CORROSION INHIBITION OF BRASS IN CHLORIDE SALT SOLUTION APPLYING WILD RASPBERRY FRUIT AS A GREEN, NON-TOXIC INHIBITOR OF CORROSION

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ABSTRACT
The paper presents an examination of the possibility of applying wild raspberry fruit extract as a green inhibitor of general corrosion of brass in 3% NaCl. Wild raspberry fruits were collected from the Moševac near Maglaj city, Bosnia and Herzegovina. Wild raspberry fruit extract was obtained by ultrasonic method. By UV/VIS spectrophotometry analysis a significant content of polyphenol was found in the wild raspberry fruit extract.
*Results obtained by DC techniques (by the methods of Tafel extrapolation and linear polarization) prove that the corrosion rate decreases in the presence of the wild 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 3% NaCl solution, wild raspberry fruit extract can be used as an inhibitor of brass corrosion in concentracion of 0.04828 g/*L.

1. INTRODUCTION

Pure copper is rarely used as a structural material, especially when exposed to a chloride environment. Therefore, more resistant copper alloys, such as brass, are used for these purposes instead of copper. Brass is the primary alloy of copper and zinc, the most widespread, and has a very diverse range of applications. Copper-zinc alloys are primarily used for casting ingots, blocks, billets, and similar forms that undergo plastic deformation, but some types are also used for casting shaped castings [1].
Brass is susceptible to the electrochemical process of selective corrosion, in which zinc dissolves upon contact with an electrolyte, a process known as dezincification, leaving behind a porous layer of copper [2].
The examination of brass in NaCl solutions of varying concentrations confirmed the presence of copper and zinc in the electrolyte solution after electrochemical measurements. This indicates the formation of a surface protective layer and the dissolution of the alloy, which is diffusion-controlled and related to the difference in the radius of Cu^{2+} and Zn^{2+} ions [2, 3]. The mechanism of dissolution and layer formation on the surface of brass is explained as follows [2, 3]:
In the initial stage of zinc corrosion, ZnO oxide is formed as a reaction product of reaction (1) or (2):

$$Zn^{2+} + H_2O \rightarrow ZnO + 2H^+ \tag{1}$$

$$Zn + H_2O \rightarrow ZnO + 2H^+ + 2e^- \tag{2}$$

Copper also transitions into an oxide formed as a product of reaction (3) or (4):

$$2Cu^+ + H_2O \rightarrow Cu_2O + 2H^+ \quad (3)$$

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \quad (4)$$

These oxide layers form immediately after brass comes into contact with the chloride medium, but they are not stable or compact enough to prevent further oxidation. Chloride ions cause the dissolution of brass at higher anodic potentials, leading to the formation of CuCl and $CuCl_2^-$ compounds according to reactions (5, 6, and 7) [2, 3, 4].

$$Cu^+ + Cl^- \rightarrow CuCl \quad (5)$$

$$2CuCl \rightarrow Cu^+ + CuCl_2 \quad (6)$$

$$CuCl + Cl^- \rightarrow CuCl_2^- \quad (7)$$

On the cathodic surface, the oxygen released from the solution reacts with the electrolyte according to reaction (8), while on the anodic surface, active copper dissolution occurs, and a Cu-chloro complex is formed, as shown in reaction (9) [2]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (8)$$

$$Cu + 2Cl^- \rightarrow CuCl_2^- + e^- \quad (9)$$

Based on the reactions, it can be concluded that an increased concentration of Cl^- ions prevents the formation of a passivating layer and promotes dissolution reactions. The literature [2, 3] mentions that at Cl^- ion concentrations greater than 1 mol/dm^3, higher Cu complexes ($CuCl_3^{2-}$, $CuCl_4^{3-}$) are formed. Appropriate corrosion inhibitors are used as effective protection for brass against corrosion.

In order to preserve the environment, the development of new environmentally friendly corrosion inhibitors is focused on natural, biologically-based, non-toxic, and biodegradable molecules. For this reason, there is still intensive research aimed at finding new effective yet non-toxic compounds. Plant extracts contain a large number of organic compounds, and one of these is phenolic compounds. It has been found that some of these compounds possess anticancer, antimutagenic, and antioxidant properties [5].

