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Testing the effectiveness of raspberry flower extract as an inhibitor of copper's corrosion in 3% NaCl

ABSTRACT

The paper presents an examination of the possibility of applying raspberry flower extract (Rubus idaeus L.) as a green inhibitor of general corrosion of copper in 3% NaCl. Raspberry flowers (Rubus idaeus L.) sort Polka were collected from the Moševac near Maglaj city, Bosnia and Herzegovina. Raspberry flower extract in ethanol was obtained by ultrasonic extraction. A significant content of polyphenol was found in the raspberry flower extract by UV/VIS spectrophotometry analysis.

Results obtained by DC techniques (by the methods of Tafel extrapolation, potentiodynamic polarization and linear polarization) prove that the corrosion rate decreases in the presence of the raspberry flower extract. Tests performed by the method of electrochemical impedance spectroscopy prove that the tested extracts slow down the kinetics of the corrosion process, which is visible through the increase in resistance. The results of the conducted tests prove that in an aggressive medium, such as 3% NaCl solution, Polka raspberry flower extract can be used as an inhibitor of copper's corrosion.

Keywords: *extraction, raspberry flower, inhibitor, Tafel extrapolation, potentiodynamic polarization, linear polarization, electrochemical impedance spectroscopy*

1. INTRODUCTION

Copper is a metal that has extensive application due to its good properties. It is used in electrical engineering to produce wires, sheets, pipes, and production of alloys. It is relatively resistant to the effects of the atmosphere and many chemicals. However, it is known to be subject to corrosion in aggressive environments. The use of copper corrosion inhibitors is necessary in these cases because the formation of a passive protective layer cannot be expected. The development of new environmentally-friendly corrosion inhibitors is directed towards natural biological, non-toxic, biodegradable molecules to preserve the environment. Therefore, intensive efforts are still being made to find new effective but non-toxic compounds.

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Plant extracts contain a large number of organic compounds, and one of many is phenolic compounds. Phenols are aromatic compounds with one or more hydroxyl groups (-OH) that bind directly to the carbon atom of the benzene ring. Some of them have been found to possess anticancer and antimutagenic properties as well as antioxidant properties. Some of them express the possibility of forming chelated complexes with metals [1].

According to previous research on the dissolution of copper in chloride medium, the anodic reaction is reversible mainly due to the strong, thermodynamically more favorable complexation of copper ions with chloride ions [2-4]. The cathodic response is dominated by oxygen reduction, which is considered to be irreversible. Copper with chloride ions can form several complexes [3]: $CuCl$, $CuCl_2^-$, $CuCl_3^{2-}$ or $CuCl_4^{3-}$. The formation of the CuCl layer takes place according to the reaction:

$$Cu + Cl^- \rightarrow CuCl \quad (1)$$

CuCl is poorly soluble in NaCl solution, resulting in the formation of a ion $CuCl_2^-$ complex:

$$CuCl + Cl^- \rightarrow CuCl_2^- \quad (2)$$

It is generally accepted that the anodic dissolution of Cu depends on the concentration of Cl^- ions and does not depend on the pH of the solution. At concentrations of Cl^- ions greater than 1 mol dm^{-3}, it is possible to form more complex complexes such as $CuCl_3^{2-}$ and $CuCl_4^{3-}$ [5-7].

The cathodic reaction in neutral solutions is:

$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \quad (3)$$

During hydrolysis $CuCl_2^-$ ions in NaCl solution can cause precipitation of copper (I) oxide:

$$2CuCl_2^- + H_2O \rightarrow Cu_2O + 2H^+ + 4Cl^- \quad (4)$$

or by direct oxidation of copper [4, 8, 9]:

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \quad (5)$$

When a passive film is created on a metal (e.g., Cu_2O) that does not have good protective properties, pitting corrosion will occur [10] in the presence of aggressive ions which is very dangerous because it quickly penetrates deep into the metal mass and can lead to cracking of the structure under stress. Pitting corrosion most often occurs during the transition from active to the passive state. Cu_2O stability depends on the concentration of chloride ions. The use of inhibitors and alloying reduces the possibility of pitting corrosion.

