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Application of biochar derived from sour cherry pit and kombucha scoby for the removal of lead (II) ions from wastewater

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Abstract

Heavy metals are persistent environmental contaminants that pose severe risks to both ecosystems and human health mainly due to their high toxicity and bioaccumulation. These pollutants originate from natural processes like volcanic activity and human activities such as mining and industrial operations. Their non-biodegradable nature leads to bioaccumulation in the food chain, resulting in elevated concentrations in humans. In order to solve the problems connected to heavy metal presence in the natural environment and wastewaters in particular, special attention is focused on biosorbents, which are usually cheaper (i.e. compared to active carbon), but still highly efficient. For this purpose, different biological materials such as microorganisms (bacteria, fungi, algae), agricultural by-products, etc., with high metal-binding capacities, are increasingly investigated as particularly effective in treating diluted effluents. In this work, the emphasis is put on investigating the application of biochar resulted in the pyrolysis of biowaste cherry pits and kombucha SCOBY in the removal of heavy metals, specifically lead from wastewaters. In this investigation, the adsorption capacity and efficacy of those two adsorbents and their adsorption kinetics were examined using pseudo-first- and pseudo-second-order kinetic models, and the Weber-Morris diffusion model. It was also monitored whether the mechanism of mixing (macromixing using a magnetic stirrer and micro mixing using an ultrasonic bath) has effects on the kinetics of the adsorption process. The selected method of analysis, regarding the nature of the analyte, was the atomic absorption spectroscopy.

Keywords: biosorbent, pyrolysis, kombucha SCOBY, ultrasonic mixing, kinetic study, lead removal

1. INTRODUCTION

Heavy metals such as lead, cadmium, mercury, and arsenic pose a considerable threat to ecosystems and human health. Even at minimal concentrations, these toxic elements can interfere with essential biological functions resulting in impaired growth, reproductive issues, and metabolic disturbances. Over time, heavy metals accumulate in the tissues of living organisms, leading to biomagnification through the food chain. This bioaccumulation presents serious risks for all forms of living organisms. Major contributors to metal pollution include industrial operations, mining activities, agricultural runoff, and urban wastewater discharges. The persistent and non-biodegradable nature of these metals allows them to remain in the environment indefinitely, resulting in prolonged contamination (Ismail & Mokhtar 2020). The adverse effects of heavy metal pollution extend beyond individual organisms, causing significant physiological harm and disrupting the balance of aquatic ecosystems by altering species diversity and population dynamics. Therefore, it is imperative to address metal pollution effectively to protect aquatic life and promote public health (Aziz et al. 2023; Živanić et al. 2023).

Traditional techniques such as precipitation, coagulation, ion exchange, and membrane filtration are utilized to eliminate heavy metal ions from wastewater. However, these methods often present challenges including high costs, inadequate efficiency—particularly at low contaminant concentrations—and technical complexity. The urgent need for the development of effective, cost-efficient, and rapid purification alternatives has driven researchers to explore a variety of adsorption methods (Hussain et al. 2024). These techniques are gaining popularity because of their simplicity, widespread availability, and low operational costs. Activated carbon remains the most commonly used adsorbent due to its high surface area and excellent adsorption properties. Nevertheless, its widespread practical application is hindered by several constraints, notably the substantial production costs, issues related to its regeneration, and environmental concerns during its disposal. In response, alternative adsorbents such as bio-adsorbents and modified materials have been investigated. These materials offer promising eco-friendly solutions with enhanced performance and reduced costs (Saravanan, Karishma, Kumar, Thamarai, & Yaashikaa 2023), especially those cellulose-based (Hokkanen, Bhatnagar, & Sillanpää 2016). In addition, among different biosorbents, lignocellulosic materials are among those with the greatest potential for applications in the removal of heavy metals due to their good chelating properties, three-dimensional structure, and a large number of different functional groups as active binding sites for metal ions. In addition, their price is up to ten times lower than the price of ion-exchange resins, while their working life is only somewhat shorter. Further modification of these materials can significantly enhance their adsorption capacity and selectivity for specific contaminants (O'Connell, Birkinshaw, & O'Dwyer 2008). Physical activation methods like ultrasonication and pyrolysis, as well as chemical modifications using acids, bases, and organic compounds, have been employed to improve adsorption efficiency (Saravanan et al. 2023). These modified bio-adsorbents have demonstrated high removal rates for heavy metals, inorganic anions, and organic pollutants. Many modified adsorbents are regenerable and reusable, allowing for multiple adsorption/desorption cycles and concentrated recovery of adsorbed pollutants, and the development of these low-cost adsorbents not only addresses water pollution issues but also contributes to solving solid waste problems globally (Gupta, Nayak, Bhushan, & Agarwal 2015). Having in mind all those facts, it is not surprising that in recent years, there has been a significant focus on natural materials, particularly agro-industrial by-products, which serve a dual purpose: minimizing waste and providing an economical adsorbent for the remediation of water and wastewater pollutants (Antanasković et al. 2024; Lopicic et al. 2023).

