University of Belgrade, Technical Faculty in Bor

30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

Editor
Prof. Dr Snežana Šerbula

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PROCEEDINGS

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PREFACE

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 kept three areas in focus: ecology, environmental protection and sustainable development. The conference will be held on Mt Stara Planina in hotel Stara Planina, Serbia, 20–23 June 2023. The monograph is published on the occasion of the 30th anniversary of the conference. On behalf of the scientific and organizing committee, it is a great honor and pleasure to wish all the participants a warm welcome to the conference.

The monograph is published on the occasion of the 30th anniversary of the conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These Proceedings 103 papers from the authors coming from the universities, research institutes and industries in 11 countries: Australia, USA, Brazil, Spain, Portugal, Libya, Italy, Bulgaria, Bosnia and Herzegovina, North Macedonia, and Serbia.

As a part of this year's conference, the 5th Student Session – EcoTERS'23 is being held. We appreciate the contribution of the students and their mentors who have also participated in the conference.

The support of the Gold donor and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'23. The organizing committee would like to extend their appreciation and gratitude to the Gold donor of the conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the conference participants for their support to the EcoTER'23. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'23.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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Student Section

THE COPPER CORROSION IN CHLORIDE MEDIUM WITH ADDITION OF BLACKBERRY LEAF EXTRACT

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Abstract

The influence of blackberry leaf extract (BLE) on copper corrosion in 0.5 M NaCl solution was investigated. The extract was made as evaporated blackberry leaf water extract. The cyclic voltammetry (CV) was performed in a blank solution and a solution with the addition of 15 g/L BLE. Surface characterization was performed using scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDS). The copper surface characterization was performed on copper specimens after 1 day of immersion in a blank solution and in a solution with the addition of 15 g/L BLE. Three anodic current peaks and two cathodic current peaks were observed on the cyclic voltammogram without the addition of BLE. The CV results show that there was a reduction of anodic and cathodic current peaks in the presence of BLE, which clearly confirms that BLE reduced the amount of corrosion products. SEM-EDS results confirm that a smaller amount of copper oxide and chloride occurs on the copper surface in the presence of BLE in relation to the copper surface in the blank solution. The results show that BLE acts as a good copper corrosion inhibitor in a chloride environment.

Keywords: green inhibitor, blackberry leaf, copper, corrosion, SEM-EDS.

INTRODUCTION

Blackberry leaf is a concentrated source of valuable nutrients and bioactive constituents. It contains vitamins, steroids, and lipids in seed oil and minerals, flavonoids, glycosides, terpenes, acids, and tannins in the aerial parts. The aeral parts have pharmacological activities such as antioxidant, anti-carcinogenic, anti-inflammatory, antimicrobial, anti-diabetic, anti-diarrheal, and antiviral [1,2]. According to a survey conducted in 2005, Serbia had the largest area in the world and accounted for 69% (5300 ha) of Europe's blackberry area. Also, Serbia had the fourth-highest production in the world, with 90% of its production processed and exported [3]. Considering the importance of sustainable development and the replacement of previously toxic substances with environmentally friendly ones, blackberry leaf can be considered as an environmentally friendly corrosion inhibitor. Research shows that blackberry leaves contain caffeic acid, which is already a known copper inhibitor [4,5].

Copper is used in industrial facilities where it is exposed to seawater, chlorine-containing solutions, and hydrochloric acid used to remove rust [6,7]. It is important to note that chlorine has a negative effect on copper corrosion, so natural corrosion inhibitors can be applied to protect this highly used metal [8,9].

The influence of blackberry leaf extract (BLE) on the copper corrosion behavior in 0.5 M NaCl was previously investigated [5]. The results have shown that BLE acts as a mixed type of copper inhibitor (97.19% IE). The best results were obtained with the addition of 15 g/L BLE. For further understanding of the corrosion mechanism, this paper shows how the presence of 15 g/L BLE in a 0.5 M NaCl solution affects the protection of copper from corrosion by using cyclic voltammetry (CV). Also, surface characterization (SEM-EDS) was performed to show the difference between the copper surface after standing in a pure solution and a solution with the addition of BLE. Based on this, blackberry leaf, as a by-product of blackberry production, can be part of progress towards sustainable development and environmental protection.

EXPERIMENTAL

Solution and material preparation

The starting component for obtaining blackberry leaf extract is a dry blackberry leaf produced by “Adonis”, Serbia. Water extract was obtained by pouring hot water over dry leaves. The ratio of solid to liquid components was 1 kg:7.5 L. After 12 hours, filtering was performed on filter paper No. 1. The aqueous extract was evaporated in a rotary evaporator “Buchi R-210”. As an output product, a dark colored resin-like substance was obtained, representing blackberry leaf extract (BLE).

The solution of 0.5 M NaCl was prepared using distilled water and NaCl salt p.a. purity manufactured by “Zorka Pharma”, Šabac, Serbia. A solution containing 15 g/L BLE was prepared by adding an adequate amount of evaporated extract in a 0.5 M NaCl. Fresh solutions were prepared before each experiment. A rectangular piece of copper Cu-DHP (99.97% Cu, 0.0198% P, 0.0005% Pb) sheet was used to prepare the working electrode. It was sealed with epoxy resin to obtain a cross section of 0.06 cm^2. The copper coupons Cu-DHP for SEM-EDS analysis were made by cutting a copper sheet to dimensions of 1x1 cm.

