

Article

Adsorption of Zinc(II) Ion by Spent and Raw *Agaricus bisporus* in Aqueous Solution

Xiaoyu Zhang ^{1,†}, Caiyi Zhao ^{1,†}, Feng Xue ², Beicheng Xia ³, Yuanyuan Lu ¹, Rongrong Ying ^{1,*} and Zhewei Hu ¹¹ Nanjing Institute of Environmental Sciences, Ministry of Ecology and Environment, Nanjing 210042, China; zhangxiaoyu@nies.org (X.Z.); zhaocaiyi@nies.org (C.Z.); yylu@nies.org (Y.L.); huzhewei@nies.org (Z.H.)² Shenzhen Degree of Freedom Eco Technology Co., Ltd., Shenzhen 518116, China; 13770759516@163.com³ School of Environment Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China; xiabch@mail.sysu.edu.cn

* Correspondence: yrr@nies.org

† These authors contributed equally to this work.

Abstract: A significant environmental concern globally is the pollution of water bodies as a result of heavy metals. To date, various attempts have been made to effectively remove heavy metals, such as those that use synthetic and biogenic materials to abate and control water pollution. The biological removal of pollutants from water is an efficient and environmentally friendly technique. In this study, we evaluated the biosorption characteristics of Zn²⁺ ions from aqueous solution by spent composed of raw *Agaricus bisporus* (RAB) and *A. bisporus* (SCAB). We added different biosorption doses, metal ions, and initial concentrations of pollutants to explore the adsorption of Zn²⁺ by RAB and SCAB. We applied pseudo-first- and second-order models to investigate the biosorption kinetics. According to our results, the rate of Zn²⁺ removal from the aqueous solution using raw biomass was significantly lower than that using sodium citrate-treated biomass of SCAB. When the Zn²⁺ concentration increased from 10 mg L⁻¹ to 200 mg L⁻¹, the rate of removal of RAB decreased from 73.9% to 38.4%, and that of Zn²⁺ by SCAB decreased from 99.9% to 75.9%. As we increased the biosorbent dose, the rate of Zn²⁺ removal by SCAB increased. Interestingly, Zn²⁺ biosorption was inhibited by heavy co ions (Cu²⁺ and Pb²⁺) and light metals (e.g., Na⁺, Mg²⁺, K⁺, and Ca²⁺). When treating wastewater polluted with Zn²⁺, Pb²⁺, and Cu²⁺, SCAB showed good potential. The results of this study provide a scientific basis for an environmentally sound approach to controlling water pollution.



Citation: Zhang, X.; Zhao, C.; Xue, F.; Xia, B.; Lu, Y.; Ying, R.; Hu, Z.

Adsorption of Zinc(II) Ion by Spent and Raw *Agaricus bisporus* in Aqueous Solution. *Processes* **2024**, *12*, 717.

<https://doi.org/10.3390/pr12040717>

Academic Editor: Federica Raganati

Received: 24 January 2024

Revised: 22 March 2024

Accepted: 29 March 2024

Published: 1 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: biosorbent; *Agaricus bisporus*; Zn²⁺; kinetics; thermodynamic

1. Introduction

Technological advancements, growing population, mining and other industrial activities, and increasing urbanization have contributed to the rapid increase in the number of water bodies polluted with heavy metals, creating a major environmental problem. Developmental advances in industrial activities, such as mining operations, smelting, printing, metal plating facilities, explosive manufacturing, and dyeing, as well as consumer products, including paints, plastics, pesticides, alloys, batteries, tanneries, and ceramic glass, are responsible for this alarming extent of heavy metal pollution. Wastewater containing heavy metals generated by industrial units is being directly and indirectly discharged into the environment. The toxic heavy metals discharged into the water bodies influence the flora and fauna of aquatic ecosystem systems and negatively affect human health when these metals are transferred and enriched through the food chain [1]. Chemical precipitation, electrochemical treatment, filtration, and membrane technologies are commonly used to remove toxic metals from the wastewater [2–4]. When the concentration of heavy metals is low (e.g., 1–100 mg L⁻¹) and the volume of wastewater is high, conventional methods are extremely expensive and may even be ineffective [5,6]. Another major problem associated

with these conventional treatment processes is the generation of toxic chemical sludge, and its disposal becomes environmentally costly [7]. Thus, learning how to remove heavy metals from wastewater to an environmentally safe level in an ecofriendly and cost-effective manner is essential.

A significant amount of research has been conducted over the past 20 years to examine ways to control heavy metal pollution. In recent years, the removal of heavy metals involving biological methods has attained significant attention because of the cost-effective and environmentally friendly aspects [8]. Fungus [9–11], citrus peel [12], marine algae [13,14], bacteria [15], and other materials [16–18] are cost-effective and ecofriendly. These readily available biomaterials can effectively remove heavy metals in various forms from aqueous solution. However, the low adsorbing capability of raw biomass has limited the practical application of biosorption to heavy metals. Therefore, to enhance the biosorbent's adsorption capacity, chemical pretreatments are often applied, including washing the raw biomaterials with HNO_3 [12], calcium chloride [19], formaldehyde [20], HCl and acetone [21], and NaOH [22]. By masking or removing the surface groups or exposing metal-binding sites, pretreatment may change the functional groups and surface properties [23].

Recent studies have used Fourier transform infrared spectroscopy (FT-IR) or X-ray photoelectron spectroscopy (XPS) [24,25] to examine changes in the functional groups and study the mechanism of biosorption. The biosorption mechanism usually consists of adsorption, ion exchange, complexation, and microprecipitation [16]. The cell wall of biosorbent materials is usually composed of a large number of polysaccharides, proteins, lignin, and other polycomplexes, which can provide sufficient functional groups such as carboxyl, hydroxyl, sulfate, phosphate, amide, and amino for the binding of metal ions [26,27]. However, ion exchange, which is another important mechanism for chemical adsorption, has not attracted sufficient attention in the field of biosorption. The pH change after biosorption has not been reported, although it can help to evaluate the chemical changes in the biosorption process. Several studies have examined the leaching of Na^+ , Mg^{2+} , K^+ , and Ca^{2+} from biosorbents; however, these changes have not been compared with simultaneous changes in pH [9,28,29]. Furthermore, the combination of a simultaneous pH change and light metal ion release might explain the ion exchange involved in the process of biosorption [16].

One of the most common pollutants—and also among the most harmful—found in wastewater for both irrigational and industrial applications is zinc [30]. Zinc is a trace element that is essential for human beings and for the growth of flora and fauna, but large quantities of zinc can have an adverse impact on plants, animals, and humans [31]. According to the U.S. Environmental Protection Agency, the Zn^{2+} concentration in drinking water must be less than 3 mg L^{-1} [32].

Agaricus bisporus is a kind of large fungus, widely cultivated in China. Its subsidiary entity has the advantages of large size, easy access, low price, and good tolerance to harsh environments. It has the potential to prepare heavy metal bioadsorbent materials, which provides a good basis for the development of bioadsorbent materials and related mechanism research. Although most of the raw biomass materials used for biosorption are cheap and readily available, the cost involved in the preparation of biosorbents must also be considered. Hence, regeneration of the biosorbent can lower processing costs and also recover the adsorbed heavy metals. Thus, nondestructive regeneration of biosorbents by ecofriendly, economical, and effective desorbing eluants is a valuable option for eliminating heavy metals from industrial wastewater. Several studies have investigated the recycling of raw biosorbents [24,33,34]. The number of effective sorption–desorption cycles of many biosorbents, however, do not meet ideal applications. Thus, in this study, we (1) examined the role of the initial biosorbent dosage, the Zn^{2+} concentration, and aqueous metal ions; (2) tested the Zn^{2+} adsorption capacity of sodium citrate-treated *Agaricus bisporus* (SCAB); (3) studied the Zn^{2+} adsorption mechanism from multiple angles; (4) explored the effect of SCAB on the removal of Zn^{2+} from aqueous solution and determined the number of possible sorption–desorption cycles. To reduce and remove water pollution caused by

toxic heavy metals, the results of this study offer a scientific basis and an environmentally sound approach.

2. Materials and Methods

2.1. Biosorbent Preparation

The raw fungal biomass of *A. bisporus* (RAB) was obtained from a commercial company. The fruit bodies were washed thoroughly with deionized water to remove impurities and dirt, then dried for 24 h in an 80 °C oven. To obtain a uniform particle size, the dried biomass was crushed and sieved through 250–380 µm American Society for Testing Material–standard sieves. The sieved biomass was treated per gram with between 0.1 L and 10 mM of sodium citrate in a rotary shaker for 0.5 h at 150 rounds per minute. Before use, the treated biomass was dried for 24 h at 80 °C and then stored in a desiccator.

