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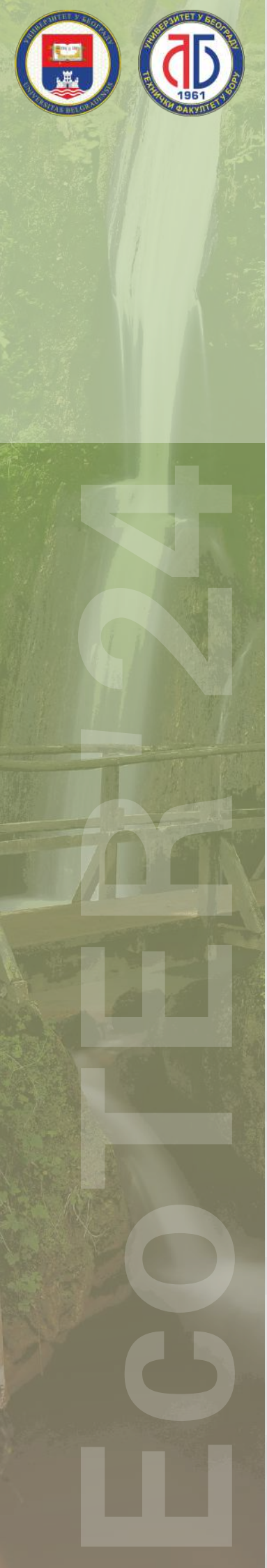

31st International conference

Ecological Truth & Environmental Research

Editor
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PROCEEDINGS

Hotel Sunce, Sokobanja, Serbia
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PREFACE

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 focuses on showing the latest research findings and innovations in the field of ecology, environmental protection and sustainable development. The conference will be held in Sokobanja (Serbia) in hotel Sunce in the period of 18–21 June 2024.

The aim of the conference is to connect the experts in various fields in order to transform attitudes and behaviors in everyday practices, as well as in the industry and economy sector which is essential for achieving the desired changes that our society must undergo.

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 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 Society of Young Researchers – Bor.

These Proceedings encompass 119 papers from the authors coming from the universities, research institutes and industries in 15 countries: Brazil, Norway, USA, Spain, Austria, Libya, Italy, Israel, Slovenia, Croatia, Romania, Bulgaria, Montenegro, Bosnia and Herzegovina, North Macedonia, and Serbia. It is a great honor and pleasure to cordially wish a warm welcome to all the participants of the conference.

As a part of this year's conference, the 6th Student Section – EcoTERS'24 will be held. We appreciate the contribution of the students and their mentors who have also participated in the conference and hope that students will continue to explore and to be curious, since education is a never-ending process, and knowledge is continuously growing.

The organization of the EcoTER'24 conference has been financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The support of the Donors and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'24 conference. The organizing committee would like to extend their appreciation and gratitude to the Platinum donors of the conference – Serbia ZiJin Copper doo Bor and HBIS SERBIA, to the Gold donor of the conference – Elixir Group, as well as to the Silver donor of the conference – Serbian Chamber of Engineers.

We would like to express our sincere appreciation to all the authors who have contributed to the Proceedings. We would also like to express our gratitude to the members of the scientific, organizing and honorary committees, reviewers, speakers, chairpersons and all the conference participants for their support of the EcoTER'24. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'24.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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THERMODYNAMIC ANALYSIS AND INFLUENCE OF THE pH VALUE ON THE BIOSORPTION OF COPPER IONS ONTO HAZELNUT SHELLS

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Abstract

The thermodynamic analysis of the copper ions biosorption process using hazelnut shells as a biosorbent, as well as the influence of the pH value on the biosorption capacity, are presented in this paper. The thermodynamic parameters that were analyzed are: activation energy (E_a), change in Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), under standard conditions, at different temperatures (25°C, 35°C, and 45°C). The values of the calculated thermodynamic parameters indicate that the biosorption of copper ions onto hazelnut shells is favored at temperatures lower than the room temperature, that the process itself is endothermic and disordered, in which copper ions are bound to the surface of the hazelnut shell by chemisorption. The pH analysis showed that the pH value of the solution has a significant effect on the biosorption capacity, whereby the biosorption capacity increases proportionally with the increase in the pH value of the solution.