Electrochemical experiments

The three-electrodes electrochemical cell was used for performing electrochemical experiments. The working electrode was made of copper Cu-DHP, counter electrode was made of platinum sheet, and saturated calomel electrode was used as reference electrode. Experiments were performed at room temperature. The working electrode surface was polished before experiments using a polishing cloth with alumina slurry (0.3 μm), washed with distilled water and ethanol. The “Gamry interface 1010e potentiostat/galvanostat/zra” (Gamry instruments, USA) was used for conducting experiments. The BLE influence on copper corrosion in a chloride medium was investigated using cyclic voltammetry. The cyclic voltammograms were recorded in 0.5 M NaCl without and with the addition of 15g/L BLE in a potential range from -1 V to +1 V (SCE), with a scan rate of 20 mV/s. The “Gamry Framework software” was used for setting parameters and performing experiments, while

“Gamry Echem Analyst” was used for analyzing output data, as well as for drawing graphics (both Gamry instruments, USA).

Metal surface characterization

The copper surface was characterized using scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDS “VEGA 3 LMU”, Tescan, USA). The copper specimens were immersed in the solution after preparing the surface. The analysis was performed after standing for 1 day in a blank solution and in a solution with the addition of 15 g/L BLE.

RESULTS AND DISCUSSION

Cyclic Voltammetry (CV)

Cyclic voltammograms obtained for copper in 0.5 M NaCl solution with and without the addition of 15 g/L BLE are shown in Figure 1.

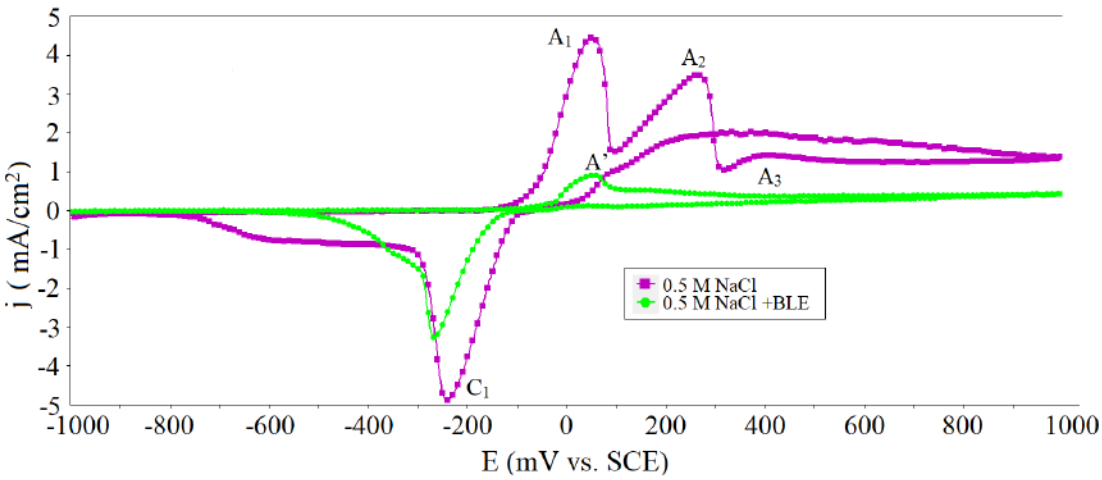

Figure 1 *Cyclic voltammograms obtained for copper in 0.5 M NaCl solution with and without the addition of 15 g/L BLE*

The following current peaks were observed on the cyclic voltammogram obtained in 0.5 M NaCl solution without the addition of BLE: A_1, A_2, A_3, A’, and C_1. Copper dissolution starts around E = -150 mV vs. SCE followed by peaks A_1 and A_2. According to the literature, it can be assumed that current peaks A_1 and A_2 correspond to the formation of CuCl and $CuCl_2^-$ [11–15]. The mechanism of copper corrosion takes place starting with the following reaction [16]:

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

after which it is adsorbed or deposited on the surface of Cu-DHP. Further, this molecule is transformed into a complex [16]:

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

The anodic current peak A_3 can be attributed to the formation of copper oxide [17–19]. This additional oxidation of copper is assigned to the current peak A' [17]. These reactions can be represented as follows [16]:

$$CuCl_2^- \rightarrow Cu^{2+} + 2Cl^- + e^- \quad (3)$$

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

$$Cu_2O + 1/2\, O_2 + Cl^- + H_2O \rightarrow Cu_2(OH)_3Cl + OH^- \quad (5)$$

The cathodic peak C_1 observed on the CV curve for blank solution indicates the reduction of corrosion products [20].