This paper presents the effect of Polka variety raspberry flower extract from the Moševac site near Maglaj, Bosnia and Herzegovina as an inhibitor of general corrosion of copper using electrochemical methods. Raspberry Polka is one of the best varieties of raspberries. It is an everbearing raspberry, a newer variety of raspberry, originally from Poland, created by the crossing of varieties: *Autumn Bliss, Lloyd George* and *Rubus crataegifolius*, introduced in 2001 and entered in the official registers in 2003. The specificity of the variety is that it can be grown without reinforcement. Raspberry flower extract is a relatively cheap, readily available, and renewable natural product rich in various organic compounds such as polyphenolic compounds, organic acids, vitamins, etc., which makes it a potential corrosion inhibitor.

2. EXPERIMENTAL PART

To examine the effect of raspberry (*Rubus idaeus* L.) flower extract, we used the 99.8% purity copper as the corrosion characteristics of copper. Raspberry flower extract in ethanol was obtained by ultrasonic extraction. Extraction was performed in the ultrasonic bath under defined conditions: frequency (20-40 kHz), power (250-500 W), temperature (40 ºC) and extraction time (30 min). Ethanol was used as the solvent. After treatment, the extract was filtered and evaporated to dryness. The extract obtained in this way was stored in dark bottles in a refrigerator at a temperature of +4 ºC. The content of total phenols in Polka raspberry flower extract was determined spectrophotometrically, on the PerkinElmer, Lambda 650, UV – VIS spectrophotometer device, by the Folin-Ciocalteu method. The results of total phenols analyzes in this extract is shown in Table 1.

Table 1. Content of total phenols in Polka raspberry flower extract obtained by methods ultrasonic extractions

Tabela 1. Sadržaj ukupnih fenola u ekstraktu cvijeta maline sorte Polka, dobijenog ultrazvučnom ekstrakcijom

Sample	A_1	A_2	A_3	mg/g extract		
UCPM	0,6824	0,6476	0,5939	159,17	150,55	137,24

Meaning of markings: UCPM – flower Polka Maglaj – ultrasonic;
A_1, A_2, A_3 - measured values of concentrations for replica samples (g dm^{-3})

The chemical composition of copper was tested at Kemal Kapetanović Institute in Zenica on the PerkinElmer, AA 800, Atomic Apsorption Spectrometry device.

Following polarization measurement methods were used in this research during electrochemical tests of the corrosion process by DC techniques:

- Tafel extrapolation method;
- potentiodynamic polarization method;
- linear polarization method.

To examine the corrosion process by AC - techniques was used electrochemical impedance spectroscopy (EIS). For testing the inhibitory effect of raspberry flower on corrosion of copper in 3%

NaCl solution were used copper samples of the following dimensions:

- Samples dimensions d = 15 mm and d from 1 to 2 mm were used for polarization tests.
- For the application of the electrochemical impedance spectroscopy method, samples dimensions 13x13 mm were used.

Before each measurement, the copper work surface was mechanically grinded with grindpaper of different grit and on the device, degreased in ethanol, and washed with distilled water. Copper polarization measurements by DC techniques were performed in a corrosion cell on a Potentiostat / Galvanostat device, PAR, model 263A-2, and PowerCORR® software package. The electrochemical cell contains three electrodes. A carbon electrode is used as an auxiliary electrode, and a saturated calomel electrode (SCE) is used as a reference electrode. The working electrode (1,0 cm^2) is a cylindrical body (disk) and is located inside a space made of glass and metal. Sample preparation and care were done according to the ASTM G5 standard [11]. Tests were performed at room temperature, 20 ± 1 °C. The surface of the working electrode was 1,0 cm^2. Taffel extrapolation method implies scanning of working electrode potential on the order of ± 250 mV in relation to its Open Circuit Potential (E_{OCP}), at the speed of 0.5 mVs^{-1}. Linear polarization method implies scanning of working electrode potential in a narrow range of potentials ± 20 mV at the speed of 0.5 mVs^{-1}.