Keywords: thermodynamic analysis, biosorption, copper ions, pH value, hazelnut shells.

INTRODUCTION

Water, making up more than 70% of the Earth's surface, is our most valuable natural resource, without which life would not be possible [1]. However, as a result of continuous population growth, agricultural activities, industrialization and other geological, environmental and global changes, its pollution is increasing and in many parts of the world safe drinking water is not available [2].

Bearing in mind the development of mining, extractive and processing metallurgy, pollution by heavy metals, due to their non-degradable and persistent nature, leads to permanent contamination of the environment, and represents a serious environmental problem [3]. The solubility of heavy metals in the water environment is very high, which is why living organisms can absorb them. If they accumulate in the body beyond the permitted limits, they can cause serious health problems, which is why the treatment of wastewater contaminated with heavy metals, before their release into the environment, is necessary [4].

Removal of heavy metals from industrial wastewater can be achieved by various conventional methods. These treatment methods include: chemical precipitation, coagulation, complexation, adsorption with activated carbon, ion exchange, solvent extraction, electrodeposition, cementation, etc. [5]. The application of the mentioned methods does not

always give satisfactory results. Developing a new process – the biosorption process, which can become an alternative to conventional methods, certain advantages can be achieved when it comes to industrial wastewater treatment [6]. The main advantages of biosorption compared to conventional wastewater treatment technologies are its low cost, high efficiency, minimization of chemical or biological sludge, the ability to regenerate adsorbents, and the possibility of metal recovery after adsorption [7].

Adsorption of metal ions from aqueous solutions is a reversible process, which is why a change in temperature has an impact on its development. Thermodynamic parameters, such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0), are evaluated to better understand the effect of temperature on the adsorption process [8].

In this work, the influence of the change in the pH value of the solution on the capacity of the biosorption process was investigated, along with the thermodynamic of the process.

MATERIALS AND METHODS

Hazelnut shells were ground and sieved on a set of laboratory sieves, and the fraction (-1+0.4) was used for the experiments.

In order to examine the influence of the pH value of the solution on the biosorption capacity of copper ions, a series of experiments was performed using copper ions solutions of different pH values, ranging from 2–5. The pH value of the solution was adjusted by adding 0.1M HNO_3 and 0.1M KOH. The initial concentration of copper ions in the solution (0.2 g dm^{-3}), as well as the stirring rate and adsorption time (60 minutes) were constant.

In order to determine the thermodynamic parameters, 1 g of biosorbent was brought into contact with 50 mL of a solution of copper ions with a concentration of 0.2 g dm^{-3}, at temperatures of 25°C, 35°C and 45°C, for 90 minutes. The suspension was then filtered and the concentration of copper ions was determined in the obtained solution.

RESULTS AND DISCUSSION

Effect of pH value change on biosorption capacity

The experimental data obtained for the effect of the pH are shown in Figure 1.

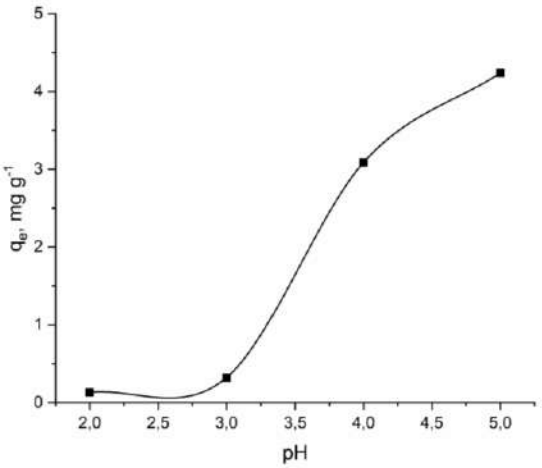

Figure 1 *Change in biosorption capacity with change in the solution pH*

It can be seen from Figure 1 that the removal of metal ions from an aqueous solution by biosorption is highly dependent on the pH value of the solution. At pH=2, the biosorption capacity was 0.131 mg g^{-1}, while it reached its maximum value of 4.237 mg g^{-1} at pH=5. Lower values of biosorption capacity at lower pH values are the result of higher concentration of H^+ ions in the solution, which "compete" with copper ions for active sites in the structure of hazelnut shells [9].