Comparing the CV curve obtained in the presence of BLE with the CV curve without the addition, it can be observed that the area under the anodic polarization curve decreases in the presence of BLE. Surface reduction indicates the formation of smaller amounts of corrosion products [19]. The anodic peak A_1 is significantly smaller. Other anodic peaks were not detected in the presence of BLE. This indicates that the presence of inhibitor significantly reduces the formation of copper chloride, while the formation of oxides is completely prevented. The obtained results indicate that BLE molecules adsorb on the copper surface and prevent copper corrosion [5,16,19]. The decrease of cathodic current peak C_1 indicates that the reduction process is taking place but with a much lesser extent than in 0.5 M NaCl solution without the addition [20]. The results obtained by cyclic voltammetry indicate that BLE affects both the cathodic and anodic processes. There is a greater influence on the oxidation process, especially on the process of copper oxide formation.

Metal surface characterization

The backscattered electron (BSE) images were obtained by scanning electron microscopy. Micrographs were obtained from the copper surface after immersion in 0.5 M NaCl solution for 1 day in the absence (Figure 2a) and presence of 15 g/L BLE (Figure 2b). The chemical composition of each surface was determined by EDS for the entire surface as shown in Figure 2. The chemical composition of the elements is shown in Table 1 and expressed in atomic percentages. Spectrum 1 refers to the copper surface in 0.5 M NaCl, while the values for Spectrum 2 refer to the copper surface after standing in a solution with the addition of BLE.

The presence of oxygen and chlorine in the corresponding Spectrum 1 confirms the existence of corrosion products on the Cu-DHP surface after standing in blank solution. In contrast, in the presence of BLE, the copper surface is well protected from corrosion (Figure 2b). Also, the Spectrum 2 of the copper surface in the presence of BLE shows that there is no chlorine detected on the surface. The amount of oxygen is significantly lower, which may be a consequence the inhibitor organic components adsorbed on the copper surface. The presence of BLE molecules on the copper surface is additionally confirmed by the presence of carbon in Spectrum 2 [20]. The earlier research of BLE chemical composition shows that BLE contains caffeic acid, quercetin-3-O-glucoside and kaempferol-3-Oglucoside [5]. SEM-EDS analysis confirms that inhibitor molecules adsorb on the copper surface and protect the metal from corrosion in the presence of chloride ions.

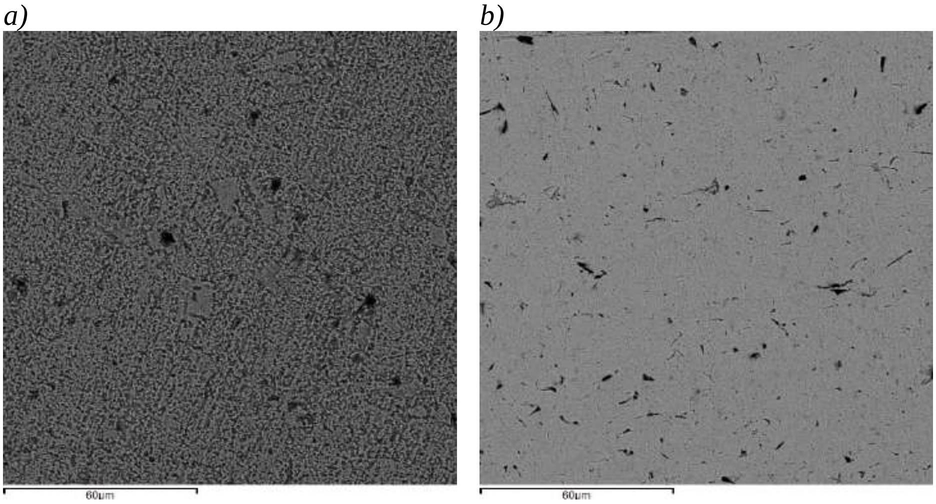

Figure 2 *BSE SEM images of copper specimens after 1 day of immersion in 0.5 M NaCl a) without and b) with 15 g/L BLE*

Table 1 *Chemical composition of copper after standing for 1 day in 0.5 M NaCl solution (Spectrum 1) and in a solution with the addition of 15 g/L BLE obtained by EDS (Spectrum 2)*

Spectrum	Elements, at%			
	O	Cl	Cu	C
1	50.82	1.33	47.85	-
2	11.65	-	38.35	49.99

CONCLUSION

Based on the investigated electrochemical behavior of the Cu-DHP in a 0.5 M NaCl solution, without and with the addition of blackberry leaf extract, the following can be concluded: The results obtained by cyclic voltammetry show that tree current peaks were detected on the anodic polarization curve and two current peaks were detected on the cathodic polarization curve for copper in 0.5 M NaCl. The anodic peaks correspond to the formation of CuCl, $CuCl_2^-$ and Cu_2O. The cathodic peaks correspond to additional oxidation of copper and reduction of corrosion products. With the addition of 15 g/L BLE, the surface area below the polarization curves is smaller than the surface area below the polarization curve recorded without the addition of BLE. Since BLE affects both anodic and cathodic peaks, it can be concluded that it acts as a mixed type of copper inhibitor in chloride medium. SEM and EDS results show that there is no chloride in the presence of BLE, and oxygen amount is significantly reduced. The presence of carbon unequivocally confirms the presence of adsorbed BLE molecules on the copper surface.

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