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Original scientific paper

INVESTIGATION OF INHIBITORY EFFECT OF THE RASPBERRY FRUIT EXTRACT (*Rubus idaeus* L.) ON CORROSION OF COPPER IN 3% NaCl SOLUTION

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ABSTRACT

The paper presents an examination of the possibility of applying raspberry fruit extract (*Rubus idaeus* L.) as a green inhibitor of general corrosion of copper in 3% NaCl. Raspberry fruits (*Rubus idaeus* L.) sort Polka was collected from the Starposle near Kakanj, Bosnia and Herzegovina. Raspberry fruit extracts in ethanol were obtained by the Soxhlet extraction and the ultrasonic method. By UV/VIS spectrophotometry analysis, a significant content of polyphenols was found in the raspberry fruit extracts. Due to the great importance of gallic acid, the concentration of gallic acid was also determined using liquid chromatography.
Corrosion testing of copper by the DC techniques was performed on a measuring device consisting of an electrochemical cell and a potentiostat/galvanostat, and electrochemical impedance spectroscopy measurements were performed using a potentiostat/galvanostat.
Results obtained by the DC technique (by the method of Tafel extrapolation) prove that the corrosion rate decreases in the presence of the raspberry fruit 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 a 3% NaCl solution, Polka raspberry fruit extract can be used as an inhibitor of copper's corrosion.

Keywords: raspberry fruit, Tafel extrapolation, electrochemical impedance spectroscopy

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1. INTRODUCTION

Copper is a metal that has extra 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. 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]. Gallic acid (3, 4, 5-Trihydroxybenzoic acid) is one of the best-known representatives of phenolic compounds commonly used to express the mass fraction of total phenols or phenolic subgroups in plant extracts [2]. Gallic acid participates in the formation of hydrolyzing gallotannins, and its condensation produces dimer-ellagic acid, which is also part of ellagitannin. According to most literature data, some of the most significant compounds from the class of polyphenols in raspberry fruit is ellagic acid and ellagitannins [3].

According to previous research on the dissolution of copper in a chloride medium, the anodic reaction is reversible mainly due to the strong, thermodynamically more favorable complexation of copper ions with chloride ions [4,5,6]. The cathodic response is dominated by oxygen reduction, which is considered to be irreversible. Copper with chloride ions can form several complexes [5]: 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 an 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 compounds such as $CuCl_3^{2-}$ and $CuCl_4^{3-}$ [5,7,8]. 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 (l) oxide:

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

or by direct oxidation of copper [6,5]:

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

When a passive film is created on a metal (e.g. Cu_2O) that does not have good protective properties and pitting corrosion will occur [9] 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 the 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. Many studies have focused on natural organic compounds from plant material. Natural antioxidants are affordable, available, and renewable compounds obtained by extraction from plant material or synthesized. Studies have shown that many of these compounds can be used as effective inhibitors of copper corrosion [10, 11, 12, 13].

Effective environmental corrosion inhibitors show a high tendency for adsorption. The adsorption mechanism of organic inhibitors on the metal/solution partitioning surface may consist of one or more steps. In the first step, the adsorption of the organic inhibitor on the metal surface usually involves the replacement of one or more water molecules initially adsorbed on the metal surface [15]:

$$Inh_{(sol)} + xH_2O_{(ads)} \rightarrow Inh_{(ads)} + H_2O_{(sol)} \quad (6)$$

where:
Inh(sol) - inhibitor in solution,
Inh(ads) – adsorbed inhibitor,
x – number of water molecules displaced by the inhibitor.

The inhibitor combined with the metal ion M^{2+} formed on the metal surface as a result of the metal oxidation or dissolution process, creating a metal-inhibitor complex [14]:

$$M \rightarrow M^{2+} + 2e^- \quad (7)$$

$$M^{2+} + Inh(ads) \rightarrow [M\text{-}Inh]_{(ads)}^{2+} \quad (8)$$

Depending on the relative solubility of the resulting complex, further dissolution of the metal can be further inhibited or catalyzed [14].