The electrochemical impedance spectroscopy method (EIS) was used to determine the kinetic parameters of the electrochemical reaction of copper corrosion in 3% NaCl solution without and in the presence of raspberry flower extracts. Measurements were performed using the IviumSoft software package on IVIUM® Vertex One potentiostat / galvanostat. The surface of the working electrode was 1,69 cm^2. Data were obtained at open circuit potential in the frequency range 10 kHz to 10 mHz using an amplitude of alternating voltage of 10 mV.

Polka variety raspberry (*Rubus idaeus* L.) flowers were collected at the Maglaj-Moševac site. The Moševac site near Maglaj is far from industrial plants.

3. RESULTS AND DISCUSSION

Figure 1 shows the polarization curves of copper in 3% NaCl without and with the addition of flower extract in different concentrations, obtained by the Tafel extrapolation method. Table 2 shows the corrosion parameters of copper in 3% NaCl without and with the addition of flower extract in different concentrations, determined by the Tafel extrapolation method.

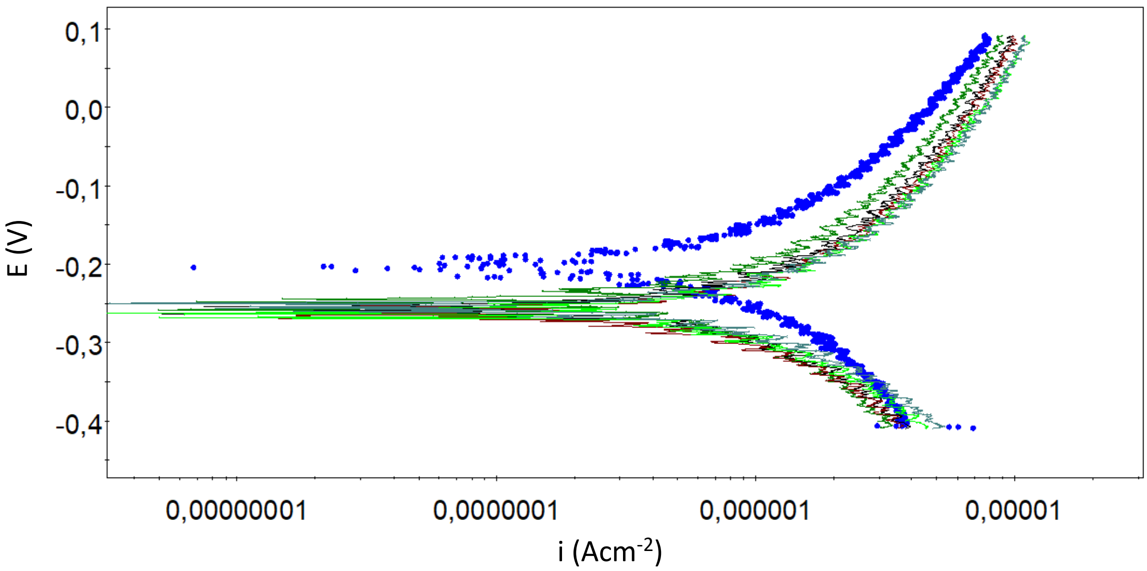

Figure 1. Polarization curves of copper in 3% NaCl obtained by the Tafel extrapolation method

---- 3% NaCl; ---- 3% NaCl+0,01612 gdm^{-3}; ---- 3% NaCl+0,03221gdm^{-3}; ---- 3% NaCl+0,04828 gdm^{-3}; ---- 3% NaCl+0,06432 gdm^{-3}; ---- 3% NaCl+0,08033gdm^{-3}

Slika 1. Polarizacijske krive bakra u 3% NaCl dobivene metodom Tafelove ekstrapolacije

---- 3% NaCl; ---- 3% NaCl+0,01612 gdm^{-3}; ---- 3% NaCl+0,03221gdm^{-3}; ---- 3% NaCl+0,04828 gdm^{-3}; ---- 3% NaCl+0,06432 gdm^{-3}; ---- 3% NaCl+0,08033gdm^{-3}