2.2. Zn^{2+} Solution Preparation

Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) was used to prepare Zn^{2+} solutions. The required quantity of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water to prepare the stock solution of Zn^{2+} (1 g L^{−1}). This solution was used to prepare different working concentrations of the dilute solutions. In all of the experiments, 0.1 M HCl and 0.1 M NaOH solutions were used to adjust the pH of the Zn^{2+} solutions to 4.0. All of the analytical-grade chemicals and reagents were used without further purification.

2.3. Batch Experiments

2.3.1. Effect of Biosorbent on Zn^{2+} Biosorption by RAB and SCAB

Then, 3 to 20 g L^{−1} of SCAB was added to 250 mL Erlenmeyer flasks containing a concentration of 100 mL Zn^{2+} solution. The temperature was maintained at 25 °C and the pH at 4.0. The experiments were performed by using equivalent amounts of raw *A. bisporus* (RAB) biomass under the same conditions to study the efficiency of the SCAB treated with sodium citrate.

2.3.2. Effect of Zn^{2+} Concentration on Zn^{2+} Biosorption by RAB and SCAB

We investigated how SCAB biosorption of Zn^{2+} was affected by the initial Zn^{2+} concentration, which ranged from 20 to 200 mg L^{−1}. The same experimental conditions were used to add RAB, further examining the effect of sodium citrate on SCAB.

2.3.3. Effect of Adsorption Time on Zn^{2+} Biosorption by SCAB

The 13 g L^{−1} SCAB was placed in 22 mg L^{−1}, 65 mg L^{−1}, 85 mg L^{−1}, and 135 mg L^{−1} zinc solution at 25 °C and a pH of 4.0, and the remaining zinc ion concentration in the solution was sampled at 5, 10, 20, 30, 40, and 60 min after the start of the reaction.

2.3.4. Effect of Co-Ions on Zn^{2+} Biosorption by SCAB

The competition for binding sites on the biomass was investigated by adding other metal ions to Zn^{2+} solutions.

Then, 0 mM of Na⁺, 1 mM of Mg²⁺, 5 mM of K⁺, and 10 mM of Ca²⁺ were added to the Zn^{2+} solutions to examine how light metal ions affected the biosorption properties of Zn^{2+} by SCAB. The quantity of light metal ions relative to their in molar equivalents was calculated because the concentration was quite high in practical wastewater.

Next, 50 mg L^{−1}, 75 mg L^{−1}, and 100 mg L^{−1} Cu²⁺ and Pb²⁺ were added to the Zn^{2+} solutions to examine how heavy metal ions affected the biosorption properties of Zn^{2+} by SCAB. The ratios of Cu²⁺/Pb²⁺ to Zn^{2+} in solution were set to 1:1, 1.5:1, and 2:1 because a 50 mg L^{−1} concentration of Zn^{2+} was maintained.

After the biosorption experiments were completed, the biosorbent was immediately removed by filtering the samples with a 0.45 µm filter membrane. An inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin-Elmer Instruments, Optima

5300 DV, Waltham, MA, USA) was used to determine the concentration of Zn^{2+} in the filtered solutions.

2.3.5. Specific Surface Area Detection of Bioadsorbent Materials

The RAB and SCAB were pretreated with vacuum pump at 348 K for 10 h. Then, an automatic nitrogen adsorption instrument (ASAP 2010, Micromeritics, Norcross, GA, USA) was used to detect the specific surface area of multi-point BET.

2.4. Light Metal Ion Release

To determine the relationship between the quantity of light metal ions released and the quantity of Zn^{2+} ions adsorbed, we sampled the solutions following the biosorption of 20–200 mg L^{-1} Zn^{2+} solutions by SCAB. We employed the charge balance method ($\text{Sum} = \text{Na}^+ / 2 + \text{K}^+ / 2 + \text{Mg}^{2+} + \text{Ca}^{2+}$) to calculate the quantity of light metal ions released.

2.5. Results of Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectroscopy (Thermo Nicolet IS10, Waltham, MA, USA) was used to study the chemical characteristics of RAB and SCAB before and after biosorption of Zn^{2+} . A ratio of 1:200 of the dried and sieved biomass samples was mixed with potassium bromide (KBr) (SP). The samples were compacted under high pressure into pellets. The FT-IR spectra ($500\text{--}4000\text{ cm}^{-1}$) were collected, and the pure KBr background from the sample spectra were subtracted.

2.6. Results of Sorption–Desorption Cycles

To study the possibility of regeneration and reuse of SCAB, 10 mM sodium citrate was used as both eluent and the regenerant. Then, 13 g L^{-1} SCAB was used to treat the 100 mg L^{-1} Zn^{2+} solution at 25 °C and a pH of 4.0; 100 mL of 10 mM sodium citrate was used to desorb the Zn^{2+} onto the biosorbent. Both the sorption duration and desorption duration were 30 min. Excessive distilled water was used to wash the biosorbent and remove the sodium citrate. Then, vacuum filtration was used to dry the biosorbent and prepare it for next process. The sorption–desorption cycle was repeated 10 times. After each sorption or desorption process, the contents of Zn^{2+} in the remaining solution were analyzed by using ICP-OES.

2.7. Experimental Data Analysis

2.7.1. Capacity of Biosorption

To evaluate the biosorption capacity, we calculated the amount of Zn^{2+} adsorbed by the biomass according to the following equation:

$$E\% = (C_0 - C_e) / C_0 \times 100, \quad (1)$$

$$q_e = (C_0 - C_e) V / W, \quad (2)$$

where $E\%$ represents biosorption efficiency; q_e represents the amount of Zn^{2+} adsorbed by SCAB (mg g^{-1}); C_0 represents the initial Zn^{2+} concentration (mg L^{-1}); C_e represents the Zn^{2+} concentration at equilibrium (mg L^{-1}); V represents the solution volume (L); and W represents the biosorbent weight (g). The experiments were completed at 25 °C (room temperature).

2.7.2. Equilibrium Isotherms

Langmuir, Freundlich, Dubinin–Radushkevich (D-R), and Temkin isotherms were used to calculate the biosorption equilibrium data.

Sorption occurs on only one ion per binding site, according to the Langmuir model, and the sorbent surface has just one type of binding site [9]. The linear form of this model is expressed as follows:

$$C_e / q_e = 1 / Q_0 b + C_e / Q_0, \quad (3)$$

where C_e represents the equilibrium Zn^{2+} concentration in solution (mg L^{-1}); q_e represents the amount of equilibrium absorption (mg g^{-1}); the Langmuir constant Q_0 (mg g^{-1}) represents the capacity of the monolayer adsorption; and b (L mg^{-1}) represents adsorption heat.

The Freundlich model can be used to calculate surface heterogeneity and multilayer adsorption to binding sites on the sorbent's surface [35]. The linear form of this empirical expression follows:

$$\log q_e = \log K_f + \log C_e/n, \quad (4)$$

where C_e represents the Zn^{2+} equilibrium concentration in solution (mg L^{-1}); q_e represents the amount of equilibrium absorption (mg g^{-1}); K_f ($\text{mg g}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$) represents the adsorbent's adsorption; and $1/n$ represents the heterogeneity of the surface [36].

Because the D-R isotherm does not assume constant sorption potential or a homogeneous surface, it is less specific than the Langmuir isotherm [37]. D-R can be calculated as follows:

$$\ln q_e = \ln q_m - \beta \epsilon^2, \quad (5)$$

where, β represents a constant related to the mean free energy of adsorption per mole of adsorbate ($\text{mol}^2 \text{kJ}^{-2}$); q_m represents the capacity for theoretical saturation; and ϵ represents the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R represents the universal gas constant and T represents the absolute temperature.

A decrease in sorption heat is linear in the Temkin isotherm rather than logarithmic, as in the Freundlich equation. This isotherm can be calculated as follows:

$$q_e = RT \ln(A_T C_e)/b_T, \quad (6)$$

where A_T (L mg^{-1}) and b_T represent the Temkin isotherm constants; R represents the universal gas constant; and T represents the absolute temperature.

2.7.3. Biosorption Kinetics

Several studies have described heavy metal experimental data for biosorbent removal using two kinetic models [38,39].

