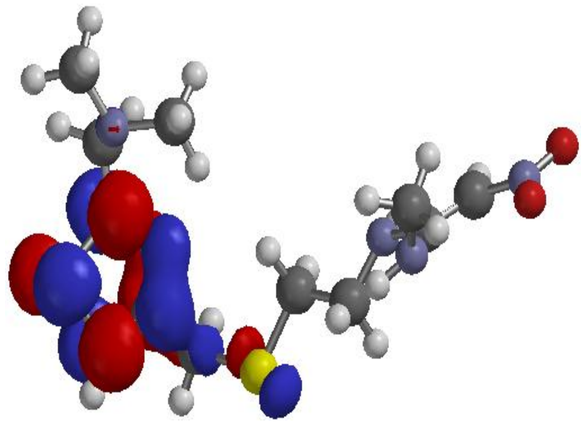
Slika 14. (a) EDX za α-mesing (slobodan) (b) α-mesing u 1M HCl (prazan) (c) α-mesing u 1M HCl sa prisustvom 300 ppm isteklog nizatidin leka

4. QUANTUM CHEMICAL CALCULATIONS

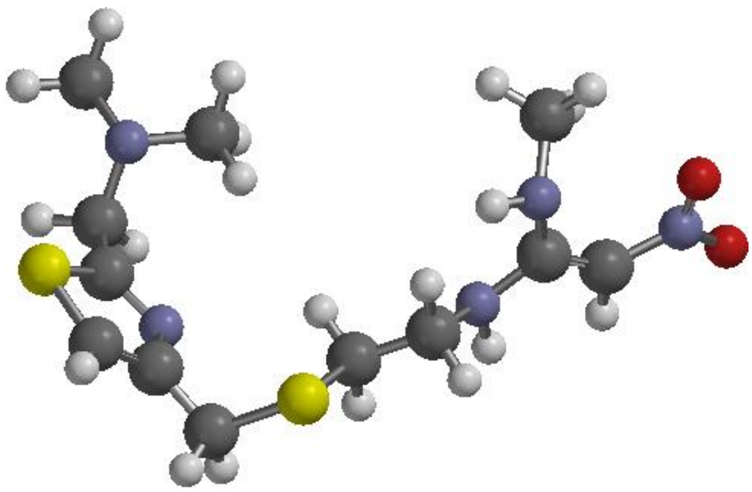
The energy of frontier molecular orbitals can be associated with the reactivity of compounds and the corrosion inhibitive power of inhibitors [51]. The obtained data given in Table 11 such as LUMO and HOMO forms (E_{HOMO} and E_{LUMO}) and energy gap ΔE are the output of the DFT calculations. Generally, the inhibitor's active power is always associated with E_{HOMO} and E_{LUMO} [52]. Higher adsorption can be indicating from the higher value of E_{HOMO}, which means higher capacity of inhibitors to donate electrons in certain chemical interaction. Whereas, the low values of E_{LUMO} is indicative of the higher affinity of the inhibitor to accept electrons under some chemical interaction conditions. The energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), the lesser ΔE, the easier the electron transfer from HOMO to LUMO and the higher adsorption ability of the expired nizatidine drug on brass, hence the IE will be greater. All outcome data in Table 11 displayed that the expired nizatidine drug has the lowest total energy which means that the adsorption of the expired nizatidine drug is higher Fig. (15) provides the electron density maps of HOMO and LUMO for the tested expired nizatidine drug.



HOMO



LUMO



Molecular orbital

Figure 15- (HOMO) and (LUMO) of molecular orbit

Slika 15. HOMO i LUMO molekularne orbitale

Table 11. Data obtain from quantum chemical properties for expired nizatidine drug.

Tabela 11. Podaci dobijeni iz kvantnih hemijskih svojstava za istekli lek nizatidin.

$E_{HOMO,}$ (ev)	-9.40
$E_{LUMO,}$ (ev)	-0.99
ΔE, (E_L-E_H)	8.41
μ, (Dipole moment)	8.530

5. INHIBITION MECHANISM

Considering the result data of the tests in our study, we explore the mechanism of dissolution protection of α-brass in 1M HCl by expired nizatidine drug. The interactive drug molecules displaced the water molecules located at brass/solution interface. In general, it is possible that the adsorption of drug at the brass / solution interface is the first step in the mechanism of action of drug in destructive environments. The adsorption of the drug molecules at the brass / solution interface may due to: "i) Electrostatic attraction among inhibitor and brass molecules ii) Interaction of unshared pairs of electrons in the expired nizatidine drug with the brass iii) Interaction of electrons iii) Interaction of electrons π with brass" vi) A summation of the preceding. The expired nizatidine drug action mechanism for α-brass in 1HCl was discussed in terms of physical adsorption on the α-brass interface. This proved from the effect of temperature (%IE decreases by raising temperature). The α-brass surface with its positive charge prefers the adsorption of Cl^- to produce a negative charge surface. This molecule (nizatidine) will present in the protonated form, so it can adsorb directly on the negative surface of α-brass [53] in acidic medium by electrostatic attraction as shown below.

