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Moringa oleifera plant extract as a copper corrosion inhibitor in binary acid mixture (HNO₃ + H₃PO₄)

ABSTRACT

The behavior of Cu in 1 M mixture of nitric and phosphoric acids containing different concentrations of moringa oleifera leaves (MOL) extract has been studied by weight loss (WL) and electrochemical techniques [potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM)]. The maximum inhibition efficiency was found to be 89% at concentration 0.300 mol L⁻¹ of the extract at 298K after 3 hours immersion period. The inhibition efficiency (IE) increased with increasing the extract concentration while decreased with increasing the temperature indicates that the extract is physically adsorbed on Cu surface. The adsorption of the extract follows Langmuir adsorption isotherm. Some thermodynamic parameters of activation and adsorption processes were also determined and discussed. Surface analysis was also studied.

Keywords: Copper corrosion; (HNO₃ + H₃PO₄), Moringa oleifera leaves extract; EIS, EFM, AFM, SEM.

1. INTRODUCTION

Copper and its alloys are widely used materials for their excellent electrical and thermal conductivities in many applications such as electronics and recently in the manufacture of integrated circuits [1-4]. Cu is relatively noble metal, requiring strong oxidants for its corrosion or dissolution. The most widely used corrosive solution contains nitric acid, so this medium has induced a great deal of research on copper corrosion [5-17]. The present study used a mixture of concentrated nitric acid and phosphoric acid to test the strength and efficiency of the inhibitor and the metal under extremely hard acidic conditions. One of the most important methods in the corrosion protection of Cu is the use of organic inhibitors. These last decades, researches are reoriented to the application of non-toxic inhibitors called green or eco-friendly environment inhibitors. Natural plants were added in the form of extracts, oil or pure compounds, may play a major role to keep the

environment more healthy, safely and under pollution control. Among the various natural plant extracts products, MOL extract [18] was used as corrosion inhibitor. The use of these natural compounds extracted from plants as corrosion inhibitors have been reported by several authors [19-26].

2. EXPERIMENTAL METHODS

2.1. Materials

All chemicals were of analytical grade. Cu with 99.8 % purity was used. Approximately 1 mol L⁻¹ HNO₃/H₃PO₄ mixture was prepared by diluting the appropriate volume of the concentrated chemically pure grade acid 70% and 85%, with bi-distilled water. The Cu specimens were rectangular of (20 mm x 20 mm x 2 mm). A WL method was used to determine the IE based on the Cu weights in the absence and presence of MOL extract as inhibitor.

2.2. Preparation of MOL extract

The present investigation was carried out using the plant namely MOL. The used parts were the leaves of MOL tree. The sample were picked from the trees of Talkha sanitation plant and ground into a fine powder to give 500 g of powdered materials, a known quantity of the material was Soxhletated using bi-distilled water. Finally the extract was lyophilized, weighed and preserved at 4° C and kept for use when required [27]

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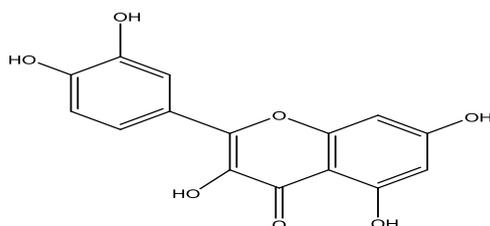
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2.3. Weight Loss (WL) Method

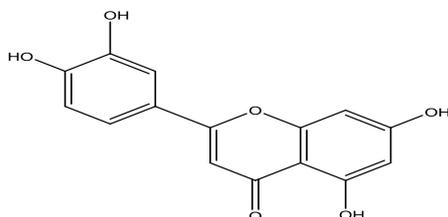
The Cu specimens were abraded with successive emery papers, degreased in acetone, rinsed in bi-distilled water and finally dried and weighed. The test pieces were suspended by suitable glass hocks, and under the surface of the test solution by about 1 cm. WL measurements were performed for 3 hours at the temperature range from 25–45°C. The average WL at a certain time for each set of the six samples was taken.

2.4. Electrochemical method

The electrochemical measurements were performed in a conventional three-electrode electrochemical cell, consisting of platinum electrode, as an auxiliary electrode, saturated calomel electrode (SCE), as the reference and Cu metal as the working electrode. The working electrode was abraded with emery papers before each measurement. The chemical structures, names, molecular weights and molecular formulas of the main components present in MOL extract are presented below:



Quercetin, $C_{15}H_{10}O_7$, 302.2357 g/mol



Luteolin, $C_{15}H_{10}O_6$, 286.2363 g/mol

2.5. Thermodynamic study

Parameters such as temperature, equilibrium constant (K_{ads}) and change of Gibbs free energy for adsorption (ΔG_{ads}°) are required for thermodynamic investigation. The value of ΔG_{ads}° is an indicator about the type of interaction between inhibitor and metal surface, whether it shows a chemical or physical adsorption. The value of K_{ads} obtained from the proposed model of adsorption isotherm can be assumed as the K_{ads} required in the thermodynamic study [28]. The thermodynamic expression required to perform the type of adsorption in relation to corrosion inhibition is described as follows:

$$\Delta G_{ads}^{\circ} = -RT \ln (55.5 K_{ads}) \quad (1)$$

($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $T = \text{temperature}$; $55.5 = \text{concentration of water (mol/L) in solution}$).

3. RESULTS AND DISCUSSION

3.1. Weight loss (WL) method

Figure 1, shows the variation of WL of Cu with time in $1 \text{ mol L}^{-1} \text{ HNO}_3/\text{H}_3\text{PO}_4$ mixture containing various concentrations of the extract at 289 K. From the plots, it is evident that the WL of Cu decreased with the increasing of extract concentration. The degree of surface coverage (θ) and (% IE) were calculated using the following equation:

$$\% \text{ IE} = \theta \times 100 = [1 - (CR_{inh} / CR_{free})] \times 100 \quad (2)$$

where CR_{free} and CR_{inh} , are the corrosion rates in the absence and in the presence of MOL extract, respectively. It can be seen that the maximum IE of 89% is achieved at 0.300 mol L^{-1} of extract concentration and % IE increases with increasing the extract concentration. The (CR) and the (%IE) at different concentrations of extract for the corrosion of Cu after 90 min of immersion in $1 \text{ mol/L HNO}_3/\text{H}_3\text{PO}_4$ mixture at 298 K were presented in Table 1. Arrhenius plots and the activation parameters for extract adsorption on Cu in $1 \text{ mol L}^{-1} \text{ HNO}_3/\text{H}_3\text{PO}_4$ mixture in absence and presence of various concentrations of MOL extract were presented in Table 2 and shown in Figures 2 and 3.