Effective ecological corrosion inhibitors exhibit a high tendency for adsorption. The adsorption mechanism of organic inhibitors on the metal/solution interface can consist of one or more steps. In the first step, the adsorption of the organic inhibitor onto the metal surface typically involves the replacement of one or more water molecules initially adsorbed on the metal surface [6]:

$$Inh(sol) + xH_2O(ads) \rightarrow Inh(ads) + H_2O(sol) \quad (10)$$

where is:

Inh(sol) - inhibitor in solution,

Inh(ads) – adsorbed inhibitor,

x – number of water molecules displaced by the inhibitor.

The inhibitor then combines with the metal ion M^{2+} formed on the metal surface as a result of metal oxidation or dissolution, forming a metal-inhibitor complex [6]:

$$M \rightarrow M^{2+} + 2e^- \quad (11)$$

$$M^{2+} + Inh(ads) \rightarrow [M\text{-}Inh]_{(ads)}^{2+} \quad (12)$$

Depending on the relative solubility of the resulting complex, it can either inhibit or catalyze further metal dissolution [6].

This paper presents the effect of wild raspberry fruit extract from the Maglaj-Moševac region, Bosnia and Herzegovina, as a corrosion inhibitor for brass, using electrochemical methods. The wild raspberry fruit extract is considered a relatively inexpensive, easily available, and renewable natural product rich in various organic compounds such as polyphenolic compounds, organic acids, vitamins, etc., making it a potential non-toxic corrosion inhibitor.

2. EXPERIMENTAL PART

The wild raspberry fruits were collected from the Moševac area near Maglaj, Bosnia and Herzegovina.

The extraction was performed in an ultrasonic bath under defined conditions: frequency (20-40 kHz), power (250-500 W), temperature (40ºC), and extraction time (30 minutes) [7]. Ethanol was used as the solvent. After the treatment, the extract was prefiltered and evaporated to dryness. The extract obtained in this way was stored in dark bottles in the refrigerator at a temperature of +4 ºC.

The fact that plants contain several thousand secondary metabolites creates the need for the development of a rapid and precise extraction method, such as ultrasonic extraction.

The total phenolic content was determined spectrophotometrically, using a UV–VIS spectrophotometer, PerkinElmer, Lambda 650, by the Folin-Ciocalteu method.

For testing the effect of wild raspberry fruit extract as a corrosion inhibitor for brass, brass with the chemical composition provided in Table 1 was used. The chemical composition of the brass was analyzed at the "Kemal Kapetanović" Institute in Zenica, Bosnia and Herzegovina, using a Perkin Elmer 3110 Atomic Absorption Spectrometer.

Table 1. *Chemical composition of brass*

Element	Percentage (%)
Cu	57.0
Zn	39.5

In the electrochemical corrosion testing using DC techniques, this study employed the polarization method of Tafel extrapolation and the linear polarization method.

The polarization resistance values were monitored using the linear polarization method. The polarization resistance was determined based on the open circuit potential in the polarization range of ± 20 mV.

The change in the potential of the working electrode from the open circuit potential was measured in both the cathodic and anodic directions using the Tafel extrapolation method, within a range of ± 250 mV at a scan rate of 0.5 mV/s.

For corrosion testing using AC techniques, electrochemical impedance spectroscopy (EIS) was used.

Impedance as a function of frequency was measured using the electrochemical impedance spectroscopy method. The principle of this method is to apply a small amplitude sinusoidal potential (±5–10 mV) to the working electrode, which oscillates around the corrosion potential at different frequencies.

For testing the inhibitory effect of wild raspberry fruit on the corrosion of brass in 3% NaCl, brass samples with the following dimensions were used:

- For polarization DC testing, samples with a diameter (d) of 15 mm and thickness (δ) ranging from 1 to 2 mm were used;

- For the application of the electrochemical impedance spectroscopy method, samples with dimensions of 13x13 mm were used.