The first is the Lagergren model, which generally expresses a pseudo-first-order rate model as follows:

$$\log(q_e - q_t) = \log q_e - k_1/2.303, \quad (7)$$

The corresponding pseudo-second-order model is as follows:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e, \quad (8)$$

where q_e and q_t represent the quantities of Zn^{2+} ions adsorbed on the biosorbent at equilibrium and at time t (min.), respectively; k_1 represents the first-order adsorption rate constant (min^{-1}); and k_2 represents the second-order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

2.7.4. Biosorption Thermodynamics

Changes in Gibbs free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°), which are the most common thermodynamic parameters, were calculated as follows:

$$K_c = C_{e,ad}/C_e, \quad (9)$$

$$\Delta G^\circ = -RT \ln K_c, \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad (11)$$

where $C_{e,ad}$ and C_e represent the Zn^{2+} concentration on the biosorbent and the residual Zn^{2+} concentration at equilibrium (mg L^{-1}); K_c represents the equilibrium constant; R represents the gas constant ($8.3145 \text{ J mol K}^{-1}$); and T represents the solution temperature (K).

3. Discussion of Results

3.1. Effect of *A. bisporus* Pretreatment

In this study, when the Zn^{2+} concentration increased from 10 to 200 mg L^{-1} , the rate of Zn^{2+} removal by SCAB lowered from 99.9% to 75.9%, and the rate of RAB removal lowered from 73.9% to 38.4% (Figure 1a). This result indicated that the sodium citrate-treating method improved the biosorption capability of *A. bisporus* biomass and made the decreasing trend less significant. Because the trend in saturation when using a higher initial metal concentration for the biosorbent created a finite number of surface binding sites, the removal rate with high Zn^{2+} concentration decreased [40]. Our findings aligned with a previous study, which found that *Chlorella coloniales* was effective for Cr, Co, Fe, and As bioaccumulation; however, bioaccumulation efficiency decreased when the concentration of heavy metal was high [41].

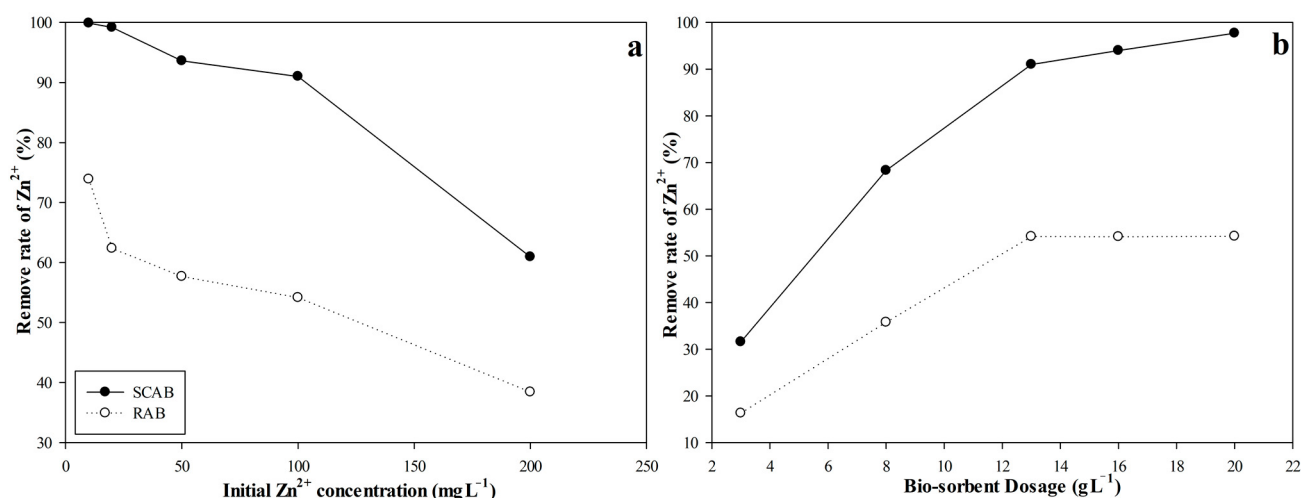


Figure 1. Removal rate of Zn^{2+} by the sodium citrate-treated *Agaricus bisporus* (SCAB) and the raw *Agaricus bisporium* (RAB): (a) with different initial Zn^{2+} concentrations; and (b) with different biosorbent dosages.

When the biosorbent dosage was changed from 3 to 20 g L^{-1} , the rate of Zn^{2+} removal by SCAB rose from 31.6% to 97.7%. Under matching experimental conditions, the rate of RAB removal increased only from 16.3% to 54.2% (Figure 1b). We attributed this increased rate of Zn^{2+} removal with a high dose of the biosorbent to an increase in the surface area as well as in the number of binding sites. The exchangeable ions that were available for adsorption increased, which was tied to the amount of biosorbent needed in the process of biosorption [42]—that is, when the biomass amount increased, the metal ion biosorption per gram of biomass decreased [41,43–46]. Therefore, when the biomass dose increased, the final amount of heavy metal removal was also enhanced; however, the biosorption capacity of the heavy metal ions decreased [41,47–49]. The removal rate of both SCAB and RAB did not rise significantly when the biosorbent dose was more than 13 g L^{-1} . The reduced effective sorption area that results from biosorbent aggregation likely was responsible [50].

The 13 g L^{-1} SCAB was placed in 22 mg L^{-1} , 65 mg L^{-1} , 85 mg L^{-1} , and 135 mg L^{-1} zinc solution at 25 °C and a pH of 4.0, and the remaining zinc ion concentration in the solution was sampled at 5, 10, 20, 30, 40, and 60 min after the start of the reaction. The kinetic curve for zinc ion showed that the amount of biosorption sharply increases with increasing contact time in the initial stage (0–20 min) and then gradually increases to reach an equilibrium value. The higher reaction rate originates from the large number of convenient adsorption sites on the surface or inside of the adsorbent. As the reaction proceeds, the available sites are gradually saturated, and the adsorption rate cannot be further improved.

3.2. Effect of Co-Ions on Zn^{2+} Biosorption by SCAB

Heavy metal ions in industrial effluents are always accompanied by light metal ions (e.g., Na^+ , Mg^{2+} , K^+ , and Ca^{2+}). The concentration of light metal ions normally is higher than that of heavy metal ions. The sorption capacity of commercial ion exchange resins is affected by light metal ions [19]. Even at a concentration of 10 mM, the effect of Mg^{2+} on Zn^{2+} uptake was somewhat insignificant. The rate of Zn^{2+} removal by SCAB decreased by about 39.6% when the Na^+ concentration was 10 mM. The removal rate decreased by 16.3% and 12.5%, however, with the same Ca^{2+} and K^+ concentrations (Figure 2), which indicated SCAB's relatively higher affinity for Zn^{2+} than for the light metal ions.

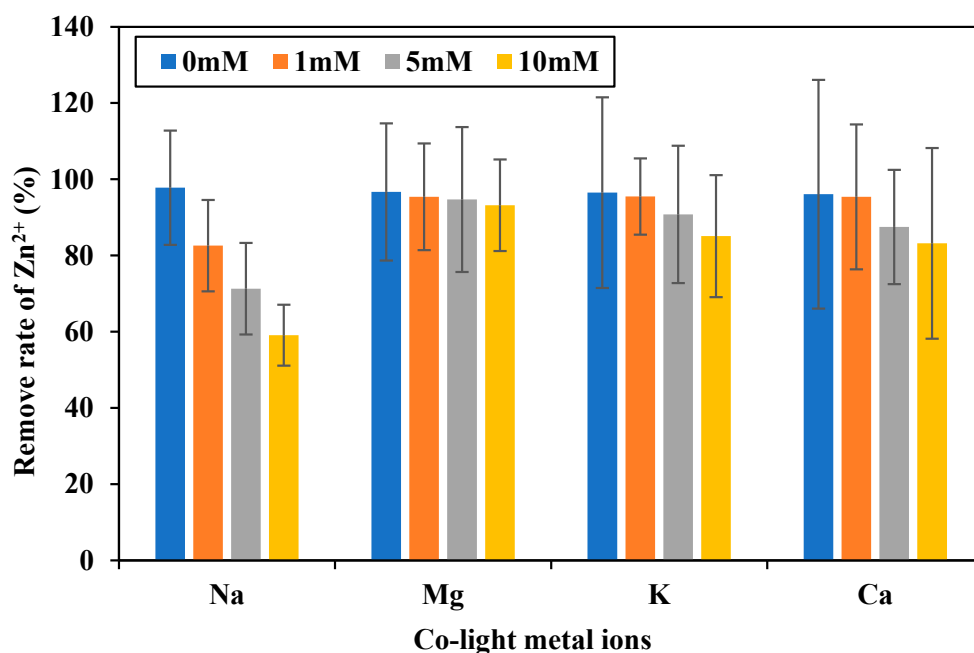


Figure 2. Light metal ions have an impact on the Zn^{2+} biosorption by the sodium citrate-treated *Agaricus bisporus* (SCAB) at an initial concentration of 1 mM.