Table 1. Corrosion Rate (CR) and inhibition efficiency (%IE) at different concentrations of extract for the corrosion of Cu after 90 min of immersion in $1 \text{ mol/L HNO}_3/\text{H}_3\text{PO}_4$ mixture at 298 K

Tabela 1. Koroziona brzina (CR) i efikasnost inhibitora (% IE) kod različitih koncentracija inhibitora za koroziju bakra posle 90 minuta potapanja u smeši $1 \text{ mol/L HNO}_3/\text{H}_3\text{PO}_4$ na 298 K

Conc., mol L^{-1}	CR, $\text{mg cm}^{-2} \text{ min}^{-1}$	% IE
Blank	0.0242	--
0.050	0.0106	56.3
0.100	0.0076	68.4
0.150	0.0074	74.1
0.200	0.0049	79.8
0.250	0.0041	83.1
0.300	0.0026	89.3

Table 2. Activation parameters for the adsorption of extract on Cu in $1 \text{M HNO}_3/\text{H}_3\text{PO}_4$ mixture in absence and presence of various concentrations of extract

Tabela 2. Parametri aktivacije za adsorpciju ekstrakta na Cu u smeši $1 \text{M HNO}_3/\text{H}_3\text{PO}_4$ u odsustvu i prisustvu različitih koncentracija ekstrakta

Conc., mol L^{-1}	E_a^* , kJ mol^{-1}	ΔH^* , kJ mol^{-1}	$-\Delta S^*$, $\text{J mol}^{-1} \text{ K}^{-1}$
Blank	70.5	29.5	260.6
0.050	88.9	37.5	262.5
0.100	94.2	38.4	263.9
0.150	91.0	39.8	265.7
0.200	103.7	43.9	266.4
0.250	110.5	46.9	266.5
0.300	123.5	52.5	266.6

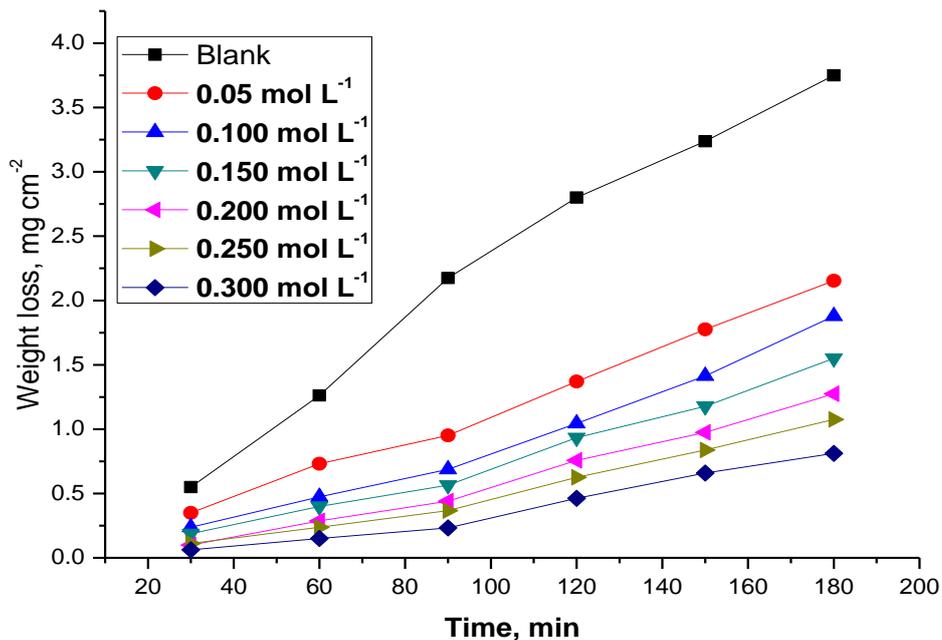


Figure 1. WL-time curves for the corrosion of Cu in 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ mixture in the absence and presence of different concentrations of extract at 298 K

Slika 1. Kriva WL - vreme za koroziju Cu u 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ smeši u odsustvu i prisustvu različitih koncentracija ekstrakta biljke na 298K

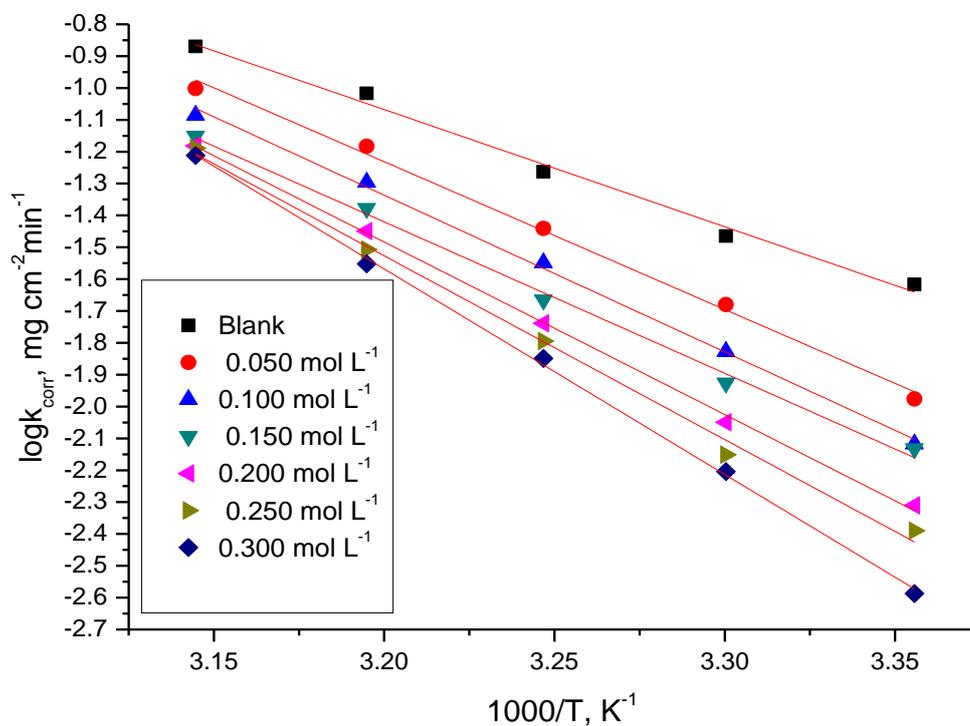


Figure 2. Arrhenius plots for Cu after 90 minute of immersion in 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ mixture in the absence and presence of various concentrations of the extract