Table 2. Corrosion parameters of copper in 3% NaCl determined by Tafel extrapolation method

Tabela 2. Korozioni parametri bakra u 3% NaCl određeni metodom Tafelove ekstrapolacije

Concentracion of the extract in the cell, g dm^{-3}	E_{corr} (mV)	i_{corr} (μA cm^{-2})	b_c (mV dec^{-1})	b_a (mV dec^{-1})
0	-215,11	$5{,}69\cdot10^{-1}$	220,12	239,94
0,01612	-247,75	$4{,}99\cdot10^{-1}$	190,93	234,61
0,03221	-257,40	$2{,}60\cdot10^{-1}$	79,76	81,02
0,04828	-263,09	$9{,}90\cdot10^{-1}$	222,40	236,36
0,06432	-263,74	$5{,}81\cdot10^{-1}$	119,35	142,24
0,08033	-254,99	$2{,}51\cdot10^{0}$	403,44	496,81

The results shown on figure 1 and in table 2 showed that the corrosion rate decreases in the presence of raspberry flower extract, and that the flower extract of concentration 0,03221 g dm^{-3} provides the greatest protection of copper against corrosion in 3% NaCl.

Figure 2 shows results of testing the influence of raspberry flower extract on the corrosion characteristics of copper using the method of potentiodynamic polarization.

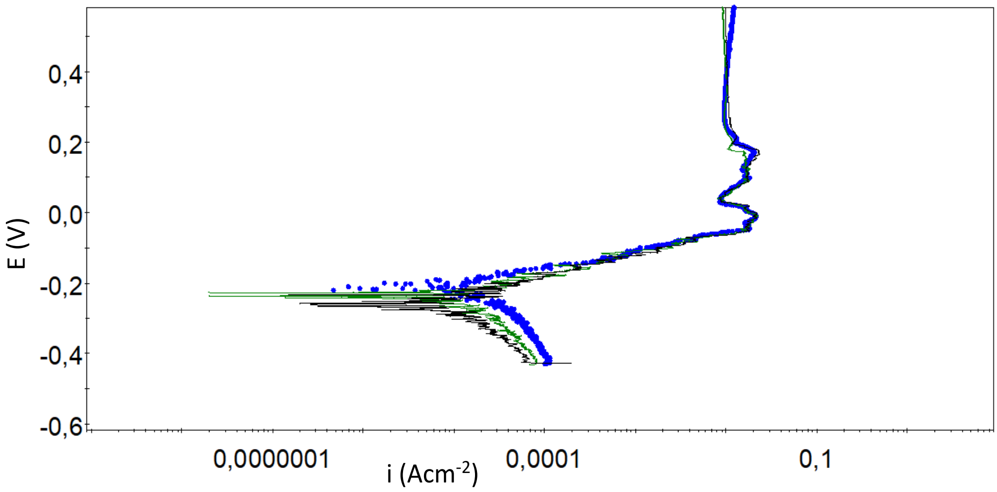

Figure 2. Potentiodynamic polarization curves of copper in 3% NaCl without and with the addition of flower extract: ---- 3% NaCl; ---- 3% NaCl+0,01612 gdm^{-3}; ---- 3% NaCl+0,04828 gdm^{-3}

Slika 2. Potenciodinamičke polarizacijske krive bakra u 3% NaCl bez i uz dodatak ekstrakta cveta maline: ---- 3% NaCl; ---- 3% NaCl+0,01612 gdm^{-3}; ---- 3% NaCl+0,04828 gdm^{-3}

The anode part of the polarization curves (figure 2) is characterized by the dissolution of copper in a corrosive medium, and can be divided into three separate areas:

- linear Tafel area,
- pseudopassive area and
- the area where the current density increases [5].