When multiple metal ions are present in natural and polluted water, it often has an interactive effect that does not occur in the presence of single toxic metallic species. Therefore, how various heavy metal ions interact must be considered in the biosorption process [51]. Using SCAB, we effectively removed Pb^{2+} (99.7–98.6%), but the effect of interfering ions was higher, resulting in a decrease from 90.2 to 44.0% for Zn^{2+} in the presence of Pb^{2+} . This result showed that Zn^{2+} biosorption was hindered by Pb^{2+} . In contrast, when the Cu^{2+} concentration increased from 50 to 100 $mg\ L^{-1}$, the rate of Cu^{2+} removal decreased from 96.6% to 80.5% and the rate of Zn^{2+} removal decreased from 39.3% to 20.2%. As the ratio of Pb^{2+} or Cu^{2+} to Zn^{2+} increased, the removal rate of Zn^{2+} in the Cu-Zn binary metal system decreased more than that in the corresponding Pb-Zn binary metal system, which suggested that Cu^{2+} shared more binding sites with Zn^{2+} on the surface of SCAB than Pb^{2+} . In addition, both lead and copper ions could be effectively removed from the solution by SCAB, which could also be applied to these heavy metals as a biosorbent.

3.3. Effect of Biosorption on Solution pH

Research has shown that heavy metal uptake is affected by pH [52,53]. Past studies have primarily examined the pH value in initial biosorption when considering the capacity of biosorbents for heavy metal uptake [53], but they have rarely considered pH value changes following biosorption. In this study, we set the initial solution pH at 4.0. Figure 3 shows the value of the solution pH after Zn^{2+} biosorption by SCAB. As the initial Zn^{2+} concentration increased, the solution pH value also increased (Figure 3a). This result

showed that H^+ could be removed from the solution onto the biosorbent surface as a result of the involvement of an ion exchange mechanism. Additionally, the change in the pH solution was limited at a higher initial Zn^{2+} concentration. As shown in Figure 3b, with an increase in the dose of the biosorbent in solution, the solution pH also increased. This result may have been caused by more exchangeable and releasable components, such as Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , as well as additional binding sites when the dose of the ion exchange mechanism was higher. The involvement of the biosorption process relative to the ion exchange mechanism will be addressed in a follow-up study.

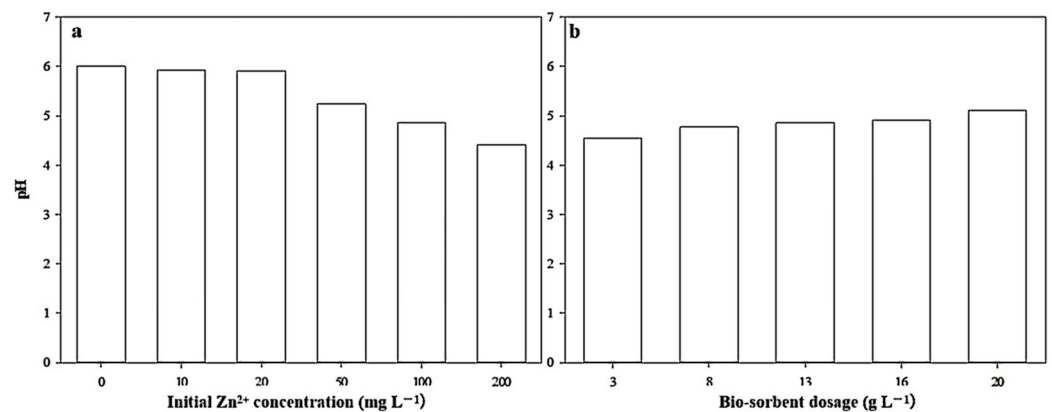


Figure 3. Solution pH value following Zn^{2+} biosorption by the sodium citrate-treated *Agaricus bisporus* (SCAB): (a) with various initial Zn^{2+} concentrations; and (b) with various biosorbent dosages.

3.4. Ion Exchange during Biosorption

According to Chen et al. [54], a generalized type of functional group such as carboxyl, hydroxyl, sulfate, phosphate, and amine groups (represented as R^{2-}) is part of the metal ion adsorption process. Most complex functional groups have light metal ions such as Ca^{2+} (CaR), which can be stripped away through the ion exchange process. In aqueous solution, H^+ ions could replace Ca^{2+} when the biosorbents were applied according to the following reaction:

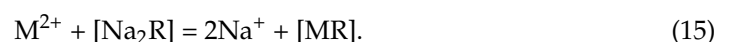
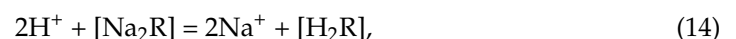


- (1) During biosorption, a similar exchange occurs between Ca^{2+} ions and heavy metal ions (represented as M^{2+}), as shown in Equation (13):



- (2) The driving force behind the equilibrium on the right side of the equation was the stronger affinity of M^{2+} for R^{2-} . As demonstrated in Equation (12), when the Ca^{2+} in the solution exchanged the H^+ in the biosorbent, the solution's pH increased.

Because Na^+ was the most common light metal released and contributed the most to the ion exchange of Zn^{2+} in the biosorption process, Equations (12) and (13) can be rewritten as follows:



- (3) During the uptake of Zn^{2+} , ion exchange was essential; however, it appeared that the nonstoichiometric exchange of ions meant that the ion exchange mechanism was not solely responsible for the biosorption of Zn^{2+} by SCAB.

Light metal ions (e.g., calcium ions) can saturate many biosorbents and then can exchange them with heavy metal ions from the solution. As a result, the release of the light metal ions and the adsorption of heavy metal ions can occur simultaneously [54]. We observed that light metal ions, including Na^+ , Mg^{2+} , K^+ , and Ca^{2+} , were released simul-

taneously with Zn^{2+} adsorption (Figure 4a). As the initial Zn^{2+} concentration increased, the four light metal ions in solution also increased, which demonstrated that light metal ions might be released as a result of an ion exchange with Zn^{2+} . After treating the raw biomass with sodium citrate, the main exchangeable light metal ion was Na^+ , in contrast to other studies, which found Ca^{2+} on the surface of SCAB [20,55]. The quantity of light metal ions released was proportional to Zn^{2+} adsorption (Figure 4b). The involvement of an ion exchange mechanism was demonstrated by the simultaneous release of light metal ions and Zn^{2+} adsorption. After Zn^{2+} biosorption by SCAB, the solution pH increased, which showed that light metal ions replaced H^+ from solution on the surface of SCAB (Figure 3). Conversely, when the initial Zn^{2+} concentration increased, pH changes were limited, which showed that Zn^{2+} rather than H^+ replaced the light metal ions on the biosorbent. This was most notable when the initial Zn^{2+} concentrations were high.

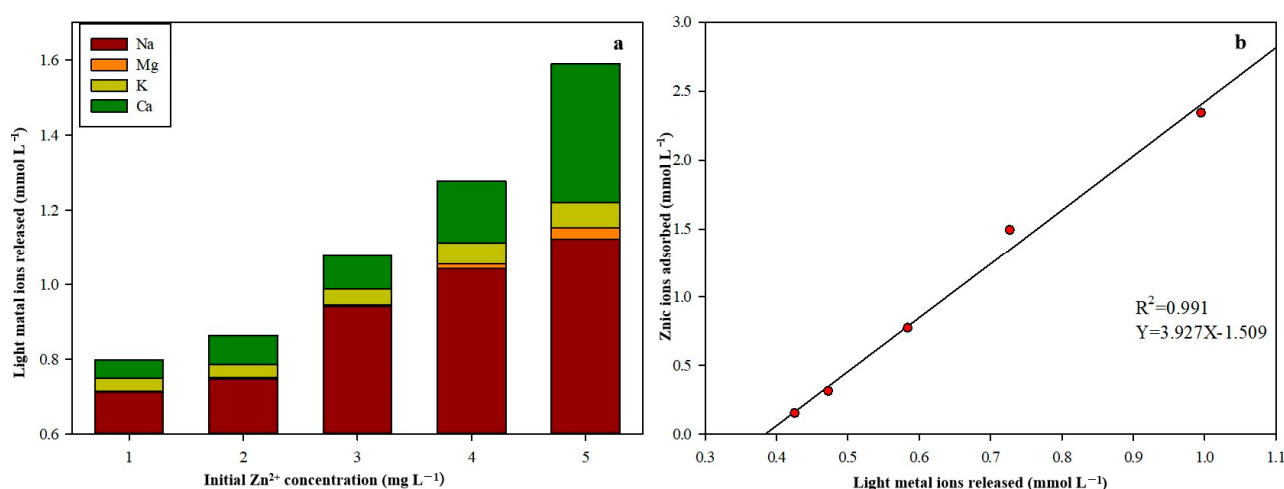


Figure 4. Ions released during Zn^{2+} biosorption by the sodium citrate-treated *Agaricus bisporus* (SCAB): (a) four light metal ions released with various initial Zn^{2+} concentrations; and (b) the relationship between the quantity of light metal ions released and the quantity of Zn^{2+} ions adsorbed.