Slika 2. Arrheniusove krive za Cu nakon 90 minuta uranjanja u smešu 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ u odsustvu i prisustvu različitih koncentracija ekstrakta

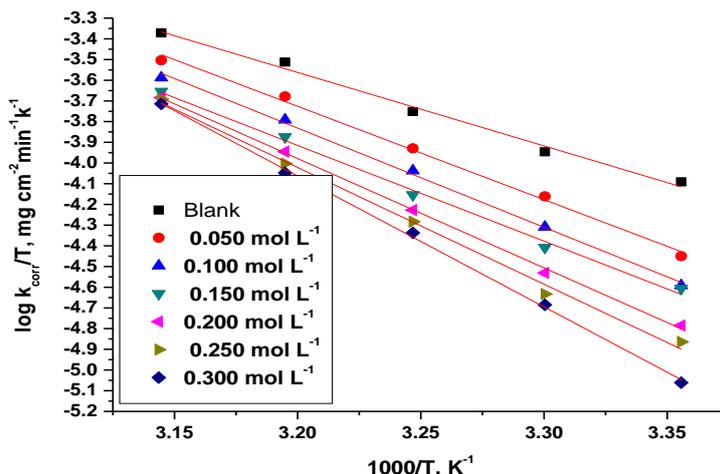


Figure 3. Transition plots for Cu after 90 minute of immersion in 1M HNO₃/H₃PO₄ mixture in the absence and presence of various concentrations of the extract

Slika 3. Prelazne krive za Cu posle 90 minuta potapanja u smešu 1M HNO₃/H₃PO₄ u odsustvu i prisustvu različitih koncentracija ekstrakta

3.2. Adsorption isotherms

Adsorption isotherm values are important to explain the mechanism of corrosion inhibition of organo-electrochemical reactions. The most frequently used isotherm is the Langmuir isotherm (Figure 4):

$$C/\theta = 1/K_{ads} + C \tag{3}$$

Where, C is the inhibitor concentration in the bulk of the solution, θ is surface coverage and $K_{ads} = 1/\text{intercept}$. ΔG°_{ads} values at all studied temperatures can be calculated from the following equation:

$$\Delta G^{\circ}_{ads} = -RT \ln (55.5K_{ads}) \tag{4}$$

Where R is the universal gas constant, T is the absolute temperature and 55.5 is molar concentration of water in the solution in M/L. The heat of adsorption (ΔH°_{ads}) was calculated according to Van't Hoff equation:

$$\text{Log } K_{ads} = (-\Delta H^{\circ}_{ads} / 2.303 RT) + \text{constant} \tag{5}$$

The values of ΔS°_{ads} can be calculated using the following equation:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T \Delta S^{\circ}_{ads} \tag{6}$$

Thermodynamic parameters for the adsorption of extract on Cu in 1M HNO₃/H₃PO₄ mixture at different temperatures were listed in Table 3.

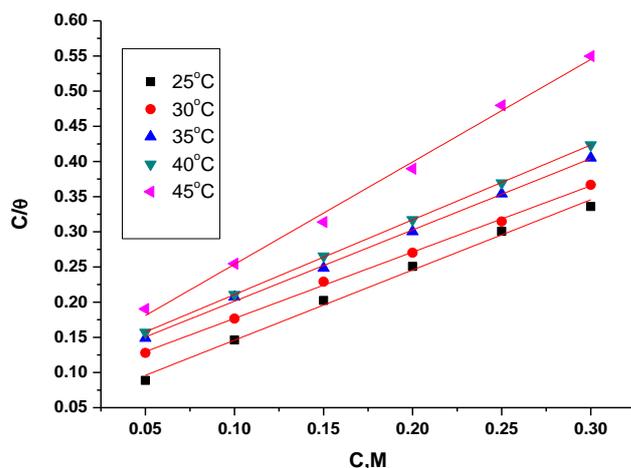


Figure 4. Langmuir adsorption isotherm of the extract on Cu in 1M HNO₃/H₃PO₄ mixture at different temperatures

Slika 4. Langmuirova adsorpcijska izoterma ekstrakta na Cu u smeši 1M HNO₃/H₃PO₄ na različitim temperaturama

Table 3. Thermodynamic adsorption parameters for the adsorption of the extract on Cu in 1M HNO₃/H₃PO₄ mixture at different temperatures

Tabela 3. Termodinamički parametri za adsorpciju ekstrakta na Cu u smeši 1M HNO₃/H₃PO₄ na različitim temperaturama

$-\Delta S_{ads}^{\circ}$, J mol ⁻¹ K ⁻¹	$-\Delta H_{ads}^{\circ}$, kJ mol ⁻¹	$-\Delta G_{ads}^{\circ}$, kJ mol ⁻¹	K_{ads} , M ⁻¹	Temp., K
44.9	30.9	17.6	21.70	298
48.0		16.4	12.10	303
47.9		16.2	10.00	308
46.6		16.3	9.560	313
45.4		16.5	9.240	318

The negative values of ΔG_{ads}° reflect that the adsorption of studied extract on Cu in 1M HNO₃/H₃PO₄ mixture is spontaneous process [29]. ΔG_{ads}° values increase (become less negative) with an increase of temperature which indicates the occurrence of exothermic process due to the extract desorption from the Cu surface [30]. It is usually accepted that the value of ΔG_{ads}° around -20 kJ mol⁻¹ or lower indicates the electrostatic

interaction between charged metal surface and charged organic molecules in the bulk of the solution [31]. The ΔH_{ads}° value was obtained from the slope of the line in Fig.5. The negative sign of ΔH_{ads}° reveals that the adsorption of extract molecules is an exothermic process. Generally, an exothermic adsorption process suggests either physisorption or chemisorption while endothermic process is attributed to chemisorptions [32]. Generally, enthalpy values up to 41.9 kJ mol⁻¹ are related to the electrostatic interactions between charged molecules and charged metal (physisorption) while those around 100 kJ mol⁻¹ or higher are attributed to chemisorption. In the case of investigated extract; the absolute values of enthalpy are relatively low, approaching those typical of physisorption. The value of ΔS_{ads}° in the presence of the investigated extract is large and negative that is accompanied with exothermic adsorption process [33]. The experimental data give good curves fitting for the applied adsorption isotherm as the correlation coefficients (R^2) were in the range 0.950-0.997. K_{ads} values decrease with the increase of temperature from 25 to 45°C.