This paper presents the effect of Polka variety raspberry fruit extract from the Starposle site near Kakanj*,* 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 the official registers in 2003. The specificity of the variety is that it can be grown without reinforcement. Raspberry fruit 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. EKSPERIMENTAL PART

Polka variety raspberry (*Rubus idaeus* L.) fruits were collected at the Starposle-Kakanj site, Bosnia and Herzegovina. The Starposle site near Kakanj is far from industrial plants.

2.1. Obtaining extracts and samples of raspberry fruit for HPLC analysis

Defrosted raspberry fruits were ground in a blender, and as such, used in the Soxhlet apparatus. Ethanol was used as the solvent. The extraction lasted for six hours, after which the obtained extract was evaporated to dryness. The extracts obtained in this way were stored in dark bottles in a refrigerator at a temperature of +4 °C. The obtained extract samples were of resinous consistency and well-soluble in ethanol.

Extractions were also performed in the ultrasonic bath under defined conditions: frequency (20-40 kHz), power (250-500 W), temperature (40°C), and extraction time (30 min) [15].

The fact that plants contain several thousand secondary metabolites creates a need to develop fast and precise extraction methods.

Dry fruit extracts (about 0.5 g), obtained by Soxhlet extraction and ultrasonic method, were dissolved in 50% methanol in an ultrasonic bath. Then filtered to remove impurities and transferred to vials. The content of total phenols was determined spectrophotometrically, on the PerkinElmer, Lambda 650, UV – VIS spectrophotometer device, by the Folin-Ciocalteu method.

2.2. Galic acid analysis using RP-HPLC-UV/Vis technique

Many scientists are showing great interest in gallic acid, which has contributed to its analysis in raspberry fruit extracts. Gallic acid analysis of Polka raspberry fruit extracts was performed by high-performance liquid chromatography on reversed phases on Shimadzu Prominence Modular HPLC with UV/Vis detector, mobile phase degasser, pump, autosampler, and column oven. Analysis of gallic acid was performed on a Nucleosil C18 column (250 mm x 4.6 mm, particle size 5 µm; Macherey-Nagel).

As the mobile phase, a solvent system was used: A (1% formic acid) and B (acetonitrile) at a flow rate of 1 ml/min and using the following linear gradient: 0–10 min from 10 to 25% A; 10–20 min linear rise to 60% A, 20–30 min linear rise to 70% A. The column was balanced to initial conditions, 10% A, 10 min with an additional 5 min for stabilization [3]. The gallic acid standard was dissolved in 50% methanol.

Chromatograms were recorded at 280 nm for hydroxybenzoic acid derivatives (gallic).

Based on the obtained chromatograms and the calibration diagram of the standard gallic acid solution, the gallic acid concentrations in the extracts were calculated (g/l) [3]. The gallic acid standard of different concentrations is shown in Table 1 [3, 15].

Table 1. Standard solution of gallic acid of different concentrations for HPLC analysis

Standard solution	Concentration 1 (g/l)	Concentration 2 (g/l)	Concentration 3 (g/l)
Gallic acid	0.0525	0.1050	0.4200

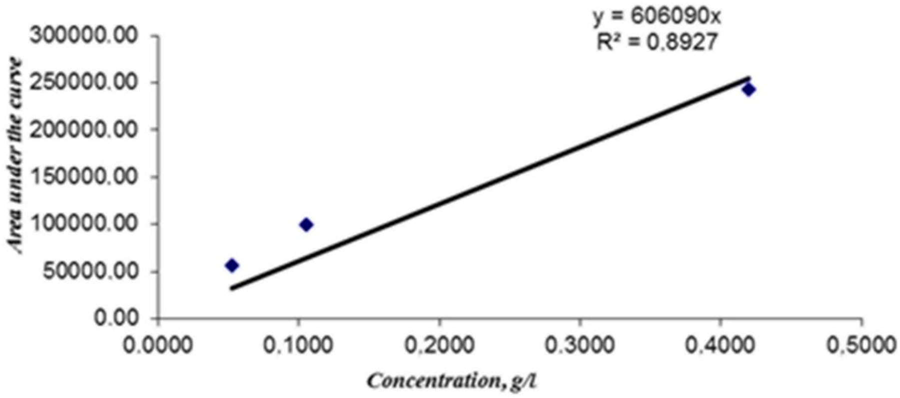

Figure 1. Calibration curve for gallic acid

To examine the effect of raspberry (*Rubus idaeus* L.) fruit extract, we used 99.8% purity copper as the corrosion characteristics of copper. The chemical composition of copper has been tested at Kemal Kapetanović Institute in Zenica on the device Atomic Absorption Spectrometry, AAS-3110.