3.5. Functional Groups in Zn^{2+} Biosorption

Specific surface area refers to the total area of the unit mass of the material, including the external area and the internal surface area (micropore area). By studying the specific surface area, the contact degree between adsorbed material can be fully understood. Specific surface area is an important index to evaluate the efficacy of adsorbent. It was determined that the specific surface area, micropore area, and surface area of the SCAB were 9.68 m²/g, 1.05 m²/g, and 8.62 m²/g, respectively, which were 3.57 times, 4.56 times, and 4.36 times higher than that of the RAB. The increase in specific surface area will help increase the contact surface between SCAB and zinc ions in solution. More adsorption sites will also be exposed, which is conducive to the binding of zinc ions in the solution with effective adsorption sites.

Four bands showed decreased intensity and band shifts (Figure 5). The absorbance peak of the hydroxyl group stretch decreased from 3423 to 3398 cm⁻¹ after biosorption. The absorbance peaks of the aromatic nitro groups' absorbance peaks reached a symmetric stretch of 1380 cm⁻¹ and an asymmetric stretch of 1551 cm⁻¹, and absorbance peaked at 617 cm⁻¹. These results likely were caused by the shift in the phosphate groups. We also observed shifts in the FT-IR spectra of the aromatic nitro, phosphate, and hydroxyl group peaks. These results indicated that these groups had an impact on SCAB biosorption of Zn^{2+} .

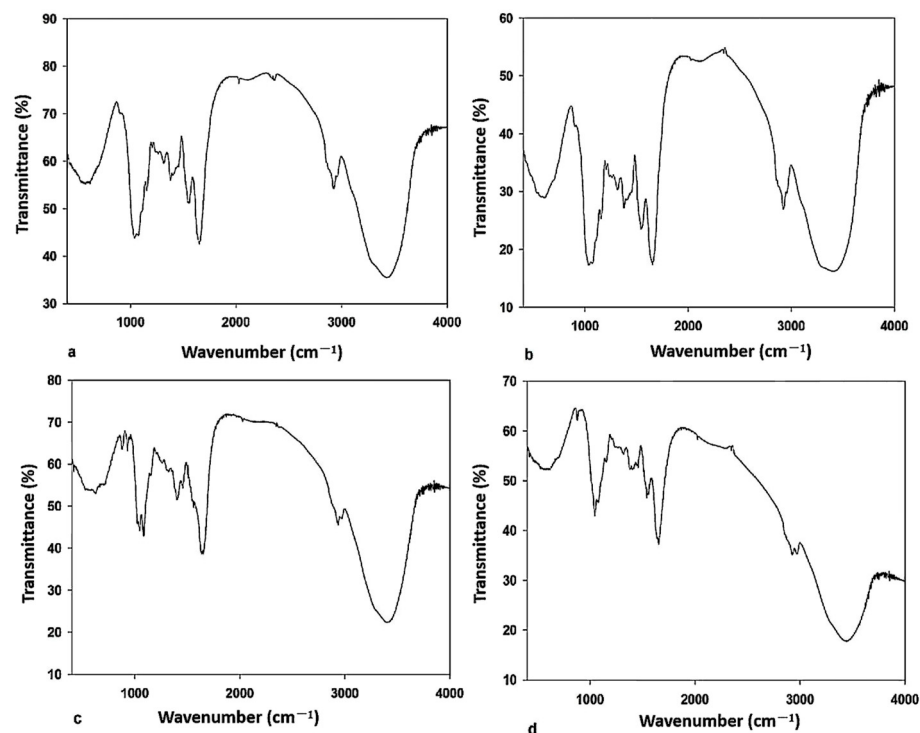


Figure 5. SCAB and RAB FT-IR spectra: (a) SCAB before biosorption; (b) SCAB after biosorption; (c) RAB before biosorption; and (d) RAB after biosorption.

The stretching vibration of the absorbance peak of the hydroxyl group increased from 3405 to 3448 cm^{-1} . We attributed the peak at 1637 cm^{-1} to the C=O bond in the carboxyl group, which was evident for Zn-loaded RAB but not for RAB. We attributed the peaks at 2973 and 1383 cm^{-1} to the alkyl and aliphatic nitro groups, which were not evident for RAB but were for Zn-loaded RAB. The phosphate groups may have been responsible for changes in absorbance peaks in the fingerprint zone ($<1000 \text{ cm}^{-1}$). The FT-IR spectra showed that changes in aliphatic nitro, hydroxyl, carboxyl, and phosphate group peaks were responsible for RAB biosorption of Zn^{2+} . Therefore, the primary functional groups that were involved in Zn^{2+} biosorption were affected by the sodium citrate-treating method.

3.6. SCAB Regeneration and Reuse

The regeneration efficiency of biosorbent after metal desorption relies on the exploitation of biosorption technology to remove heavy metals [56]. The rate of Zn^{2+} removal of 100 mg L^{-1} lowered from 96.81% to only 94.11% after 10 biosorption–desorption cycles (Figure 6). The slight SCAB loss from the open-reaction system may have been the cause. Hence, the Zn^{2+} removal efficiency by SCAB did not decrease significantly after 10 biosorption–desorption cycles.

The desorption results showed that most of the adsorbed Zn^{2+} could be effectively eluted from SCAB by the sodium citrate solution after each cycle. During desorption cycle processing, the desorption rate slightly increased, which could be attributed to the incomplete desorption of Zn^{2+} on some binding sites in the previous cycle and to the activation of these Zn^{2+} -binding sites in the subsequent cycle.

In summary, the adsorbent seems to be performing well by reaching 10 cycles with removal efficiency above 90%. Sodium citrate solution could be used as both regenerant and eluant and did not affect the biosorption properties of SCAB.

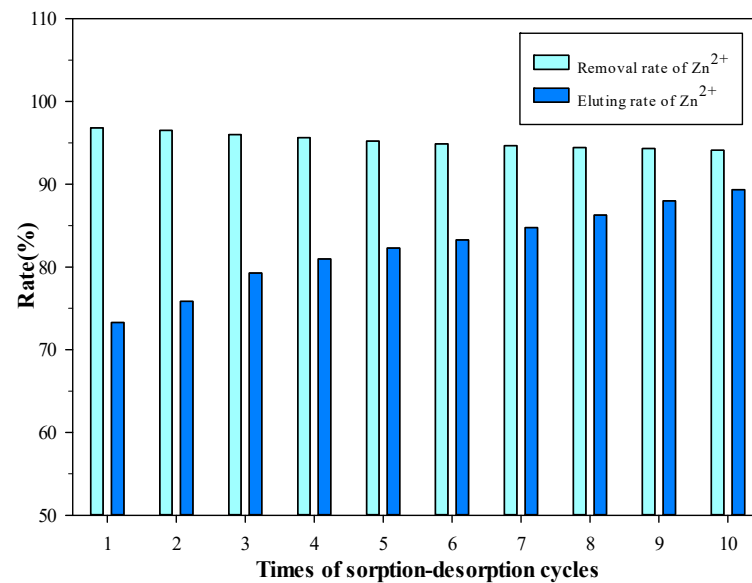


Figure 6. Removal and elution rate for successive cycles of the sodium citrate-treated *Agaricus bisporus* (SCAB) biosorption of Zn²⁺.

3.7. Equilibrium Isotherms

Certain constants, including values that express biosorbent affinity and surface properties, can be reflected in an adsorption isotherm [55]. To design an optimal biosorption system to remove metal ions from effluents, we established an appropriate relationship for these equilibrium isotherms to characterize these constants. We analyzed batch experimental data using four equilibrium isotherms (i.e., the Langmuir, Freundlich, D-R, and Temkin isotherms). We calculated the corresponding constants for the Zn²⁺ biosorption by SCAB (Table 1). We used the Langmuir isotherm (Equation (3)) to calculate the Zn²⁺ monolayer adsorption capacity (Q_0) of SCAB, which was 19.607 mg g⁻¹. We used the Freundlich isotherm (Equation (4)) to calculate the constants K_f and $1/n$, which were 4.518 mg g⁻¹ L^{1/n} g⁻¹ and 0.692, respectively. The Zn²⁺ biosorption of on SCAB was favorable, as shown by the values of $1/n$ between 0 and 1 [57].

Table 1. Model results for the correlation coefficients and constants.