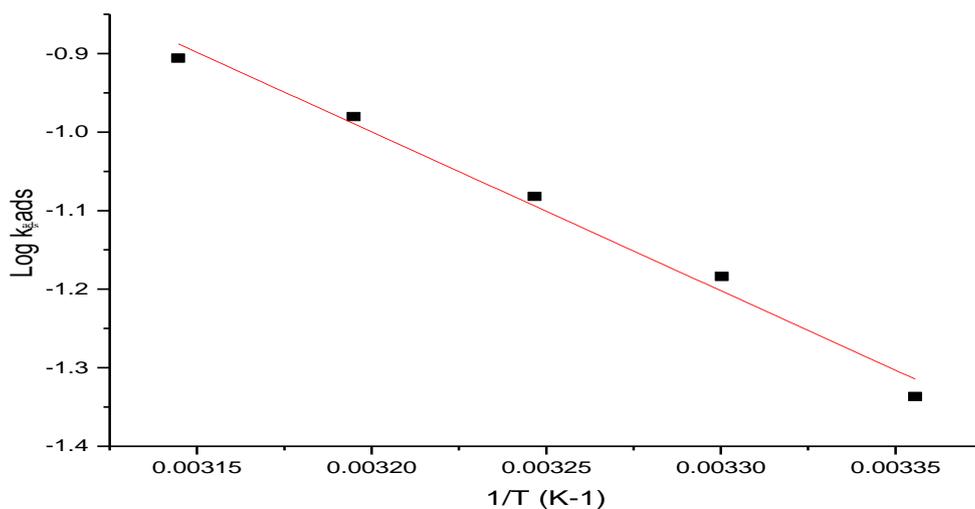


Figure 5. Log K_{ads} was plotted against $1/T$ (K⁻¹) for MOL extract

Slika 5. Log K_{ads} je prikazan u odnosu na $1/T$ (K⁻¹) za MOL ekstrakt

3.3. Potentiodynamic polarization (PP) measurements

Polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions. Figure 6 presents the results of the effect of the extract on the cathodic and anodic polarization curves of Cu in 1M HNO₃/H₃PO₄ mixture. It could be observed that both the cathodic and anodic reactions were suppressed with the addition of investigated

extract, which suggested that extract components reduced anodic dissolution and also retarded the oxygen reduction reaction. Electrochemical corrosion kinetics parameters, i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_a , β_c) and corrosion current density (i_{corr}) obtained from the extrapolation of the polarization curves were given in Table 4. The values of β_a and β_c changed slightly with increasing inhibitor concentration indicated the influence of these compounds in the extract on the kinetics of metal

dissolution. Due to the presence of some active sites, such as aromatic rings, hetero-atoms in the studied compounds for making adsorption, they may act as adsorption inhibitors. The functional groups and structure of the extract play important roles during the adsorption process. On the other hand, an electron transfer takes place during adsorption of the neutral organic compounds at metal surface [34]. As it can be seen from Table 4, the studied extract reduced both anodic and cathodic currents with a slight shift in corrosion potential (23.5 mV). According to Ferreira and others [35], if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank solution, the extract can be seen as a cathodic or anodic type. The results obtained from Tafel polarization showed good agreement with the results obtained from WL method. The θ and % IE were calculated using the following equation:

$$\%IE = \theta \times 100 = [1 - (i_{\text{corr}}/i_{\text{corr}}^{\circ})] \times 100 \quad (7)$$

where i_{corr} and i_{corr}° are the current densities in presence and absence of extract, respectively.

Table 4. Effect of concentrations of extract on the (E_{corr}), (i_{corr}), (β_c , β_a), (k_{corr}), (θ), and (%IE) of Cu in 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ mixture at 298 K

Tabela 4. Uticaj koncentracija ekstrakta na (E_{corr}), (i_{corr}), (β_c , β_a), (k_{corr}), (θ), i (% IE) Cu u smeši 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ na 298 K

Conc mol L ⁻¹	i_{corr} $\mu\text{A cm}^{-2}$	E_{corr} mV vs SCE	β_a , mV dec ⁻¹	$-\beta_c$, mV dec ⁻¹	CR, mmy ⁻¹	θ	%IE
Blank	271.0	+0.5	610	400	138.6	---	---
0.050	104.0	+3.9	111	466	50.16	0.616	61.6
0.100	102.0	-4.2	102	479	48.89	0.624	62.4
0.150	91.0	-10.0	109	481	41.50	0.664	66.4
0.200	85.7	-12.0	111	481	40.27	0.683	68.3
0.250	84.1	-22.0	99	417	38.28	0.689	68.9
0.300	78.8	-24.0	92	418	35.70	0.709	70.9

3.4. Electrochemical impedance spectroscopy (EIS) measurements

Nyquist plots of Cu in uninhibited and inhibited acid solutions containing different concentrations of the extract are presented in Figure 7a. EIS spectra obtained consists of one depressed capacitive loop (one time constant in Bode-phase plot (Figure 7b)). The increased diameter of capacitive loop obtained in 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ mixture in presence of extract indicated the inhibition of corrosion Cu. The high frequency capacitive loop may be attributed to the charge transfer reaction. Corrosion kinetic parameters derived from EIS measurements and inhibition efficiencies are given in Table 5. Double

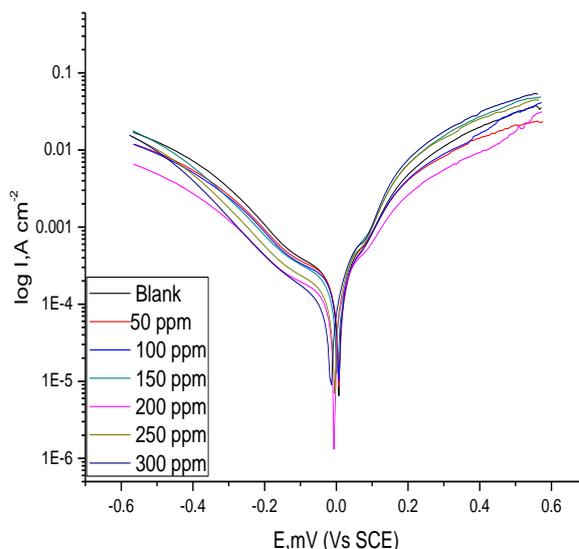


Figure 6. PP curves for the dissolution of Cu in 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ mixture in the absence and presence of different concentrations of extract at 298 K

Slika 6. PP krive za rastvaranje Cu u 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ smeši u odsustvu i prisustvu različitih koncentracija ekstrakta na 298 K

layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were obtained from EIS measurements as described elsewhere [36]. It is apparent from Table 5 that the impedance of the inhibited system amplified with the inhibitor the C_{dl} values decreased with inhibitor. This decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that extract molecules inhibit the Cu corrosion by adsorption at the metal/acid interface [37]. The depression in Nyquist semicircles is a feature for solid electrodes and often referred to as frequency dispersion and attributed to the roughness and other in homogeneities of the solid electrode [38].