The Tafel extrapolation method was used in this research during electrochemical tests of the corrosion process by DC techniques.

To examine the corrosion process by AC techniques was used electrochemical impedance spectroscopy (EIS). For testing the inhibitory effect of raspberry fruit on the corrosion of copper in a 3% NaCl solution were used copper samples of the following dimensions were:

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

Before each measurement, the copper work surface was mechanically sanded with sandpaper 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) with a potential of 0.2415 V is used as a reference electrode. The working electrode 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 [16].

The electrochemical impedance spectroscopy method (EIS) was used to determine the kinetic parameters of the electrochemical reaction of copper corrosion in a 3 % NaCl solution without and in the presence of raspberry fruit extracts. Measurements were performed using the IviumSoft software package on IVIUM® Vertex Onepotentiostat/galvanostat.

3. RESULTS AND DISCUSSION

3.1. Yield determination of Soxhlet and ultrasonic extractions

Extraction yields, *Y*, expressed as a percentage are calculated using the following formula [15]:

$$Y(\%) = (m_E / m_S) \times 100 \quad (9)$$

where
m_E - extract mass,
m_S - plant mass.

Extraction yields of Soxhlet and ultrasonic extractions are shown in Table 2. Based on the results shown in Table 2, it is safe to say that ultrasonic extraction leads to higher yields.

Table 2. Extraction yields of Soxhlet and ultrasonic extractions

Sample	SPP	UPP
Plant mass, g	66.1	110.10
Extract mass, g	3.19	6.68
Extraction Yields, %	4.83	6.07

3.2. The Results of spectrophotometric determination

Extracts of Polka raspberry fruit obtained by ultrasonic extraction showed a significantly higher total phenol content than extracts obtained using Soxhlet extraction, as shown in Table 3.

Table 3. Content of total phenols in Polka raspberry fruit extracts obtained by methods of Soxhlet and ultrasonic extractions

Sample	Total phenols, mg GA/g extract
SPP	14.92±0.87
UPP	28.51±0.91

Based on these results, it is safe to say that ultrasonic extraction leads to a higher yield of phenolic compounds in a shorter time, reducing energy consumption and phenol degradation.

Ultrasonic extraction has been shown a better and more cost-effective technique than Soxhlet extraction for the extraction of Polka raspberry fruit.

Results are expressed as mean ± SD (n = 3).

The HPLC method was used to determine the concentration of gallic acid in the tested extracts of Polka raspberry fruit. The results of HPLC analyzes of these extracts are shown in Table 4. Figures 2 and 3 show HPLC chromatograms for gallic acid detected in Polka raspberry fruit extracts.

Table 4. Results of HPLC analysis of gallic acid in Polka raspberry fruit extract obtained by Soxhlet and ultrasonic extractions

Sample	Gallic acid, µg/ml
SPP	109.90±0.92
UPP	201.66±6.44

Results are expressed as mean ± SD (n = 3).

Based on the results of spectrometric and HPLC analyses, it can be concluded that the content of total phenols and gallic acid is much higher in all samples obtained using ultrasound extraction about Soxhlet extraction.

Therefore, the extract obtained by ultrasonic extraction, which proved to be a better and more cost-effective technique than Soxhlet extraction for the extraction of Polka raspberry fruit, was further used to test copper corrosion.

Figure 4 shows the polarization curves of copper in 3% NaCl without and with the addition of fruit extract in different concentrations, obtained by the Tafel extrapolation method.