Thermodynamics of the biosorption process

The thermodynamic parameters of biosorption were calculated using the following equations [10]:

$$K_d = \frac{C_A}{C_S} \tag{1}$$

$$\Delta G^0 = -RT \ln K_d \tag{2}$$

$$\ln K_d = \left(\frac{\Delta S^0}{R}\right) - \left(\frac{\Delta H^0}{RT}\right) \tag{3}$$

$$\ln K_d = \left(\frac{-E_a}{RT}\right) + \ln A \tag{4}$$

where Kd is the equilibrium constant; C_A, the concentration of adsorbed substance at equilibrium (mol dm^{-3}); C_S, the equilibrium concentration of metal ions in solution (mol dm^{-3}); ΔG^0, the Gibbs free energy (kJ mol^{-1}); R, the universal gas constant (J mol^{-1} K^{-1}); T, the operated temperature (K); ΔH^0, the enthalpy change (kJ mol^{-1}); ΔS^0, the entropy change (J mol^{-1} K^{-1}); E_a, the activation energy (kJ mol^{-1}); A, the Arrhenius factor.

Figure 2 shows the dependence of ln K_d as a function of 1/T. Based on the given dependence and experimental data, the thermodynamic parameters of the biosorption of copper ions onto hazelnut shells were calculated and are given in Table 1.

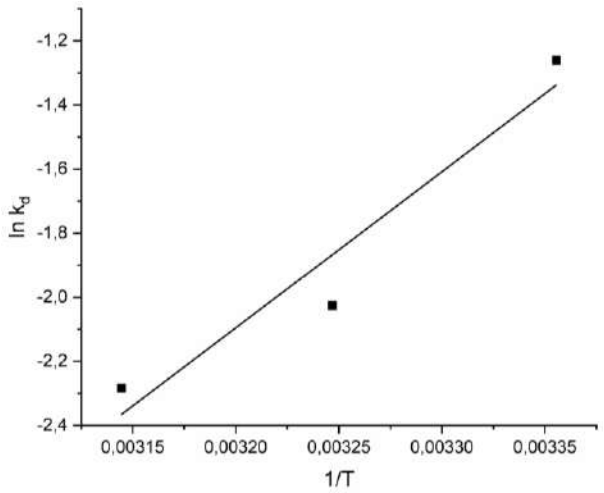

Figure 2 *Thermodynamic dependence (ln K_d = f(1/T)) for the biosorption of copper ions onto hazelnut shells*

Table 1 *Thermodynamic parameters of copper ion biosorption process onto hazelnut shells*

T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})
298	3.123			
308	5.188	4870.393	-17.681	40.492
318	6.037			

Based on the obtained values of the Gibbs free energy change, shown in Table 1, it can be concluded that the Gibbs free energy increases with an increase in temperature, as if the process itself is not feasible at room temperature, but is more favoured at lower temperatures. The obtained values of enthalpy and entropy indicate that the biosorption process of copper ions onto hazelnut shells is endothermic and disordered.

The obtained high value of activation energy (E_a) indicates that the chemical binding of copper ions to active sites in the structure of the hazelnut shell is the dominant mechanism within the examined process.

CONCLUSION

Hazelnut shells were used as a biosorbent for copper ions biosorption from synthetic solutions. The effect of changing the pH value of the solution on the capacity of the biosorption process was investigated and the thermodynamic parameters of the process were determined. Based on the performed experiments and the analysis of the obtained data, it can be concluded that the pH value of the solution has a significant influence on the biosorption capacity, whereby the biosorption capacity increases in proportion to the increase in the pH value of the solution. The values of the calculated thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0 and E_a) indicate that the biosorption of copper ions onto hazelnut shells is a more favoured process at lower temperatures than the room temperature, that the process itself is endothermic and disordered, in which copper ions bind to the surface of the hazelnut shell by chemisorption.

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