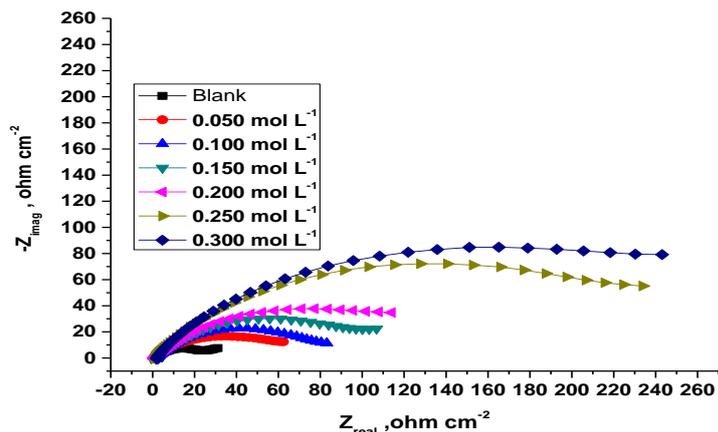


Figure 7a. The Nyquist plots for the corrosion of Cu in 1M HNO₃/H₃PO₄ mixture in the absence and presence of different concentrations of extract at 298 K

Slika 7a. Nyquist-ove krive za koroziju Cu u smeši 1M HNO₃/H₃PO₄ u odsustvu i prisustvu različitih koncentracija ekstrakta na 298 K

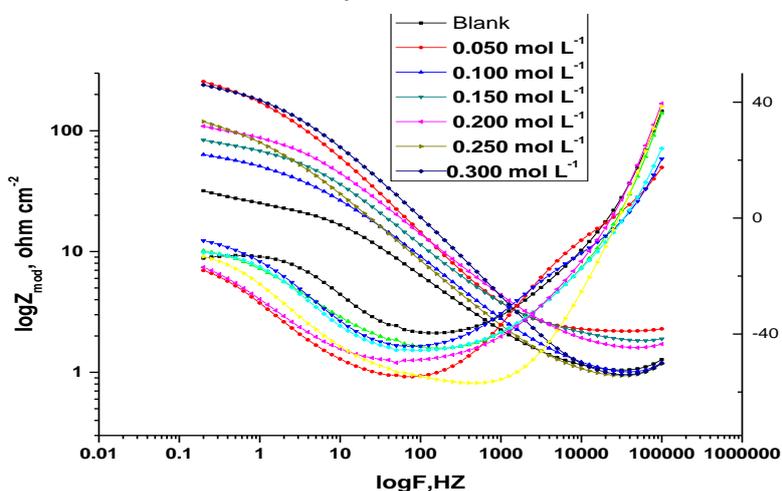


Figure 7b. The Bode plots for corrosion of Cu in 1M HNO₃/H₃PO₄ mixture in the absence and presence of different concentrations of extract at 298 K

Slika 7b. Bode-ove krive za koroziju Cu u smeši 1M HNO₃/H₃PO₄ u odsustvu i prisustvu različitih koncentracija ekstrakta na 298 K

Table 5. The EIS parameters for the corrosion of Cu in 1M HNO₃/H₃PO₄ mixture, in the absence and in the presence of different concentrations of extract at 298 K

Tabela 5. Parametri EIS za koroziju Cu u smeši 1M HNO₃/H₃PO₄ u odsustvu i u prisustvu različitih koncentracija ekstrakta na 298 K

Conc., mol L ⁻¹	R _{ct} , Ω cm ²	C _{dl} × 10 ⁴ , F cm ⁻²	θ	% IE _{EIS}
Blank	28.75	6.1149	-----	-----
0.050	63.85	5.8140	0.550	55.0
0.100	84.20	4.464	0.659	65.9
0.150	112.70	4.330	0.745	74.5
0.200	134.10	3.835	0.786	78.6
0.250	231.80	3.208	0.876	87.6
0.300	272.00	2.4083	0.894	89.4

In this behaviour of solid electrodes, the parallel network: charge transfer resistance-double layer capacitance is established where an inhibitor is present. For the description of a frequency

independent phase shift between an applied ac potential and its current response, a constant phase element (CPE) is used, which is defined in impedance representation as in the following equation:

$$Z_{CPE} = Y_0^{-1} (i\omega)^{-n} \quad (8)$$

Where, Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $i^2 = -1$ is the imaginary number and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [39]. Depending on the value of n , CPE can represent resistance ($n = 0$, $Y_0 = R$), capacitance ($n = 1$, $Y_0 = C$), inductance ($n = -1$, $Y_0 = L$) or Warburg impedance ($n = 0.5$, $Y_0 = W$). Figure 8 showed the electrical equivalent circuit employed to analyze the impedance spectra. Excellent fit with this model was obtained for all experimental data. The (θ) and % IE were calculated using the following equation:

$$\%IE = \theta \times 100 = [1 - (R_{ct}/R_{ct}^{corr})] \times 100 \quad (9)$$

where R_{ct} and R_{ct}^{corr} are the charge transfer resistances in absence and presence of extract, respectively.

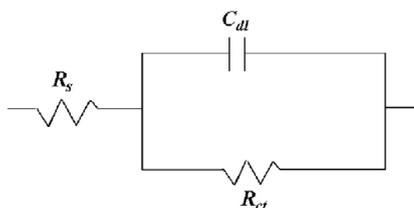


Figure 8: Equivalent circuit used to model impedance data

Slika 8: Ekvivalentno kolo koje se koristi za dobijanje modela impedanse

The results obtained from WL, PP and EIS techniques are in a good agreement but it is of interest to note that, the values of % IE given by electrochemical techniques are higher than those obtained by WL measurements; this may be due to the fact that the electrochemical measurements were carried out on freshly prepared solutions and are time independent.

3.5. Electrochemical frequency modulation (EFM) measurements

EFM is a non-destructive corrosion measurement like EIS; it is a small signal ac technique. Unlike EIS, however, two sine waves (at different frequencies) are applied to the cell simultaneously. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement [40]. The results of EFM experiments are a spectrum of current response as a function of frequency. The spectrum is called the intermodulation spectrum. The spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks (Figure 9) were used to calculate the corrosion current. The inhibition efficiencies, % IE increase with increasing the studied extract concentrations. Corrosion kinetic parameters, namely corrosion current density (i_{corr} , Tafel constants (β_a , β_c) and causality factors (CF-2, CF-3) were listed Table 6 as a function of concentration of the extract at 298 K. The causality factors in Table 6, which are very close to theoretical values according to the EFM theory, should guarantee the validity of Tafel slopes and corrosion current densities. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively [41].