Isotherm Equations		Parameters	R^2
Langmuir	Q_0 (mg g ⁻¹)	b (L mg ⁻¹)	0.950
	19.607	0.593	
Freundlich	K_f (mg g ^{1-(1/n)} L ^{1/n} g ⁻¹)	1/n	0.952
	4.518	0.268	
Dubinin–Radushkevich	q_m (mg g ⁻¹)	β (mol ² kJ ⁻²)	0.664
	50.816	7.0×10^{-9}	
Temkin	A_T (L g ⁻¹)	b_T	0.878
	1.467	2370.882	

We used the D-R constants (Equation (5)) to calculate the theoretical saturation capacity (q_m) and the free energy of adsorption per mole of the adsorbate (β), which were 50.816 mg g⁻¹ and 7.0×10^{-9} mol² kJ⁻², respectively. We used the Temkin isotherm to determine the constants of b_T (2370.882) and A_T (1.467 L g⁻¹), which showed that the adsorption of heat for all the molecules in the layer decreased in a linear fashion along with coverage as a result of the adsorbent–adsorbate interactions. We also found that a uniform distribution (up to the maximum) of binding energies characterized this adsorption [58].

The biosorption of Zn²⁺ on SCAB correlated well with the Freundlich (0.952) and Langmuir-type (0.950) isotherms. Compared with the D-R (0.664) and Temkin (0.878)

isotherms, the Freundlich (0.952) and Langmuir (0.950) isotherms correlated well with the Zn^{2+} biosorption of SCAB (Table 1). The Langmuir isotherm revealed the adsorbent's surface homogeneity, and the Freundlich adsorption isotherm revealed of the adsorbent's surface heterogeneity. Because the regression coefficients for these two isotherms were high, we found that the SCAB surface had small heterogeneous adsorption patches, which featured adsorption capabilities that were identical [59].

In order to know whether SCAB has an advantage in zinc adsorption, maximum capacity, K_f for biosorption of Zn^{2+} by various biosorbents are listed in Table 2. As can be seen from the table, the K_f value of SCAB was significantly higher than that of the reported zinc-adsorbed biomaterials, which reflected certain advantages in terms of the theoretical maximum adsorption capacity.

Table 2. Maximum capacity, K_f for biosorption of Zn^{2+} by various biosorbents.

Biosorbents	K_f	References
<i>Sargassum</i> sp.	1.44	[60]
<i>Botrytis cinerea</i>	1.13	[61]
<i>Sargassum</i>	0.41	[62]
<i>S. intermedia</i>	1.03	[63]
<i>L. minor</i>	1.06	[64]
<i>P. stratiots</i>	0.25	[61]
<i>Botrytis cinerea</i>	1.13	[58]
Plain Ca-alginate bead	0.51	[65]
SCAB	4.52	This study

3.8. Kinetic Studies

To select the optimum operating conditions for a full-scale batch metal removal process, biosorption kinetics are necessary. These kinetics offer promising biosorption efficiency characteristics [65]. To predict the biosorption kinetics, we applied the pseudo-first-order (Equation (7)) and pseudo-second-order (Equation (8)) models to evaluate the mechanism controlling biosorption.

Table 3 lists the biosorption capacity (q_e), biosorption rate constants (k_1 and k_2), and initial sorption rate (h) for Zn^{2+} biosorption by SCAB. We compared the calculated biosorption capacity ($q_{e,cal}$) with the experimental biosorption capacity ($q_{e,exp}$) and found that these values were similar to the pseudo-second-order kinetic values. We observed, however, significant differences between the experimental values and the pseudo-first-order kinetic model values. We also found that the correlation coefficients were much lower for the pseudo-first-order kinetic model than they were for the pseudo-second-order kinetic model (0.999) at all working concentrations. This result indicated that the pseudo-second-order kinetic model was better able to describe Zn^{2+} biosorption by SCAB.

Table 3. Pseudo-first-order model comparison with pseudo-second-order kinetic model; experimental and calculated q_e values for various concentrations of initial Zn^{2+} .

C_0 (mg L ⁻¹)	$q_{e,exp}$ (mg g ⁻¹)	First-Order Kinetic Model			Second-Order Kinetic Model			
		k_1 (1 min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	H (mg g ⁻¹ min ⁻¹)
22	1.746	0.099	0.004	0.824	65.437	1.748	0.999	200.000
65	4.978	0.108	0.061	0.928	4.444	5.000	0.999	111.111
75	6.449	0.122	0.242	0.969	1.395	6.494	0.999	58.824
135	9.567	0.219	2.193	0.915	0.379	9.709	0.999	35.714

3.9. Thermodynamic Parameters

Table 4 lists the equilibrium constant (K_c) as well as changes in Gibbs free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°). According to these thermodynamic param-

ters, when the temperature changed from 25 °C to 40 °C, K_c rose from 29.348 to 32.837, which demonstrated SCAB's increased biosorption capacity in keeping with an increase in temperature. As adsorption capacity increased with temperature, the kinetic energy of SCAB particles also rose at higher temperature, which caused the collision frequency between the sorbate and biosorbent to increase [66]. Temperature increases also caused the pore size of the adsorbent to change, thus improving the pore's intraparticle diffusion and increasing the adsorbent's adsorption capacity. A bond rupture in the functional groups on the biosorbent surface, however, could cause the number of active biosorption sites to increase [67]. In this study, we did not consider higher temperatures because desorption started at ≥ 50 °C.

Table 4. Thermodynamic the sodium citrate-treated *Agaricus bisporus* (SCAB) parameters at 100 mg L^{−1} concentration.

Temperature (K)	K_C	ΔG° (kJ mol ^{−1})	ΔH° (kJ mol ^{−1})	ΔS° (J mol ^{−1} K ^{−1})
298	29.348	−8.376	5.739 ^a	0.047 ^a
303	30.696	−8.630		
313	32.837	−9.090		

^a All of the temperature values are valid.

When the temperature rose from 25 °C to 40 °C, Gibbs free energy (ΔG°) changed from −8.376 to −9.090 kJ mol^{−1}. This higher negative value suggested the spontaneous nature of biosorption [68]. Because chemical adsorption generally is characterized by free energy ranging from 80 to 400 kJ mol^{−1}, the Zn²⁺ biosorption by SCAB was considered to be physical adsorption [56]. The endothermic nature of biosorption was confirmed by the positive ΔH° value. Increased randomness at the interface of the biosorbent and the Zn²⁺ solution during biosorption was demonstrated by the positive ΔS° value.

4. Conclusions

Sodium citrate-treated SCAB showed a significantly higher biosorption capability for Zn²⁺ in solution than in raw biomass. SCAB had a much higher affinity for Zn²⁺ than for light metal ions, and it preferred to adsorb Pb²⁺ and Cu²⁺ when the two ions were also present. We determined that a release of light metal ions and a change in pH following biosorption verified the involvement of the ion exchange mechanism. We confirmed changes in functional groups following pretreatment in biosorption through FT-IR. We completed 10 cycles of biosorption–desorption and verified that the removal rate of Zn²⁺ did not noticeably decrease and most of the absorbed Zn²⁺ could be eluted. The change in Gibbs free energy (ΔG°) from −8.376 to −9.090 kJ mol^{−1} with an increase in temperature showed that the physical adsorption and spontaneous biosorption process followed pseudo-second-order kinetics. The endothermic nature of biosorption was confirmed by the positive ΔH° value. This study demonstrated that SCAB treated with sodium citrate is a better alternative for the treatment of wastewaters contaminated with Zn²⁺, Pb²⁺, and Cu²⁺ ions. The world's most widely consumed mushroom species (*A. bisporus*) has high removal efficiency and high accumulation potential for heavy metal ions from mono- and polycomponent aqueous solutions. The use of sodium citrate-treated SCAB offers an efficient, cost-effective, and environmentally sound solution to treat wastewater, particularly at a time when global political views are shifting toward sustainable green technologies.

This study verified the removal efficiency of sodium citrate-treated SCAB under controlled laboratory conditions. Additional field studies are needed to better determine how to use SCAB to treat wastewater polluted by heavy metals. This limitation reveals the necessity of future work in this direction.

Author Contributions: X.Z., R.Y. and C.Z. wrote the paper; F.X. conceived and designed the paper; B.X., Z.H. and Y.L. collected and analyzed the data. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Key Research and Development Program of China (2018YFF0213402) and the National Natural Science Foundation of China (NO. 21607049).

Data Availability Statement: The data that support the findings of this study are available upon request from the authors.