The preparation and care of the samples were carried out according to the standard ASTM G5 [8].

3. RESULTS AND DISCUSSION

The extraction yield, Y, expressed as a percentage, was calculated based on the dry weight of the sample, m_S, and the weight of the extract, m_E, respectively, after the solvent was removed, according to the following formula [7]:

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

The yield of ultrasonic extraction is shown in Table 2.

Table 2. *The yield of ultrasonic extraction*

Sample	Plant mass, g	Mass of extract, g	Yield, %
UPD	96.66	5.16	5.81

Meaning of the signs: **UPD**- fruit wild raspberry - ultrasonic

Ultrasonic extraction is a better and more economically viable extraction technique, which has been shown to yield a significant content of total phenols in the wild raspberry fruit extract, as seen in Table 3. Based on these results, it can be concluded that ultrasonic extraction leads to a satisfactory yield of phenolic compounds in a short period of time, thereby reducing energy consumption and phenol degradation.

Table 3. *Content of total phenols in the wild raspberry fruit extract, obtained by the method of ultrasonic extraction*

Sample	Total phenols (mg GA/g extract)
UPD	23.41±1.73

All experiments were repeated three times. The values are expressed as mean ± standard deviation. Corrosion parameters of brass in 3% NaCl, with and without the addition of wild raspberry fruit extract, determined by the Tafel extrapolation method and the linear polarization method, are presented in Tables 4 and 5.

Table 4. *Corrosion parameters determined by Tafel extrapolation method of brass in 3% NaCl without and with the addition of wild raspberry fruit extract in different concentrations*

[Raspberry extract] g/L	$E_{cor.}$ (mV)	$I_{cor.}$ (μA cm^{-2})	b_c (mV dec^{-1})	b_a (mV dec^{-1})
Without extract	-368.271	0.4000	211.761	328.099
0.01612	-346.153	0.1301	108.583	117.081
0.03221	-308.168	0.2804	207.928	234.778
0.04828	-248.969	0.1203	94.295	101.135
0.06432	-277.499	0.1260	116.692	186.888
0.08033	-284.811	0.3611	219.250	260.793

Table 5. *Corrosion parameters determined by Linear polarization method of brass in 3% NaCl without and with the addition of wild raspberry fruit extract in different concentrations*

[Raspberry extract] g/L	$E_{cor.}$ (mV)	$I_{cor.}$ (μA cm^{-2})	*R(Ω)*
Without extract	-378.974	1.324	16420.556
0.01612	-317.414	1.173	18535.114
0.03221	-338.579	1.191	18249.167
0.04828	-335.467	0.897	24245.206
0.06432	-321.148	1.012	21478.482
0.08033	-288.412	1.213	17924.034

The results presented in Tables 4 and 5 show that the corrosion rate of brass decreases in the presence of wild raspberry fruit extract. The raspberry fruit extract at a concentration of 0.04828 g/L (0.004828 %) provides the highest protection for brass against corrosion in 3% NaCl.

The results of the investigation into the inhibitory effect of wild raspberry fruit extract on brass in 3% NaCl using electrochemical impedance spectroscopy are presented in the Nyquist diagram (Figure 1). The results were later analyzed using an equivalent electrical circuit, and the obtained corrosion parameters are shown in Table 6.