Table 6. Electrochemical kinetic parameters obtained from EFM technique for Cu corrosion in 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ mixture in the absence and Presence of different concentrations of investigated extract at 298 K

Tabela 6. Elektrohemijski kinetički parametri dobijeni iz EFM tehnike za Cu koroziju u 1M $\text{HNO}_3/\text{H}_3\text{PO}_4$ smeši u odsustvu i prisustvu različitih koncentracija ekstrakta na 298 K

θ	IE%	C.R, mpy	CF-3	CF-2	β_a , mV dec ⁻¹	β_c , mV dec ⁻¹	i_{corr} , $\mu\text{A cm}^{-2}$	Conc., mol L ⁻¹
---	----	84.43	1.9	1.95	200	190	171.1	Blank
0.523	52.3	40.26	2.5	1.90	225	183	81.59	0.050
0.653	65.3	29.29	3.2	2.00	172	119	59.36	0.100
0.500	50.0	28.28	3.3	2.00	174	98	58.47	0.150
0.702	70.2	25.13	3.2	1.99	142	86	50.93	0.200
0.734	73.4	22.48	3.5	1.90	215	82	45.55	0.250
0.790	79.0	17.76	3.0	2.019	283	80	35.98	0.300

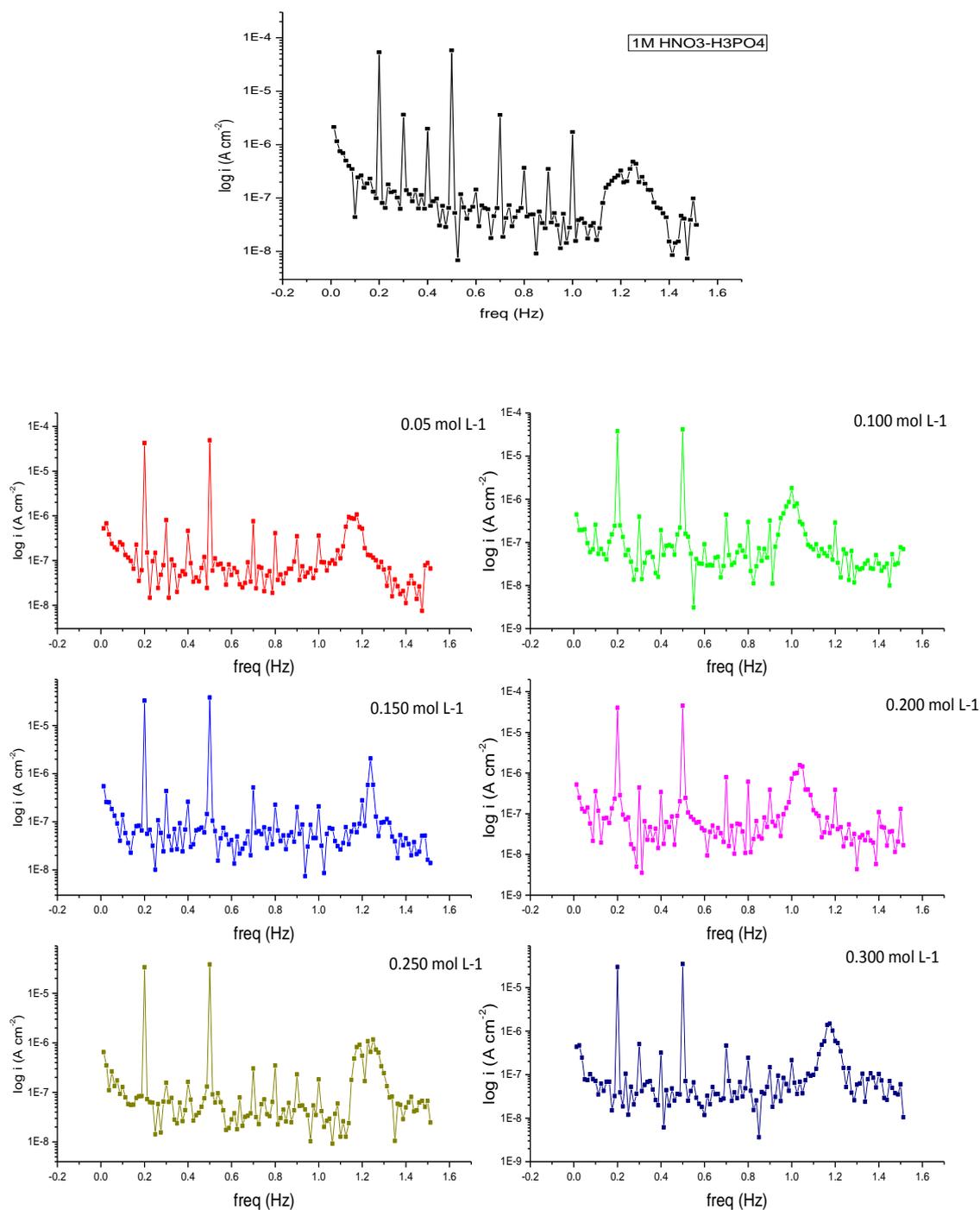


Figure 9. EFM intermodulation spectra of Cu in 1M HNO₃/H₃PO₄ mixture for extract at 298 K

Slika 9. EFM intermodulacijski spektri Cu u 1M HNO₃/H₃PO₄ za ekstrakt na 298 K

3.6. Surface Analysis [scanning electron microscopy (SEM) studies]

A photograph of the polished Cu surface before immersion in 1M HNO₃/H₃PO₄ mixture solution is shown in Figure 10. The photograph shows the surface was smooth and without pits. A photograph

of the Cu surface after immersion in 1M HNO₃/H₃PO₄ mixture solution is shown in Figure 11. The photograph revealed that, the surface was strongly damaged in the absence of MOL extract. A photograph of the Cu surface after immersion in 1M HNO₃/H₃PO₄ mixture solution containing 0.300

molL⁻¹ of extract is shown in Figure 12. It was found that the damage observed in figures disappeared and the surface was free from pits and it was smooth. It can be concluded from Figure 12 that corrosion decreased largely in the presence of extract hence corrosion was inhibited strongly when extract was present in the medium. In the

presence 0.300 mol L⁻¹ of extract, there is much less damage on the Cu surface, which further confirm the inhibit ion action. Also, there is an adsorbed film adsorbed on Cu surface .In accordance, it might be concluded that the adsorption film can efficiently inhibits the corrosion of Cu.