Conflicts of Interest: Author Feng Xue was employed by the Shenzhen Degree of Freedom Eco Technology Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Elahi, A.; Arooj, I.; Bukhari, D.A.; Rehman, A. Successive use of microorganisms to remove chromium from wastewater. *Appl. Microbiol. Biotechnol.* **2020**, *104*, 3729–3743. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Jayakumar, V.; Govindaradjane, S.; Rajamohan, N.; Rajasimman, M. Biosorption potential of brown algae, *Sargassum polycystum*, for the removal of toxic metals, cadmium and zinc. *Environ. Sci. Pollut. Res.* **2022**, *29*, 41909–41922. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Berkani, M.; Smaali, A.; Kadmi, Y.; Almomani, F.; Vasseghian, Y.; Lakhdari, N.; Alyane, M. Photocatalytic degradation of Penicillin G in aqueous solutions: Kinetic, degradation pathway, and microbioassays assessment. *Hazard. Mater.* **2022**, *421*, 126719. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Xu, Z.; Gu, S.; Rana, D.; Matsuura, T.; Lan, C.Q. Chemical precipitation enabled UF and MF filtration for lead removal. *J. Water Process Eng.* **2021**, *41*, 101987. [\[CrossRef\]](#)
5. Ayangbenro, A.S.; Babalola, O.O. A new strategy for heavy metal polluted environments: A review of microbial biosorbents. *Int. J. Environ. Res. Public Health* **2017**, *14*, 94. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Nokman, W.; Benlucvankar, V.; Packiam, S.M.; Vincent, S. Screening and molecular identification of heavy metal resistant *Pseudomonas putida* S4 in tannery effluent wastewater. *Biocatal. Agric. Biotechnol.* **2019**, *18*, 101052. [\[CrossRef\]](#)
7. Jiang, D.; Yang, Y.; Huang, C.; Huang, M.; Chen, J.; Rao, T.; Ran, X. Removal of the heavy metal ion nickel (II) via an adsorption method using flower globular magnesium hydroxide. *Hazard. Mater.* **2019**, *373*, 131–140. [\[CrossRef\]](#)
8. Şentürk, İ.; Yıldız, M.R. Highly efficient removal from aqueous solution by adsorption of Maxilon Red GRL dye using activated pine sawdust. *Korean J. Chem. Eng.* **2020**, *37*, 985–999. [\[CrossRef\]](#)
9. Bano, A.; Hussain, J.; Akbar, A.; Mehmood, K.; Anwar, M.; Hasni, M.S.; Ullah, S.; Sajid, S.; Ali, I. Biosorption of heavy metals by obligate halophilic fungi. *Chemosphere* **2018**, *199*, 218–222. [\[CrossRef\]](#)
10. Hameed, A.H.A.E.; Eweda, W.E.; Abou-Taleb, K.A.A.; Mira, H.I. Biosorption of uranium and heavy metals using some local fungi isolated from phosphatic fertilizers. *Ann. Agr. Sci.* **2015**, *60*, 345–351. [\[CrossRef\]](#)
11. Choma, A.; Nowak, K.; Komaniecka, I.; Waśko, A.; Pleszczyńska, M.; Siwulski, M.; Wiater, A. Chemical characterization of alkali-soluble polysaccharides isolated from a *Boletus edulis* (Bull.) fruiting body and their potential for heavy metal biosorption. *Food Chem.* **2018**, *266*, 329–334. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Schiewer, S.; Balaria, A. Biosorption of Pb²⁺ by original and protonated citrus peels: Equilibrium, kinetics, and mechanism. *Chem. Eng. J.* **2009**, *146*, 211–219. [\[CrossRef\]](#)
13. Alharbi, N.K.; Al-Zaban, M.I.; Albarakaty, F.M.; Abdelwahab, S.F.; Hassan, S.H.; Fawzy, M.A. Kinetic, isotherm and thermodynamic aspects of Zn²⁺ biosorption by *Spirulina platensis*: Optimization of process variables by response surface methodology. *Life* **2022**, *12*, 585. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Cepoi, L.; Zinicovscaia, I. *Spirulina platensis* as a model object for the environment bioremediation studies. In *Handbook of Algal Science, Technology and Medicine*; Academic Press: Cambridge, MA, USA, 2020; pp. 629–640.
15. Saravanan, A.; Jeevanantham, S.; Kumar, P.S.; Varjani, S.; Yaashikaa, P.R.; Karishma, S. Enhanced Zn (II) ion adsorption on surface modified mixed biomass-*Borassus flabellifer* and *Aspergillus tamaritii*: Equilibrium, kinetics and thermodynamics study. *Ind. Crop. Prod.* **2020**, *153*, 112613. [\[CrossRef\]](#)
16. Priya, A.K.; Gnanasekaran, L.; Dutta, K.; Rajendran, S.; Balakrishnan, D.; Soto-Moscoso, M. Biosorption of heavy metals by microorganisms: Evaluation of different underlying mechanisms. *Chemosphere* **2022**, *307*, 135957. [\[CrossRef\]](#)
17. Kalaimurugan, D.; Balamuralikrishnan, B.; Durairaj, K.; Vasudhevan, P.; Shivakumar, M.S.; Kaul, T.; Chang, S.W.; Ravindran, B.; Venkatesan, S. Isolation and characterization of heavy-metal-resistant bacteria and their applications in environmental bioremediation. *Int. J. Environ. Sci. Technol.* **2020**, *17*, 1455–1462. [\[CrossRef\]](#)
18. Bhatt, P.; Bhandari, G.; Turco, R.F.; Aminikhoei, Z.; Bhatt, K.; Simsek, H. Algae in wastewater treatment, mechanism, and application of biomass for production of value-added product. *Environ. Pollut.* **2022**, *309*, 119688. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Matheickal, J.T.; Yu, Q. Biosorption of lead (II) and copper (II) from aqueous solutions by pre-treated biomass of Australian marine algae. *Bioresour. Technol.* **1999**, *69*, 223–229. [\[CrossRef\]](#)
20. Chen, J.P.; Yang, L. Study of a heavy metal biosorption onto raw and chemically modified *Sargassum* sp. via spectroscopic and modeling analysis. *Langmuir* **2006**, *22*, 8906–8914. [\[CrossRef\]](#)