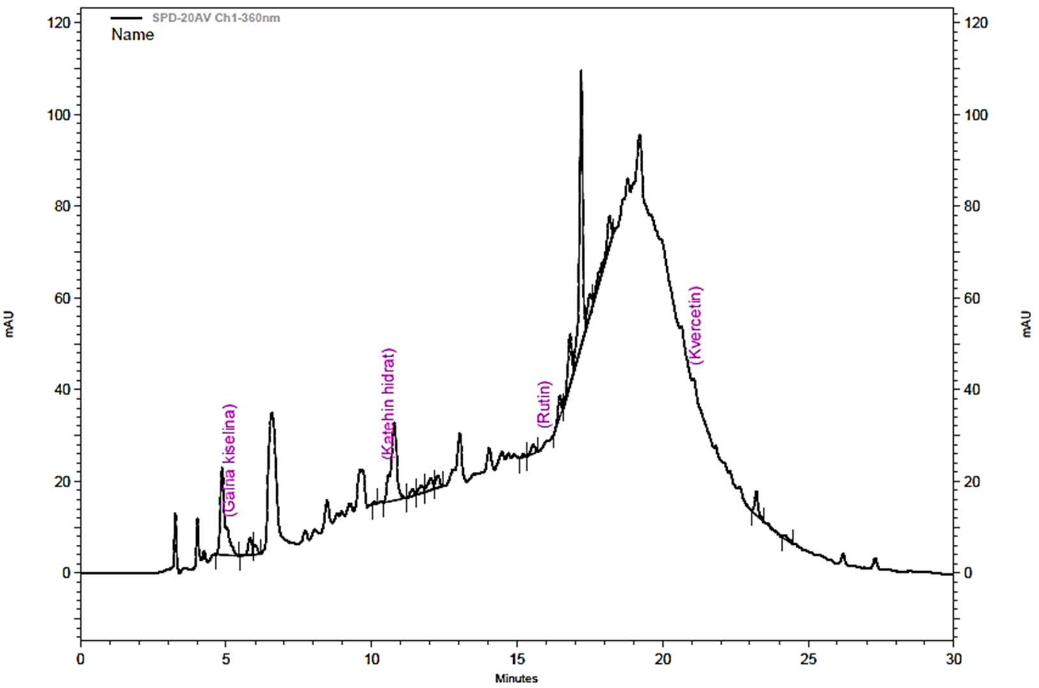

Figure 2. HPLC chromatograms of Kakanj Polka fruit - Soxhlet extraction

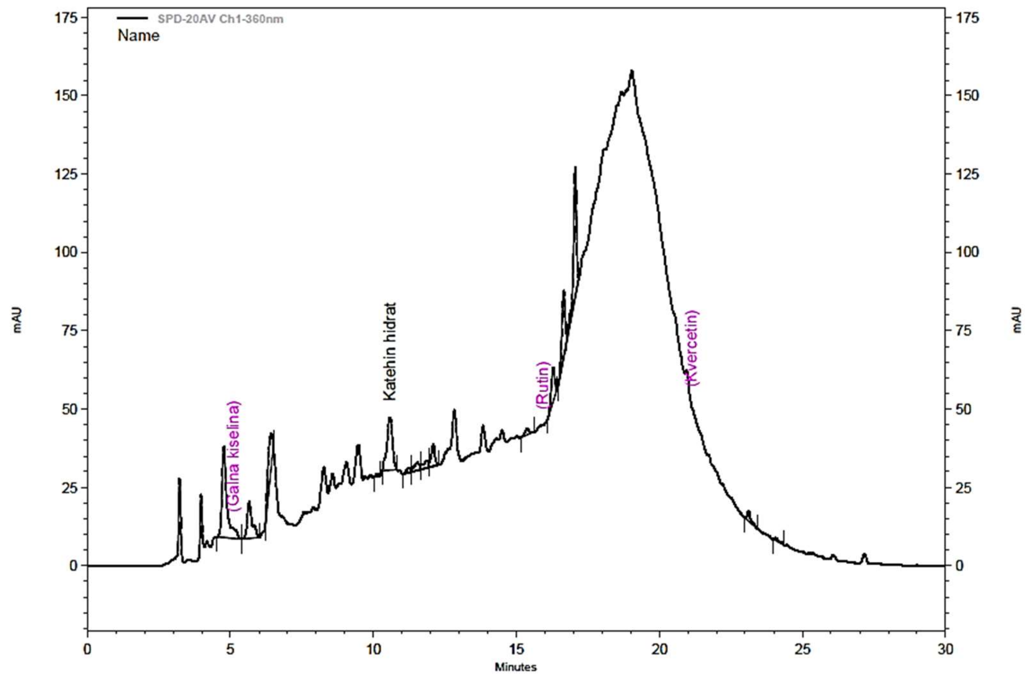

Figure 3. HPLC chromatograms of Kakanj Polka fruit - Ultrasonic extraction

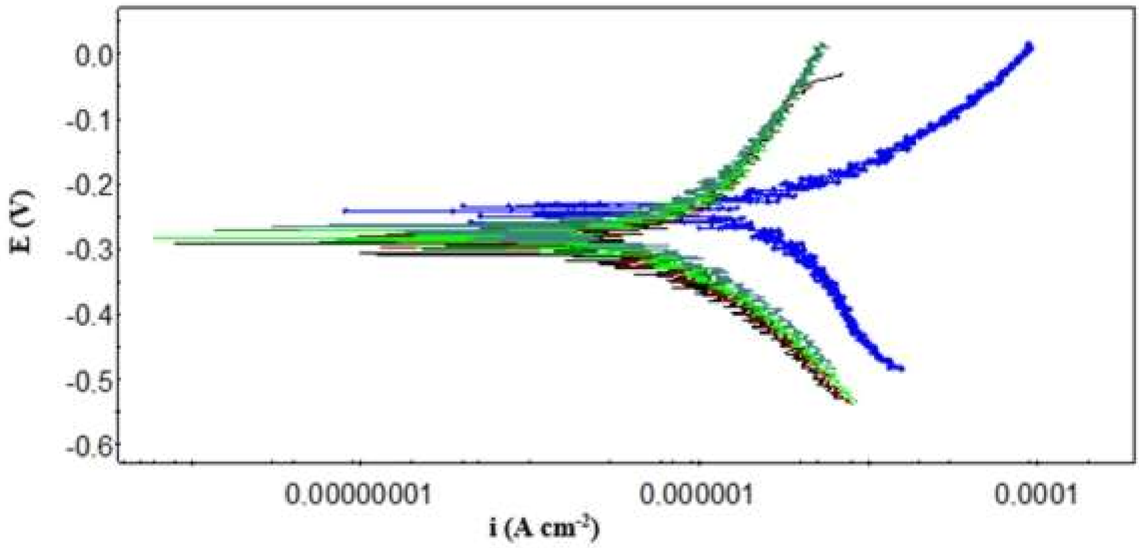

Figure 4. Polarization curves of copper in 3% NaCl without and with the addition of fruit extract in different concentrations obtained by the Tafel extrapolation method
0 g/l; 0.01612 g/l; 0.03221g/l; 0.04828 g/l; 0.06432 g/l; 0.08033g/l

Table 5 shows the corrosion parameters of copper in 3% NaCl without and with the addition of fruit extract in different concentrations, determined by the Tafel extrapolation method. HPLC chromatograms showed the presence of gallic acid in extracts of Polka raspberry fruit

The results shown in figure 4 and table 5 showed that the corrosion rate decreases in the presence of raspberry fruit extract, and that the fruit extract of concentration 0.04828 g/l provides the greatest protection of copper against corrosion in 3% NaCl because it shows the lowest corrosion current density, table 5.

The results of testing the inhibitory effect of raspberry fruit 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, and the obtained corrosion parameters are shown in Table 6.

Table 5. Corrosion parameters of copper in 3% NaCl without and with the addition of fruit extract in different determined by the Tafel extrapolation method

The concentration of the extract in the cell, g/l	$E_{kor.}$ (mV)	$i_{kor.}$ (μA cm^{-2})	b_c (mV dec^{-1})	b_a (mV dec^{-1})
0	-242.067	1.565	244.436	131.706
0.01612	-277.023	$7.798 \cdot 10^{-1}$	245.538	324.706
0.03221	-297.512	$7.541 \cdot 10^{-1}$	236.800	317.02
0.04828	-289.682	$5.715 \cdot 10^{-1}$	173.208	182.495
0.06432	-282.548	$7.893 \cdot 10^{-1}$	237.138	313.919
0.08033	-272.185	1.178	280.880	411.988