In the linear Tafel region, the polarization behavior of copper is determined by the dissolution of copper and the formation of a soluble $CuCl_2^-$ complex and its diffusion from the metal surface into the solution. At more positive potentials, corrosion products are formed on the copper surface that reduces the active dissolution of copper to a certain extent, resulting in a particular current density reduction. According to the literature, the decrease in current density is most often explained by the formation of surface compounds CuCl and Cu_2O. The formation of the CuCl compound proceeds much faster than its complexation into $CuCl_2^-$ compound and diffusion into the solution. A further potential increase leads to an increase in the current density, which indicates that the resulting surface compounds do not represent a true compact protective film, and the dissolution of copper continues with the formation of soluble Cu (II) compounds [5].

In all anode branches of copper polarization curves in the presence of different concentration extracts, it was detected that the areas in which copper dissolution occurs and the formation of a soluble $CuCl_2^-$ complex and its diffusions from the metal surface into the solution and the areas of corrosion product formation occur earlier, leading to a certain decrease in current density.

Figure 3 shows the polarization curves of copper in 3% NaCl without and with the addition of flower extract, obtained by linear polarization method. Corrosion parameters, obtained by linear polarization method, shown in table 3.

Table 3. Corrosion parameters of copper in 3% NaCl determined by linear polarization method

Tabela 3. Korozioni parametri bakra u 3% NaCl određeni metodom linearne polarizacije

Concentracion of the extract in the cell, g dm^{-3}	*R* (Ω cm^2)	E_{corr} (mV)	i_{corr} (μA cm^{-2})
0	2383,29	-177,96	9,12·10°
0,01612	2370,83	-189,29	9,17·10°
0,03221	4791,72	-221,63	4,54·10°
0,04828	4526,47	-230,44	4,80·10°
0,06432	4212,73	-227,90	5,16·10°
0,08033	2142,37	-211,15	1,02·10¹