Heavy metals represent a wide group of naturally occurring elements recognized for their significant toxicity towards both ecosystems and living organisms. These metals can be classified by their toxicity: while some, such as zinc (Zn), iron (Fe), manganese (Mn), molybdenum (Mo), copper (Cu), and nickel (Ni), become harmful mainly at high concentrations, others like cadmium (Cd), lead (Pb), mercury (Hg), and arsenic (As) can be toxic even at low levels. Commonly found in wastewater, metals such as chromium (Cr), nickel (Ni), copper (Cu), cadmium (Cd), mercury (Hg), and lead (Pb) pose environmental concerns. Lead, known for its ductility and malleability, is usually extracted from ores such as galena (PbS), cerussite ($PbCO_3$), anglesite ($PbSO_4$), and minium (Pb_3O_4). Its uses are widespread, spanning applications in batteries, cable sheathing, plumbing, glass production, and paint manufacturing, as well as in shielding against X-rays and radiation. The World Health Organization (WHO) sets the permissible limit of lead in drinking water to only 10 $\mu g/dm^3$ (Mudhoo, Garg, & Wang 2012).

Over recent decades, biochar has gained reputation as a promising biosorbent (Antanasković et al. 2024; Jagadeesh & Sundaram 2023). It is generated through the controlled thermal degradation of organic materials, including agricultural residues, forestry byproducts, sewage sludge, and algal biomass, proving effective in removing a wide range of organic and inorganic pollutants from various water sources. Research indicates that biochar possesses several advantages over conventional adsorbents, such as a large specific surface area that boosts pollutant removal efficiency, low regeneration costs, a porous structure, and the ability to reduce greenhouse gas emissions and combat global warming (Othugile, Lekgoba, Ntuli, & Makhura 2022).Common production methods for biochar include pyrolysis, gasification, and hydrothermal carbonization (Cha et al. 2016).

Agro-industrial residues like cherry pits, which are abundantly available and otherwise considered waste, represent a sustainable source for biochar production through pyrolysis. The use of such materials not only contributes to environmental sustainability by reducing waste but also offers a low-cost solution for removing hazardous contaminants from water systems. This paper investigates the potential of biochar derived from pyrolysis of cherry pits and kombucha SCOBY as adsorbents for lead ion removal from aqueous solutions, emphasizing the influence of mixing on the adsorption kinetics. The study seeks to bridge a gap in the current literature, as a review of existing research indicates a lack of targeted investigations on the application of these specific adsorbents. Furthermore, while biochar derived from other biomass

sources has been widely studied, there is limited insight into the adsorption mechanisms of biochar from cherry pits and kombucha SCOBY, especially in the context of heavy metal removal. This research aims to provide a comprehensive understanding of how these biochars perform, particularly with respect to the effects of biochar type and mixing mechanism on the kinetics of the adsorption process. By reviewing the available literature, it was noticed that no special tests of the application of these two adsorbents have been carried out so far. Given the global need for cost-efficient and sustainable water treatment solutions, this study could contribute to the development of eco-friendly materials with high adsorption capacities for pollutants like lead.