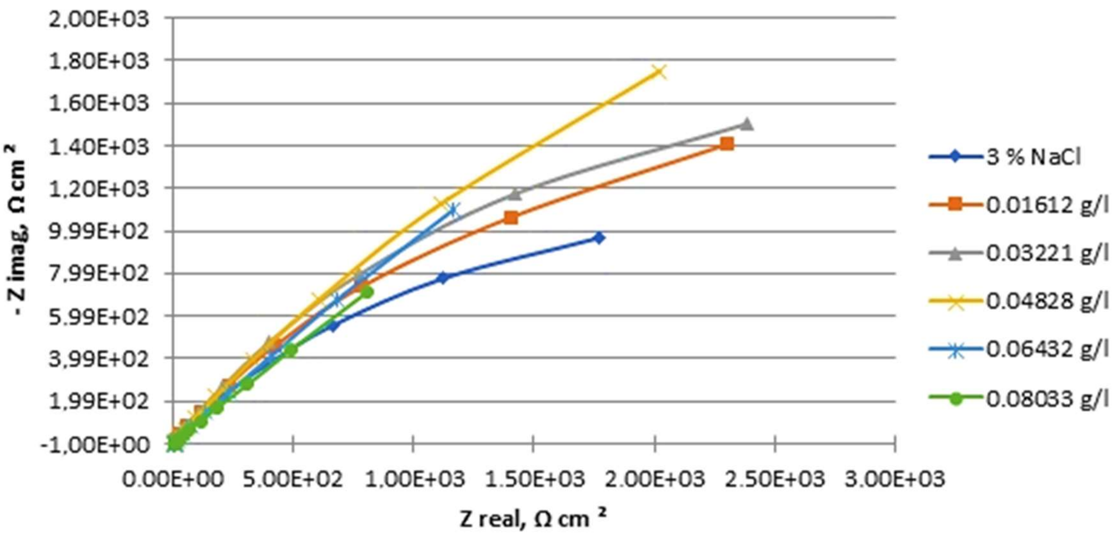

Figure 5. Nyquist copper curves in 3% NaCl without and with the addition of raspberry fruit extract

Table 6. Corrosion parameters of copper in 3% NaCl without and with the addition of fruit extract determined by electrochemical impedance spectroscopy

Concentration of the extract in the cell, g/l	R1 (Ω)	R2(Ω)	C(F)
0	93.56	1965	$5.657 \cdot 10^{-4}$
0.01612	111.4	2763	$4.875 \cdot 10^{-4}$
0.03221	106.3	2961	$4.814 \cdot 10^{-4}$
0.04828	105.8	3256	$7.007 \cdot 10^{-4}$
0.06432	79.51	2025	$1.237 \cdot 10^{-3}$
0.08033	63.55	1294	$1.748 \cdot 10^{-3}$

From Figure 5 it can be seen how the addition of the tested concentrations of raspberry fruit 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 fruit extract as well as without it obtained using the proposed model are shown in Table 6. Based on results from Table 6 it is observed that the highest corrosion resistance of copper is given by the extract concentration of 0.04828 g/l.

The concentration of gallic acid (201.66±6.44 µg/ml) in raspberry fruit extract was tested, so to conclude that gallic acid in the extract led to a decrease in copper corrosion, the effect of standard gallic acid solution at 0.03221 g/l on corrosion copper was examined. This lower concentration was taken into account because the same concentration of fruit extract showed a decrease in copper corrosion, and it is known that corrosion inhibitors are substances added in small quantities to aggressive media to reduce the rate of metal corrosion.

Figure 6 shows the polarization curves of copper in 3% NaCl without and with the addition of standard gallic acid solution, obtained by the Tafel extrapolation method. Table 7 shows the corrosion parameters of copper in 3% NaCl without and with the addition of standard gallic acid solution, determined by the Tafel extrapolation method.