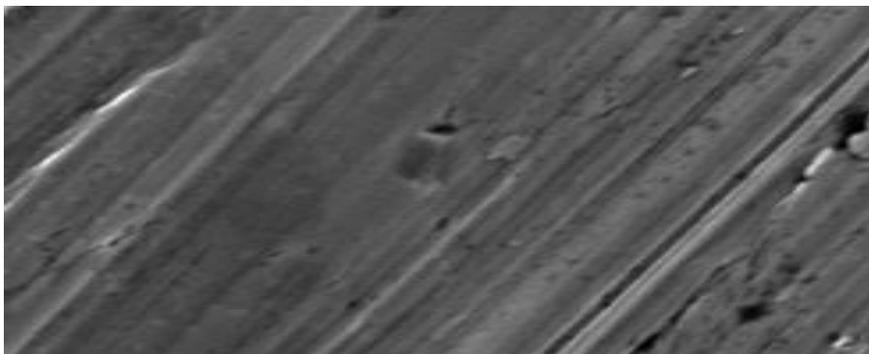


Figure 10. SEM micrographs of Cu surface before of immersion in 1M HNO₃/H₃PO₄ mixture solution

Slika 10. SEM mikrografija površine bakra pre potapanja u 1M rastvor smeše HNO₃/H₃PO₄

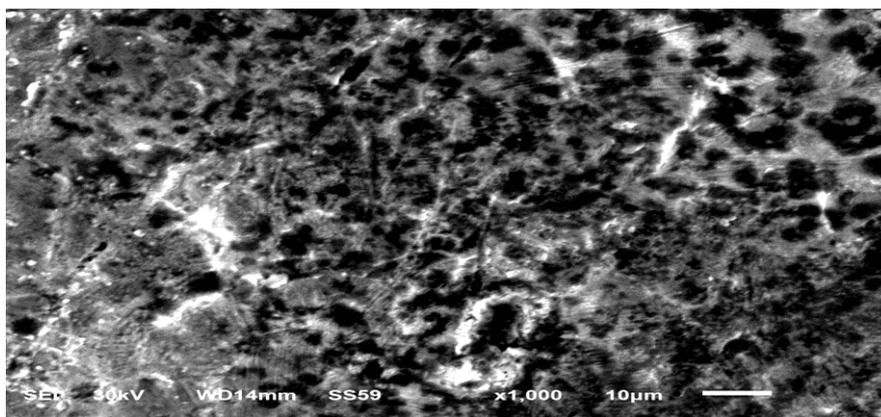


Figure 11. SEM micrographs of Cu surface after 10 h of immersion in 1M HNO₃/H₃PO₄ mixture

Slika 11. SEM mikrografija Cu površine nakon 10 h potapanja u smešu 1M HNO₃/H₃PO₄

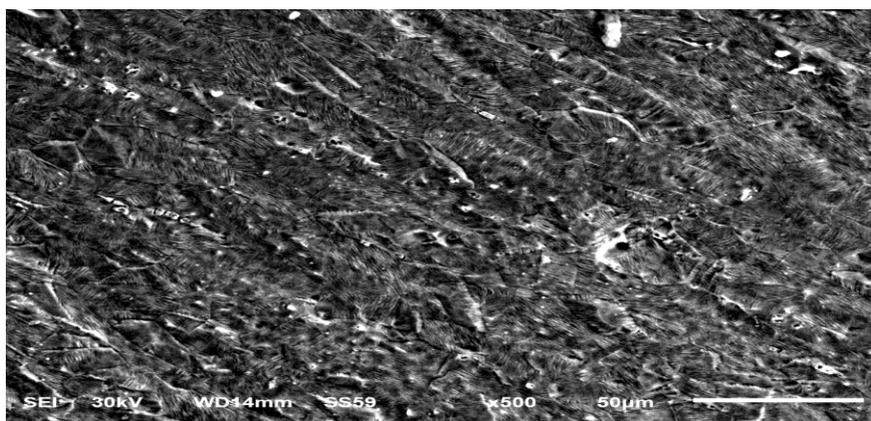


Figure 12. SEM micrographs of Cu surface after 10 h of immersion in 1M HNO₃/H₃PO₄ mixture + 0.300 mol L⁻¹ of MOL extract at 25°C

Slika 12. SEM mikrografija Cu površine nakon 10 h potapanja u smešu 1M HNO₃/H₃PO₄ + 0,300 mol L⁻¹ ekstrakta MOL-a na 25°C

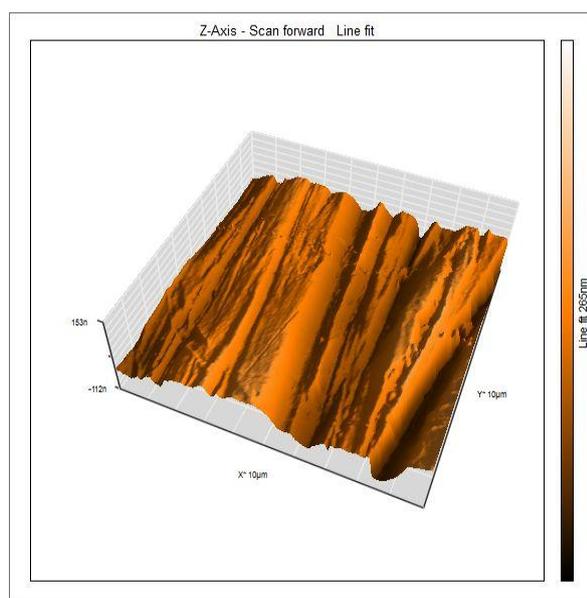
Atomic force microscopy characterization

AFM technique supplies photos with atomic or near-atomic-resolution surface topography which able to giving the surface roughness of coupons by the angstrom-scale. Atomic force microscopy (AFM) is a very higher resolution type of scanning probe microscopy on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit [42]. Fig.(13a) shows the three dimensional (3D) AFM morphologies for polished Cu surface as standard sample, Fig.(13b) shows surface immersed in 1M HNO₃/H₃PO₄ as blank sample and Fig.(13c) Cu surface immersed in 1M HNO₃/H₃PO₄ +0.300 mol L⁻¹ of MOL extract. AFM image analysis was carried out to obtain the roughness average (Sa) ,the root mean average (Sq) and the peak height (Sp) for the polished Cu (free sample), copper surface immersed in 1M HNO₃/H₃PO₄ (blank sample) and Cu surface immersed in 1M HNO₃/H₃PO₄+ 0.300 mol L⁻¹ of MOL extract. The obtained data from AFM analysis were listed in Table 7