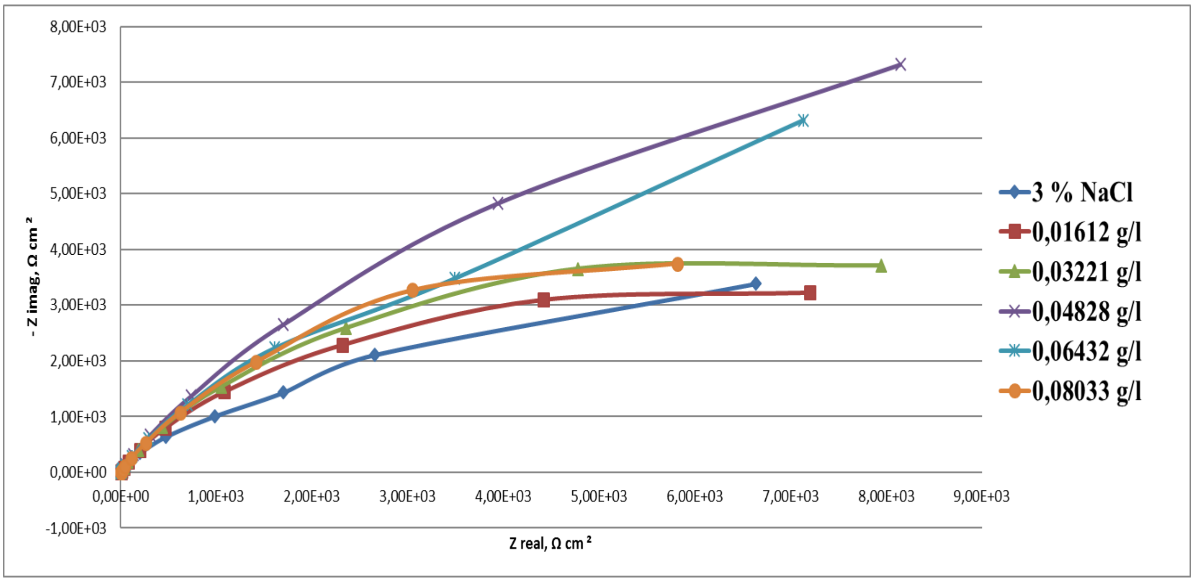

Figure 1. *Nyquist brass curves in 3% NaCl without and with the addition of wild raspberry fruit extract*

Table 6. *Corrosion parameters obtained by electrochemical impedance spectroscopy of brass in 3% NaCl without and with the addition of wild raspberry fruit extract*

[Raspberry extract] g/L	R1 (Ω)	R2(Ω)	C(F)
Without extract	283.9	7422	$2.247 \cdot 10^{-4}$
0.01612	223.5	7645	$1.297 \cdot 10^{-4}$
0.03221	221.4	8729	$1.233 \cdot 10^{-4}$

0.04828	242.6	13920	$1.776 \cdot 10^{-4}$
0.06432	257.8	11830	$2.119 \cdot 10^{-4}$
0.08033	152.3	7713	$2.109 \cdot 10^{-4}$

The corrosion parameters presented in Tables 4, 5, and 6 indicate that, using the Tafel extrapolation method, the linear polarization method, and the electrochemical impedance spectroscopy method, the extract concentration of 0.04828 g/L provides the best protection for brass in a 3% NaCl solution.
Many scientists show great interest in environmentally friendly inhibitors, plant-based compounds, and corrosion of copper and its alloys [9,10,11]. The inhibitory effect of extracts from certain plants is achieved due to the presence of tannins and other components in their composition [12].

4. CONCLUSIONS

The results obtained in this study show that the wild raspberry fruit extract, obtained by the ultrasonic method, contains significant amounts of total phenols (23.41±1.73 mg GA/g of extract), making it a potential corrosion inhibitor.
The results of the investigation into the inhibitory effect of wild raspberry fruit extract, obtained by the ultrasonic method, on brass corrosion using DC techniques confirm that the corrosion rate of brass decreases in the presence of almost all tested concentrations of the wild raspberry fruit extract.
By applying the Tafel extrapolation and linear polarization methods, it has been proven that the wild raspberry fruit extract at a concentration of 0.04828 g/L provides the highest protection for brass against corrosion in 3% NaCl.
Research conducted using the electrochemical impedance spectroscopy method (AC method) also confirms that almost all tested concentrations of wild raspberry fruit extract slow down the kinetics of the brass corrosion process, as evidenced by an increase in resistance. Furthermore, the extract concentration of 0.04828 g/L provides the highest protection for brass against corrosion in 3% NaCl, where the AC method aligns with the DC measurement methods.
The obtained results confirm that in an aggressive medium, such as a 3% NaCl solution, the tested wild raspberry fruit extract at a concentration of 0.04828 g/L can be used for brass corrosion protection at room temperature [13~~9~~].

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