2. MATERIALS AND METHODS

The experimental materials included biochar derived from sour cherry stones and kombucha SCOBY cellulose sheets, alongside a Lead(II) solution at a concentration of 30 mg/L, sourced from Sigma-Aldrich. The mixing process was conducted using either a Scilogex Magnetic Hotplate Stirrer (MS-H280-PRO) operating at 250 rpm, or a BANDELIN SONOREX DIGITEC ultrasonic bath. Lead(II) concentrations in the solution were analyzed via Atomic Absorption Spectroscopy (AAS) using the Perkin Elmer AAnalyst 300 spectrometer. Waste biomass of sour cherry stones (Prunus cerasus) was procured from the Juice Factory Vino Župa in Aleksandrovac, Serbia. After thorough washing and drying, the stones were ground using a vibrating disk mill (Siebtechnik GmbH, Germany) and sieved to achieve a particle size range of 0.1 to 0.5 mm for further investigation. The kombucha SCOBY cellulose was produced through pyrolysis of cellulose sheets formed during the fermentation of green and black tea with sugar (sucrose, $C_{12}H_{22}O_{11}$), as outlined in previous literature (Jayabalan, Malbaša, Lončar, Vitas, & Sathishkumar 2014). The cellulose was dried at 40 °C for 48 hours before grinding, following the same process as the sour cherry stones. Both materials underwent pyrolysis at 500 °C under oxygen-limited conditions in a Nabertherm 1300 muffle furnace (Nabertherm, Germany), using argon (Ar) gas at a flow rate of 100 cm^3/min, with a heating rate of 10 °C/min and a pyrolysis duration of one hour (Lopicic et al. 2023). The resultant biochars, namely sour cherry stone biochar (SCSB) and kombucha SCOBY cellulose biochar (KSCB), were subsequently utilized for adsorption studies.

A stock solution of Pb(II) at 1000 mg/L was prepared by dissolving $Pb(NO_3)_2$ in deionized water. To achieve the desired 30 mg/L concentration, this stock solution was diluted with deionized water. All experiments were conducted in triplicate within 50 mL glass bottles at ambient laboratory temperature. Detailed methodologies for batch experiments concerning lead adsorption, as well as the kinetic and isotherm studies, are thoroughly described in existing literature (Antanasković et al. 2024).

3. RESULTS AND DISCUSSION

Adsorption studies were performed in a batch mode to explore how factors such as contact time, type of adsorbent, and mixing method impact the removal of Pb(II) ions using sour cherry stone biochar (SCSB) and kombucha SCOBY cellulose biochar (KSCB). In these experiments, a 200 mL lead solution was introduced into a 400 mL glass Erlenmeyer flask, where it was mixed with 0.4 g of the selected adsorbent. The mixture was agitated using either a magnetic stirrer set at 250 rpm or an ultrasonic bath under standard conditions of pressure and temperature.

Over a period of 120 minutes, samples were collected at designated time intervals to measure the concentrations of Pb(II) ions through Atomic Absorption Spectroscopy (AAS). The primary objective was to assess which of the two biochar types exhibited superior adsorption capabilities and to investigate whether different mixing mechanisms could enhance the adsorption efficiency.

3.1. The effect of adsorbent type and mixing mechanism on Pb (II) adsorption

The experimental results detailing the effects of both the adsorbent type and mixing mechanism on the adsorption of Pb(II) ions are illustrated in Figures 1a and 1b, providing valuable insights into the optimization of biochar applications for heavy metal removal from wastewater.

The data illustrated in Figure 1 demonstrates that KSCB exhibits a greater adsorption capacity over the specified timeframe compared to SCSB, independent of the mixing method employed. This discrepancy is likely attributed to the inherent structural characteristics of the biomaterials, with the sour cherry stone possessing a denser structure (and consequently lower porosity) than the cellulose sheets derived from kombucha SCOBY. As a result, even after pyrolysis, KSCB retains a larger portion of its mass accessible for adsorption.

Moreover, the magnetic mixing technique generates larger eddies compared to ultrasonic mixing, which suggested that magnetic agitation could potentially facilitate mass transport within the bulk liquid and the boundary layer. Conversely, ultrasonic mixing was expected to improve mass transfer within the pores of the adsorbent. However, the findings reveal that the mixing method has a negligible impact on the adsorption process. This might