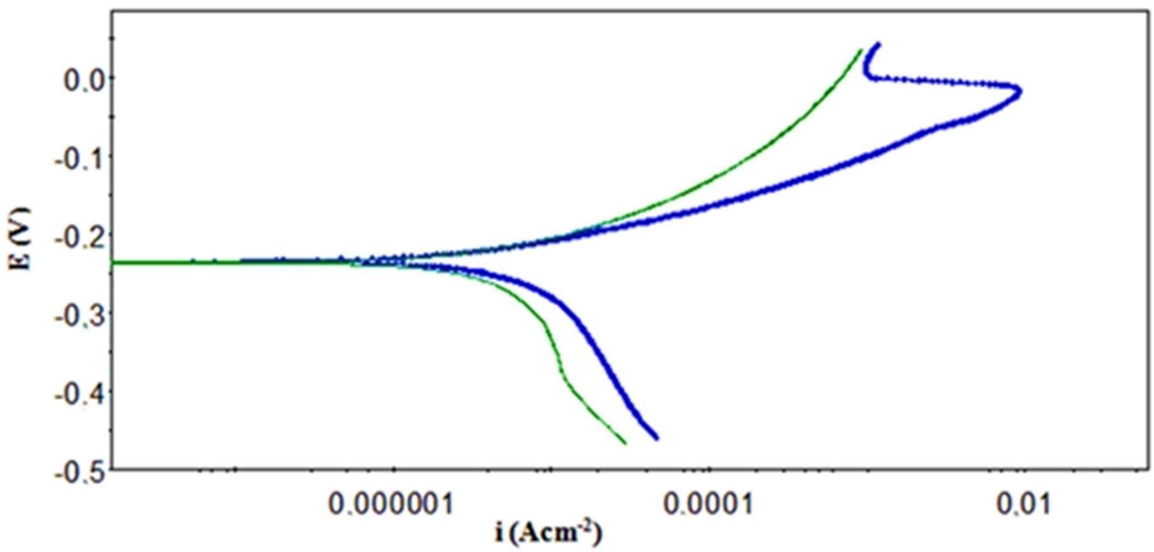

Figure 6. Anode and cathode curves of copper polarization in 3% NaCl without and with the addition of a standard solution of gallic acid
0 g/l; 0.03221g/l

Table 7. Corrosion parameters determined by the Tafel extrapolation method of copper in 3% NaCl without and with the addition of a standard solution of gallic acid

The concentration of a standard solution of gallic acid in the cell, g/l	$E_{kor.}$ (mV)	$i_{kor.}$ (μA cm^{-2})	b_c (mV dec^{-1})	b_a (mV dec^{-1})
0	-234.361	15,49	657.271	133.044
0.03221	-236.548	8.715	688.021	106.660

The results shown in figure 6 and table 7 showed that the corrosion rate decreases in the presence of standard gallic acid solution, so it can be concluded that the gallic acid contained in the tested extract led to a decrease in the corrosion rate of copper.

4. CONCLUSION

The results carried out in this paper show that the extract from raspberry fruit (*Rubus idaeus* L.) of Polka variety, obtained by the Ultrasonic method, contains significant amounts of total phenols (28.51±0.91 mg GA/g extract) then extract obtained using Soxhlet extraction (14.92±0.87mg GA/g extract) making it a potential corrosion inhibitor. HPLC chromatograms showed the presence of higher concconcentrationlic acid (201.66±6.44 µg/ml) in extrthe act obtained by the Ultrasonic method.

The results of testing the inhibitory effect of raspberry fruit extract, obtained by the Ultrasonic method, 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 the Tafel extrapolation method, it has been proven that raspberry fruit extract with a concentration of 0.04828 g/l provides the greatest protection copper against corrosion in 3% NaCl. Studies conducted by the electrochemical impedance spectroscopy method, show that almost all tested extract concentrations slow down the corrosion process kinetics, which is visible through the increase in resistance, and that a concentration of 0.04828 g/l provides the greatest protection copper against corrosion in 3% NaCl. The results of the conducted tests prove that in an aggressive medium, such as a 3% NaCl solution, "Polka" raspberry fruit extract can be used as an inhibitor of copper's corrosion at room temperature.

Conflicts of Interest

The authors declare no conflict of interest.

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