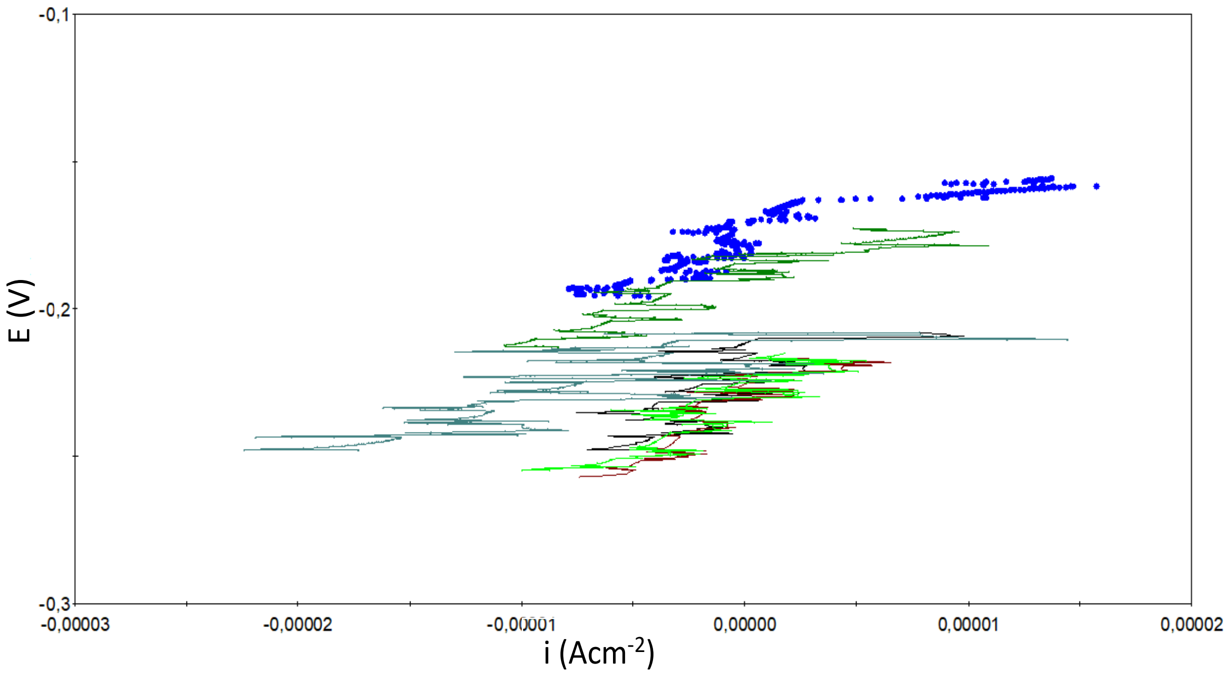

Figure 3. Polarization curves of copper in 3% NaCl: ---- 3% NaCl; ---- 3% NaCl+0,01612 gdm^{-3}; ---- 3% NaCl+0,03221gdm^{-3}; ----3% NaCl+0,04828 gdm^{-3}; ---- 3% NaCl+0,06432 gdm^{-3}; ----3% NaCl+0,08033gdm^{-3}

Slika 3. Polarizacijske krive bakra u 3% NaCl: ---- 3% NaCl; ---- 3% NaCl+0,01612 gdm^{-3}; ---- 3% NaCl+0,03221gdm^{-3}; ----3% NaCl+0,04828 gdm^{-3}; ---- 3% NaCl+0,06432 gdm^{-3}; ----3% NaCl+0,08033gdm^{-3}

The results shown on figure 3 showed that the addition of different concentrations of the extract the polarization resistance increases. Polarization resistance is a measure of the material resistance and, the higher the amount, the more resistant the material is to corrosion. Polarization measurements performed in a narrow range of potentials confirmed that the raspberry flower extract provides the greatest protection of copper against corrosion in 3% NaCl at a relatively low concentration of 0,03221 gdm^{-3} (Table 3).

The results of testing inhibitory effect of raspberry flower extract on copper in 3% NaCl by electrochemical impedance spectroscopy are shown in the Nyquist diagram, Figure 5. The results were later analyzed using an equivalent electrical circuit, Figure 4, and the obtained corrosion parameters are shown in Table 4.

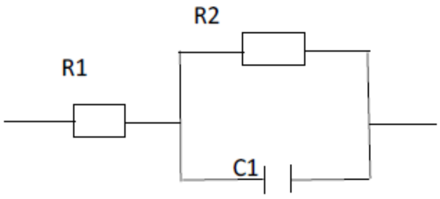

Figure 4. Scheme of the equivalent circuit of a simple electrochemical cell: C1-capacitor, R1-electrolyte resistance, R2- resistance of charge transmission

Slika 4. Šema ekvivalentnog kola proste elektrohemijske ćelije: C1-kondenzator, R1-elektrolitni otpor, R2- otpor prenosa naelektrisanja

Table 4. Corrosion parameters of copper in 3% NaCl without and with the addition of flower extract determined by electrochemical impedance spectroscopy

Tabela 4. Korozioni parametri bakra u 3% NaCl bez i uz dodatak ekstrakta od cveta dobiveni metodom elektrohemijske impedansne spektroskopije

Concentracion of the extract in the cell, g dm^{-3}	R_1 (Ω cm^2)	R_2 (Ω cm^2)	C (μF cm^{-2})
0	68,28	1407,10	2,73·10-4
0,01612	63,02	1479,29	2,21·10-4
0,03221	64,56	2251,48	2,34·10-4
0,04828	75,98	2860,36	2,11·10-4
0,06432	66,75	3333,14	1,76·10-4
0,08033	83,02	4008,88	1,72·10-4