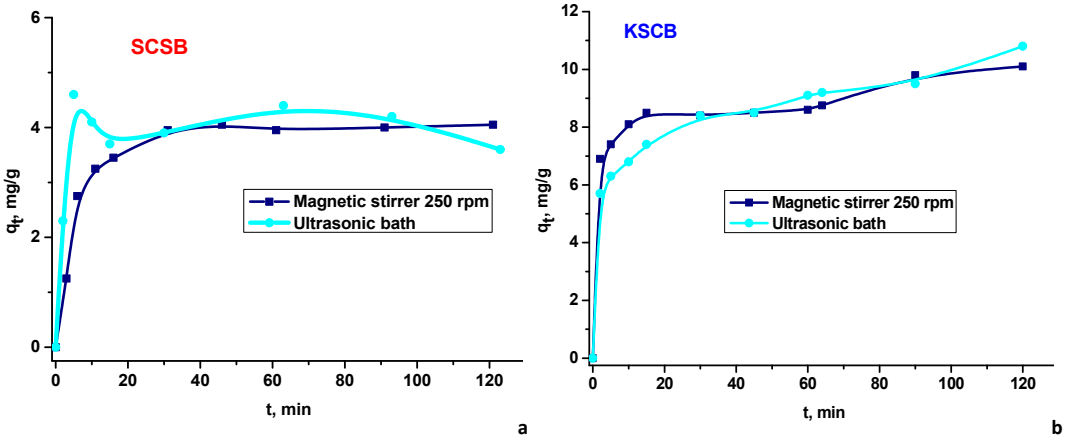

Figure 1. Influence of mixing mechanism on Pb(II) adsorption on SCSB (a) and KSCB (b).

be due to the fact that the rate-limiting step in the examined system was not the mass transport (whether in the liquid bulk, boundary layer, or adsorbent pores) but rather the adsorption itself. Despite the fact that adsorption is the slowest step, most of the adsorption process of lead (II) ion from solution was performed relatively quick within the first 20 min.

3.2. Adsorption kinetics

Numerous adsorption kinetic models have been established to characterize the reaction kinetics associated with adsorption processes. Among these, the most used are the pseudo-first-order (PFO) model, the pseudo-second-order (PSO) model, the mixed-order (MO) model, and the Elovich model. In systems adhering to the PFO model, it is typically observed that adsorption is not constrained by the adsorption in active sites; instead, in some cases it may indicate that external or internal diffusion processes are the rate-limiting steps. Conversely, systems represented by the PSO model suggest that the kinetics are primarily influenced by the adsorption onto active sites, which is considered the slowest step in the process. The MO model is therefore used when kinetics of diffusion and adsorption within the system are of the same order (Wang & Guo 2020).

Several diffusion models exist to investigate the diffusion process itself and the diffusion mechanisms, with the Weber-Morris (WM) model being predominantly utilized to identify the controlling step of the rate. In the study of Pb (II) removal kinetics, Elovich, the PFO and PSO models were applied, while WM was employed for modeling mass diffusion.

The results of modeling the investigated adsorption systems using the linear forms of Elovich, PFO, PSO and WM model are provided in Table 1, while Figure 2a, b provides the data of the WM model.

As it can be seen from Table 1, the PFO model was not suitable for kinetic modeling of either SCSB or KSCB, whereas those data closely aligned with the PSO model. This observation supports the prior assertion that the mixing mechanism does not significantly affect the kinetics of the adsorption process and that diffusion is not a rate-limiting step.

The values of $R_E = 1/(q_e{*}b)$ that can be obtained from the Elovich model indicate that the adsorption curves of Pb (II) ions adsorption on SCSB and KSCB are "rapid and mild rising curve" systems, entering what is referred to as zone II and III, and indicating relatively fast processes (Wu, Tseng, & Juang 2009a). Consequently, the adsorbents demonstrate favorable kinetic parameters for removal via adsorption.

The graphical analysis of the Weber-Morris (WM) model for lead adsorption utilizing SCSB under magnetic stirring conditions, as illustrated in Figure 2a, reveals a multi-linear pattern in the qt versus q_t vs. $t^{1/2}$ plot. Initially, during a very short time period, the process is dominated by external surface adsorption (instantaneous adsorption). This phase is succeeded by the second step (gradual adsorption), where intraparticle diffusion governs the kinetic rate. Subsequently, in the final equilibrium stage, the movement of solute from larger to micropores occurs at a reduced rate, thereby further decreasing the overall adsorption efficiency. The data for the ultrasonic bath mixing for SCSB cannot be presented by the WM model. The graphical presentation for the WM model of KSCB indicates that in the beginning of the process, when lead ions move towards the surface, the diffusion speed is unrelated to the type of stirring (same slopes for magnetic stirring and ultrasonic mixing). As they enter into pores (second step) the difference related to the type of stirring becomes more pronounced (which can be seen in the inclination) assuming that microvortices pro-

Table 1. The obtained parameters for PFO, PSO, and WM models.