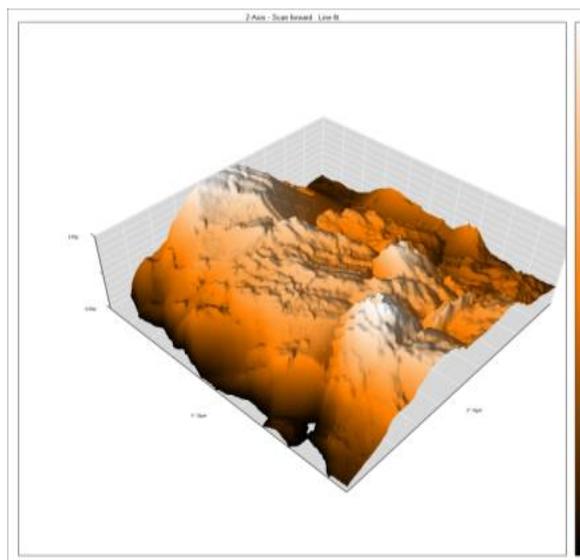
Table 7. AFM data for Cu surface with and without 0.300 mol L⁻¹ extract

Tabela 7. AFM podaci za Cu površinu sa i bez 0.300 mol L⁻¹ ekstrakta

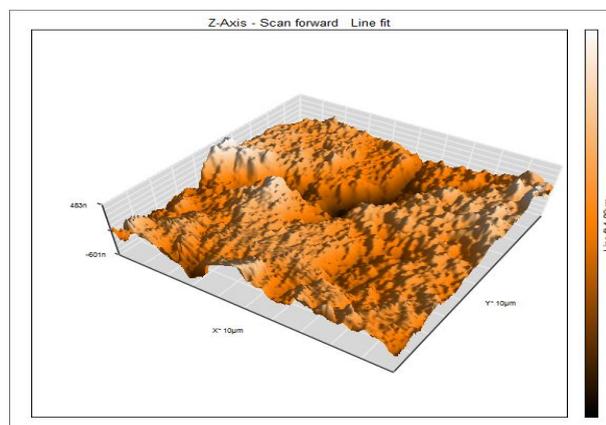
Sample	Sa	Sq	Sp
Free	21.18	25.34	40.51
Blank	697.2	809.72	1845.6
MOL extract	113.27	153.32	520.11



a) Free Cu - Slobodan Cu



b) blank - prazan



c) 0.300 mol L⁻¹ MOL extract

Fig. 13. Three dimensional (3D) AFM morphologies for polished Cu (a), blank (b) and in presence of 0.300 mol L⁻¹ extract (c)

Slika 13. Trodimenzionalne (3D) AFM morfologije za polirani Cu (a), prazan (b) i u prisustvu ekstrakta 0,300 mol L⁻¹ (c)

Mechanism of corrosion inhibition

Generally, it is assumed that the first stage in the action mechanism of the inhibition in acid medium is the adsorption of the inhibitor onto the metal surface. The process of adsorption is influenced by the nature and the charge of the metal, by the chemical structure of the organic inhibitor and the type of aggressive electrolyte. The charge of the metal surface can be determined from the potential of zero charge [43]. The Cu surface is positively charged in 1 M acidic solution. There is a tendency of the acid anions (NO₃⁻ or PO₄³⁻ ions) to be specifically adsorbed creating an excess negative charge towards the solution and

favor more adsorption of the protonated components [44]. The adsorption of extract components on Cu surface by following ways: (i) electrostatic interaction of protonated component molecules with preadsorbed NO_3^- or PO_4^{3-} ions (physisorption) (ii) interaction between unshared electron pairs of hetero-atoms (N,O,S) and vacant d-orbital of Cu-atoms (chemisorption) and (iii) donor–acceptor interactions between the π -electrons of aromatic ring and vacant d-orbital of Cu-atoms. The protonated sites of extract molecules may adsorb on the metal surface through a synergistic effect with pre-adsorbed NO_3^- or PO_4^{3-} . The accumulation of extra negative charges on the Cu surface can be transferred from the d orbital of Cu to unoccupied π^* (anti-bonding) of extract molecules (retro-donation). The combination of all ways of adsorption strengthens adsorption of extract molecules on Cu surface [45]. Finally, a layer of adsorbed extract film is formed on the Cu surface and acts as a barrier between the metal and corrosive medium, to prevent the corrosion of metal. On the basis of the above analysis and speculation, one can conclude that the studied extract is of mixed-type inhibitor, and the adsorption of the extract contains two modes of interaction, i.e. physisorption and chemisorption

4. CONCLUSIONS

The investigated extract (MOL) is considered a good corrosion inhibitor for Cu. The inhibiting action of this extract was increased with increasing the extract concentration while it decreased with increasing temperature. The %IE of this extract reached 89 % at 0.300 mol L^{-1} . The extract was adsorbed physically and spontaneously on copper surface following Langmuir adsorption isotherm. The charge transfer resistance (R_{ct}) increased while the capacitance double layer (C_{dl}) decreased by increasing the extract concentration. The surface analysis indicated the formation of protective film on the copper surface. Reasonably, good agreement was observed between the results obtained by both the WL and electrochemical measurements.

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IZVOD

EKSTRAKT BILJKE MORINGA OLEIFERA KAO INHIBITOR KOROZIJE BAKRA U MEŠAVINI BINARNE KISELINE ($\text{HNO}_3 + \text{H}_3\text{PO}_4$)

Ponašanje Cu u 1M mešavini azotne i fosforne kiseline, koje sadrže različite koncentracije ekstrakta lišća moringa oleifera (MOL), proučavano je gubitkom težine (WL) i elektrohemijskim tehnikama [potentiodinamička polarizacija (PP), elektrohemijska impedansna spektroskopija (EIS) i elektrohemijska modulacija frekvencije (EFM)]. Utvrđeno je da je maksimalna efikasnost inhibicije iznosila 89% pri koncentraciji od 0.300 molL^{-1} ekstrakta na 298K nakon 3 sata potapanja. Efikasnost inhibicije (IE) povećana je sa povećanjem koncentracije ekstrakta dok je smanjena povećanjem temperature što ukazuje na to da se ekstrakt fizički adsorbuje na Cu površini. Adsorpcija ekstrakta sledi Langmuirova izotermna adsorpcija. Određeni su i razmatrani određeni termodinamički parametri procesa aktivacije i adsorpcije. Ispitana je i analizirana i površina.

Ključne reči: korozija bakra; smeša $\text{HNO}_3 + \text{H}_3\text{PO}_4$, ekstrakt moringa oleifera; EIS, EFM, AFM, SEM.

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