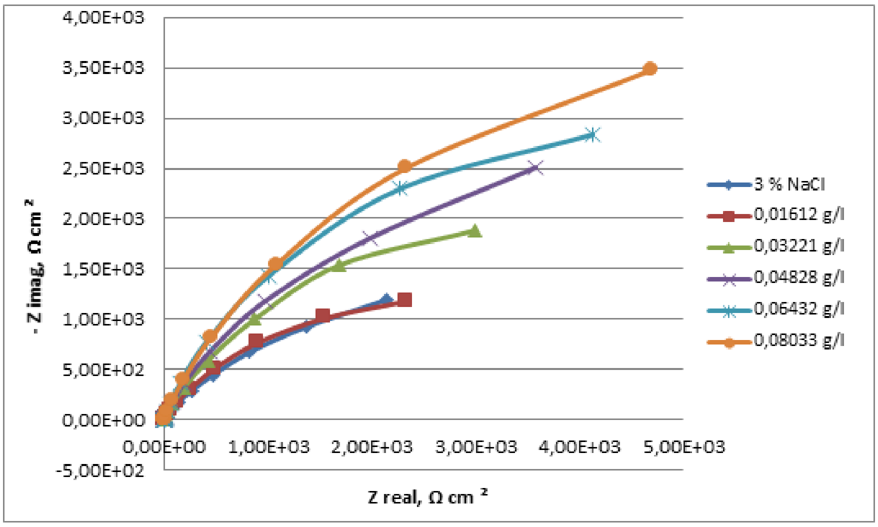

Figure 5. Nyquist copper curves in 3% NaCl without and with the addition of raspberry flower extract

Slika 5. Nyquist krive bakra u 3% NaCl bez i uz dodatak ekstrakta cveta maline

From Figure 5 it can be seen how the addition of the tested concentrations of raspberry flower extract increases the diameter of the impedance curves copper in 3% NaCl compared to the one obtained without the addition of said extract. From this, it can be concluded that the addition of this extract reduces the corrosion rate. EIS parameters for raspberry flower extract as well as without it obtained using the proposed model are shown in Table 4. Based on results from Table 4 it is observed that the highest corrosion resistance of copper is given by the extract concentration of 0,08033 gdm^{-3}.

4. CONCLUSION

The results of testing inhibitory effect of raspberry flower extract of general corrosion of copper obtained by DC techniques showed that the corrosion rate decreases in the presence of almost all tested extract concentrations. Using DC techniques (Tafel extrapolation and linear polarization methods), it has been proven that raspberry flower extract with a concentration of 0,03221 gdm^{-3} provides the greatest protection copper against corrosion in 3% NaCl. Studies conducted by the electrochemical impedance spectroscopy method, AC methods, show that almost all tested extract concentrations slow down the corrosion process kinetics, which is visible through the increase in resistance.

There are some discrepancies between the AC method and DC measurement methods, but since this is a very small range of concentrations, and therefore these deviations are negligible. The results of the conducted tests prove that in an aggressive medium, such as 3% NaCl solution, "Polka" raspberry flower extract can be used as an inhibitor of copper's corrosion at room temperature.

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IZVOD

Ispitivanje efikasnosti ekstrakta cvijeta maline kao inhibitora korozije bakra u 3% NaCl

Rad predstavlja ispitivanje mogućnosti primene ekstrakta cveta maline (Rubus idaeus L.) kao zelenog inhibitora opšte korozije bakra u 3% NaCl. Cvetovi maline (Rubus idaeus L.) sorte Polka su prikupljeni sa lokaliteta Moševac kod Maglaja, Bosna i Hercegovina. Ekstrakt cveta maline sorte Polka u etanolu dobiven je metodom ultrazvučne ekstrakcije. Analizom UV/VIS spektrofotometrijom pronađeno je da ekstrakt cveta maline sadrži značajan sadržaj polifenola.

Rezultati dobiveni DC tehnikama (metodama Tafelove ekstrapolacije, potenciodinamske polarizacije i linearne polarizacije) dokazuju da se brzina korozije smanjuje u prisustvu ispitivanog ekstrakta. Ispitivanja provedena metodom elektrohemijske impedancijske spektroskopije dokazuju da ispitivani ekstrakti usporavaju kinetiku korozionog procesa što je vidljivo kroz porast otpora. Rezultati provedenih ispitivanja dokazuju da se u agresivnom mediju, kao što je 3% rastvor NaCl, u svrhu zaštite bakra od korozije može koristiti ekstrakt cveta maline sorte Polka.

Ključne reči: *ekstrakcija, cvet maline, inhibitor, Tafelova ekstrapolacija, potenciodinamička polarizacija, linearna polarizacija, elektrohemijska impedancijska spektroskopija.*

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