Kinetic model		KSCB/MS	KSCB/US	SCSB/MS	SCSB/US
PFO	lq_e (mg/g)	2.97	3.04	1.66	1.21
	lK_1 (min^{-1})	-0.070	-0.096	-0.1305	-0.0660
	lR^2	0.5156	0.7734	0.14788	0.04085
PSO	lq_e (mg/g)	10.08	10.66	4.187	3.73
	lK_2 (min^{-1})	254.6	199.4	20.47	51.93
	lR^2	0.99142	0.9899	0.99826	0.9857
Elovich	la	586.9	44.8	2.26	76480
	lb	1.18	0.84	1.13	3.82
	lR^2	0.917		0.914	0.974
	$lR_E=1/(q_e*b)$	0.084	0.112	0.211	0.070
WM	lK_1 (min^{-1})	0.664	0.611	2.08	/
	lR^2	0.997	0.914	1	/
	lK_2 (min^{-1})	0.258	0.429	0.457	/
	lR^2	0.782	0.957	0.970	/
	lK_3 (min^{-1})	/	/	0.016	/
	lR^2	/	/	0.207	/

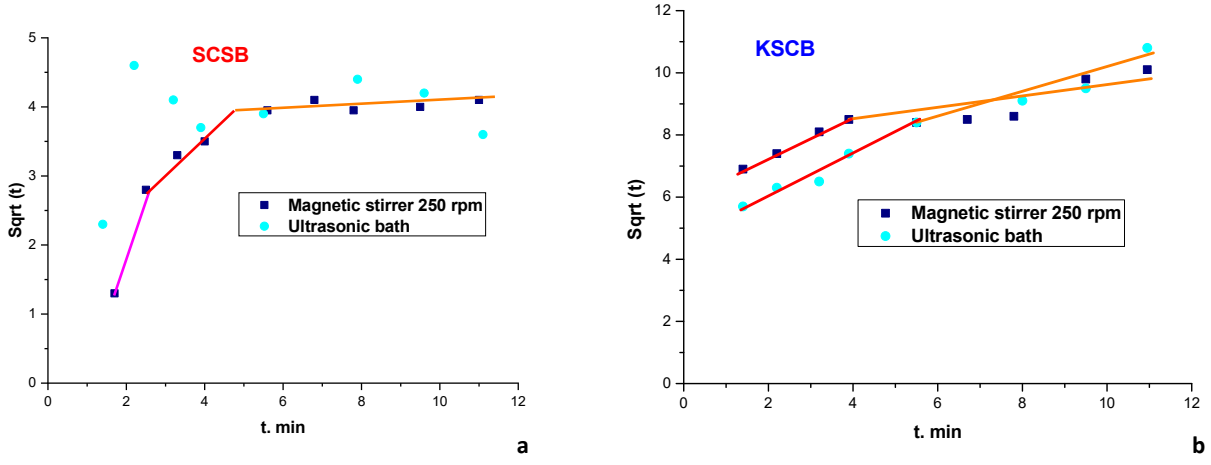

Figure 2. Weber-Morris model for SCSB (a) and KSCB (b).

duced by ultrasonic stirring can better help the Pb(II) ions in penetrating the pores, which is less pronounced with magnetic stirring. It can also be seen that the initial process step lasts longer during ultrasonic stirring because microvortices transfer lead ions form the liquid mass to the adsorbent surface more slowly in comparison to the microvortices that appear during magnetic stirring (Wu, Tseng, & Juang 2009b).

4. CONCLUSION

The conducted experiments and the subsequent analysis of results indicate that the type of adsorbent significantly influences the adsorption capacity for Pb(II) ions, while the mixing mechanism has a negligible effect on the adsorption kinetics. The findings reveal that KSCB exhibits a superior adsorption capacity, attributed to its enhanced active surface area per unit mass. The kinetics of Pb(II) ion sorption on the studied adsorbents can be modeled using the PSO kinetic model, suggesting that both adsorbents possess favorable mass transfer characteristics, thereby minimizing the impact of the mixing type. In essence, the availability of the adsorption surface is high, and the adsorption process is demonstrated to be the rate-limiting step. The kinetic parameters further imply that the investigated adsorbents enable rapid adsorption with significant capacities, underscoring their effectiveness in removing Pb(II) ions. To elucidate the adsorption mechanisms and optimize the performance of these materials further, additional investigations are necessary to examine other relevant adsorption parameters.

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