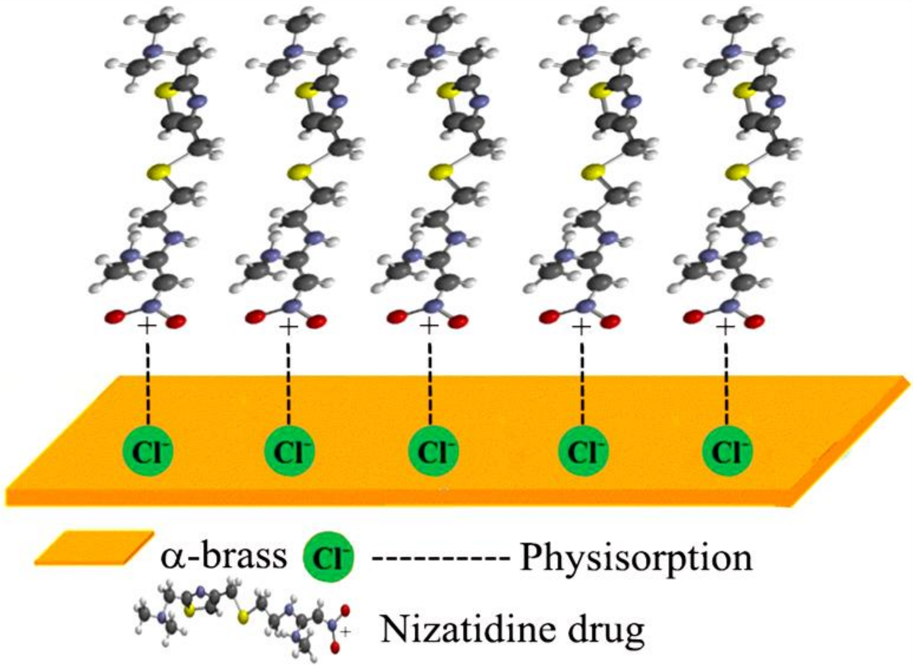


Table 12 shows a comparison %IE with presence of different drugs. The present nizatidine gives significantly important corrosion % IE compared to other drugs. Thus, the present nizatidine drug can utilized as corrosion inhibitor with promising results.

Table 12. Performance comparison of some expired drugs as corrosion inhibitors

Tabela 12. Poređenje performansi nekih lekova sa istekom roka trajanja kao inhibitora korozije

Inhibitor (drug)	sample	%IE	References
Penciillin G	mild steel	73.7	54
Domperidone	Al	89.1	55
Cloxacillin	mild steel	81.0	56
Pantoprazole	Al	59.0	57
Quinoline	mild steel	88.7	58
Nizatidine	α-brass	95.0	present work

6. CONCLUSIONS

The investigated expired nizatidine drug were investigated under conditions in 1 M HCl. From the obtained data of the study, the percentage IE from chemical and electrochemical tests were best agreement and the potential of nizatidine drug improves with lowering temperature and raising the doses of expired nizatidine in aggressive environment. PP tests exposed that nizatidine drug function as mixed kind. The obtained data from EIS test runs parallel with PP tests. The adsorption procedure conforms Langmuir isotherm. FTIR, EDX and AFM analyses also prove the formation of protective film on the surface of brass interface in 1M HCl.

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IZVOD

NIZATIDIN LEK KAO EKOLOŠKI INHIBITOR KOROZIJE ZA LEGURE α-MESINGA U VODENIM RASTVORIMA

Istekli lek nizatidine (END) proučavan je kao inhibitor α-mesinga u 1M HCl korišćenjem gubitka težine (WL) i elektrohemijskim metodama, naime, AC impedancijom (EIS), potenciodinamičkom polarizacijom (PP) i testovima elektrohemijske frekventne modulacije (EFM). Efikasnost zaštite (% IE) poboljšana je povećanjem doze isteklog leka nizatidina i smanjuje se s povećanjem temperature. Efikasnost zaštite (% IE) dostiže maksimalnu vrednost 95% pri većoj dozi istrošenog leka nizatidina na 25^{0}C. Podaci PP pokazali su da se lek nizatidin ponaša kao lek mešovite vrste. Zaštita od korozije α -mesinga od strane leka nizatidina može da se uklapa u adsorpcionu sposobnost molekula leka nizatidina na reaktivna mesta α-mesingove površine. Adsorpcija leka sledi Langmuirovu izotermu adsorpcije. Ispitivana je površinska morfologija α-mesinga. Rezultati dobijeni različitim metodama se odlično slažu.

Ključne reči: *Inhibicija kiseline, α-mesing, Nizatidin, EFM, EIS, AFM, FTIR.*

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