21. Sudha, B.R.; Abraham, T.E. Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. *Water Res.* **2002**, *36*, 1224–1236.
22. Šoštarić, T.D.; Petrović, M.S.; Pastor, F.T.; Lončarević, D.R.; Petrović, J.T.; Milojković, J.V.; Stojanović, M.D. Study of heavy metals biosorption on native and alkali-treated apricot shells and its application in wastewater treatment. *J. Mol. Liq.* **2018**, *259*, 340–349. [[CrossRef](#)]
23. Regine, H.S.; Volesky, F.B. Biosorption: A solution to pollution. *Int. Microbiol.* **2000**, *3*, 17–24.
24. Sarangi, N.V.; Rajkumar, R. Biosorption potential of *Stoechospermum marginatum* for removal of heavy metals from aqueous solution: Equilibrium, kinetic and thermodynamic study. *Chem. Eng. Res. Des.* **2024**, *203*, 207–218. [[CrossRef](#)]
25. Gu, S.; Lan, C.Q. Mechanism of heavy metal ion biosorption by microalgal cells: A mathematic approach. *J. Hazard. Mater.* **2024**, *463*, 132875. [[CrossRef](#)] [[PubMed](#)]
26. Cheng, S.Y.; Show, P.-L.; Lau, B.F.; Chang, J.-S.; Ling, T.C. New prospects for modified algae in heavy metal adsorption. *Trends Biotechnol.* **2019**, *37*, 1255–1268. [[CrossRef](#)] [[PubMed](#)]
27. Sathya, A.B.; Sivashankar, R.; Kanimozhi, J.; Devika, R.; Balaji, R. Biosorption and different native sources for preparation of biosorbents. *Emerg. Contam.* **2022**, *67*, 23–41.
28. Xu, Y.; Chen, Y. Leaching heavy metals in municipal solid waste incinerator fly ash with chelator/biosurfactant mixed solution. *Waste Manag. Res.* **2015**, *33*, 652–661. [[CrossRef](#)] [[PubMed](#)]
29. Zhang, S.; Zhang, X.; Xiong, Y.; Wang, G.; Zheng, N. Effective solidification/stabilisation of mercury-contaminated wastes using zeolites and chemically bonded phosphate ceramics. *Waste Manag. Res.* **2015**, *33*, 183–190. [[CrossRef](#)] [[PubMed](#)]
30. Seid, L.; Lakhdari, D.; Berkani, M.; Belgherbi, O.; Chouder, D.; Vasseghian, Y.; Lakhdari, N. High-efficiency electrochemical degradation of phenol in aqueous solutions using Ni-PPy and Cu-PPy composite materials. *Hazard. Mater.* **2022**, *423*, 126986. [[CrossRef](#)]
31. Joshi, H.K.; Vishwakarma, M.C.; Kumar, R.; Sharma, H.; Bhandari, N.S.; Joshi, S.K. The biosorption of Zn²⁺ by various biomasses from wastewater: A review. *J. Water Process Eng.* **2023**, *56*, 104389. [[CrossRef](#)]
32. Matouq, M.; Jildeh, N.; Qtaishat, M.; Hindiye, M.; Al Syouf, M.Q. The adsorption kinetics and modeling for heavy metals removal from wastewater by Moringa pods. *J. Environ. Chem. Eng.* **2015**, *3*, 775–784. [[CrossRef](#)]
33. Shroff, K.A.; Vaidya, V.K. Kinetics and equilibrium studies on biosorption of nickel from aqueous solution by dead fungal biomass of *Mucor hiemalis*. *Chem. Eng. J.* **2011**, *171*, 1234–1245. [[CrossRef](#)]
34. Rao, R.A.K.; Khan, M.A.; Rehman, F. Utilization of Fennel biomass (*Foeniculum vulgare*) a medicinal herb for the biosorption of Cd(II) from aqueous phase. *Chem. Eng. J.* **2010**, *156*, 106–113. [[CrossRef](#)]
35. Rudy, C.; Milhome, M.A.L.; Cavalcante, R.M.; Silveira, E.R.; Denis, D.K.; Nascimento, R.F. Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin. *Bioresour. Technol.* **2008**, *99*, 4515–4519.
36. Ofomaja, A.E.; Naidoo, E.B.; Modise, S.J. Kinetic and pseudo-second-order modeling of lead biosorption onto pine cone powder. *Ind. Eng. Chem. Res.* **2010**, *49*, 2562–2572. [[CrossRef](#)]
37. Ho, Y.S.; Ofomaja, A.E. Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution. *Process Biochem.* **2005**, *40*, 3455–3461. [[CrossRef](#)]
38. Ho, Y.S.; Wase, D.A.J.; Forster, C.F. Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat. *Environ. Technol.* **1996**, *17*, 71–77. [[CrossRef](#)]
39. Dinesh, M.; Kunwar, P.S. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. *Water Res.* **2002**, *36*, 2304–2318.
40. Jaafari, J.; Yaghmaei, K. Optimization of heavy metal biosorption onto freshwater algae (*Chlorella coloniales*) using response surface methodology (RSM). *Chemosphere* **2019**, *217*, 447–455. [[CrossRef](#)]
41. Vimala, R.; Das, N. Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: A comparative study. *J. Hazard. Mater.* **2009**, *168*, 376–382. [[CrossRef](#)]
42. Abia, D.; Nzali, S.; Acayanka, E.; Kamgang, G.Y.; Laminsi, S.; Ghogomu, P.M. Synergetic effect of gliding arc discharge treatment and biosorption for removal of nitrophenol and glycine from aqueous solution. *J. Ind. Eng. Chem.* **2015**, *29*, 156–162. [[CrossRef](#)]
43. Moyo, M.; Guyo, U.; Mawenyiyo, G.; Zinyama, N.P.; Nyamunda, B.C. Marula seed husk (*Sclerocarya birrea*) biomass as a low cost biosorbent for removal of Pb(II) and Cu(II) from aqueous solution. *J. Ind. Eng. Chem.* **2015**, *27*, 126–132. [[CrossRef](#)]
44. Munoz, A.J.; Espinola, F.; Ruiz, E. Removal of Pb(II) in a packed-bed column by a *Klebsiella* sp. 3S1 biofilm supported on porous ceramic Raschig rings. *J. Ind. Eng. Chem.* **2016**, *40*, 118–127. [[CrossRef](#)]
45. Dil, E.A.; Ghaedi, M.; Ghezalbashi, G.R.; Asfaram, A.; Purkait, M.K. Highly efficient simultaneous biosorption of Hg²⁺, Pb²⁺ and Cu²⁺ by live yeast *Yarrowia lipolytica* 70562 following response surface methodology optimization: Kinetic and isotherm study. *J. Ind. Eng. Chem.* **2017**, *48*, 162–172.
46. Nadeem, R.; Manzoor, Q.; Iqbal, M.; Nisar, J. Biosorption of Pb(II) onto immobilized and native *Mangifera indica* waste biomass. *J. Ind. Eng. Chem.* **2016**, *35*, 185–194. [[CrossRef](#)]
47. Gunasundari, E.; Kumar, P.S. Adsorption isotherm, kinetics and thermodynamic analysis of Cu (II) ions onto the dried algal biomass (*Spirulina platensis*). *J. Ind. Eng. Chem.* **2017**, *56*, 129–144.
48. Pradhan, D.; Sukla, L.B.; Sawyer, M.; Rahman, P.K. Recent bioreduction of hexavalent chromium in wastewater treatment: A review. *J. Ind. Eng. Chem.* **2017**, *55*, 1–20. [[CrossRef](#)]

49. Esposito, A.; Pagnanelli, F.; Lodi, A.; Solisio, C.; Vegliò, F. Biosorption of heavy metals by *Sphaerotilus natans*: An equilibrium study at different pH biomass concentrations. *Hydrometallurgy* **2001**, *60*, 129–141. [\[CrossRef\]](#)
50. Sheng, P.X.; Ting, Y.P.; Chen, J.P. Biosorption of heavy metal ions (Pb, Cu, and Cd) from aqueous solutions by the marine alga *Sargassum* sp. in single- and multiple-metal systems. *Ind. Eng. Chem. Res.* **2007**, *46*, 2438–2444. [\[CrossRef\]](#)
51. Zhou, K.; Yang, Z.G.; Liu, Y.C.H.; Kong, X. Kinetics and equilibrium studies on biosorption of Pb (II) from aqueous solution by a novel biosorbent: *Cyclosorus interruptus*. *J. Ind. Eng. Chem.* **2015**, *3*, 2219–2228. [\[CrossRef\]](#)
52. Masoumi, F.; Khadivinia, E.; Alidoust, L.; Mánourinejad, Z.; Shahryari, S.; Safaei, M.; Mousavi, A.; Salmanian, A.H.; Zahiri, H.S.; Vali, H.; et al. Nickel and lead biosorption by *Curtobacterium* sp. FM01, an indigenous bacterium isolated from farmland soils of northeast Iran. *J. Ind. Eng. Chem.* **2016**, *4*, 950–957. [\[CrossRef\]](#)
53. Mohapatra, M.; Rout, K.; Mohapatra, B.K.; Anand, S. Sorption behavior of Pb(II) and Cd(II) on iron ore slime and characterization of metal ion loaded sorbent. *Ind. Eng. Chem. Res.* **2009**, *166*, 1506–1513. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Chen, J.P.; Wang, L.K.; Yang, L.; Lim, S.F. Emerging biosorption, adsorption, ion exchange, and membrane technologies. In *Advanced Physicochemical Treatment Technologies*; Wang, L.K., Hung, Y.T., Shammass, N.K., Eds.; Humana Press: Clifton, NJ, USA, 2007; pp. 367–390.
55. Tran, H.T.; Vu, N.D.; Matsukawa, M.; Okajima, M.; Kaneko, T.; Ohki, K.; Yoshikawa, S. Heavy metal biosorption from aqueous solutions by algae inhabiting rice paddies in Vietnam. *J. Environ. Chem. Eng.* **2016**, *4*, 2529–2535. [\[CrossRef\]](#)
56. Wang, J.; Chen, C. Biosorbents for heavy metals removal and their future. *Biotechnol. Adv.* **2009**, *27*, 195–226. [\[CrossRef\]](#)
57. Kim, Y.; Kim, C.; Choi, I.; Rengaraj, S.; Yi, J. Arsenic removal using mesoporous alumina prepared via a templating method. *Environ. Sci. Technol.* **2004**, *38*, 924–931. [\[CrossRef\]](#)
58. Ayhan, Ş.; Mahmut, Ö. Competitive biosorption of Pb²⁺, Cu²⁺ and Zn²⁺ ions from aqueous solutions onto *Valonia tannin* resin. *J. Hazard. Mater.* **2009**, *166*, 1488–1494.
59. Ertugay, N.; Bayhan, Y.K. The removal of copper (II) ion by using mushroom biomass (*Agaricus bisporus*) and kinetic modelling. *Desalination* **2010**, *255*, 137–142. [\[CrossRef\]](#)
60. Mahmood, Z.; Zahra, S.; Iqbal, M.; Raza, M.A.; Nasir, S. Comparative study of natural and modified biomass of *Sargassum* sp. for removal of Cd²⁺ and Zn²⁺ from wastewater. *Appl. Water Sci.* **2017**, *7*, 3469–3481. [\[CrossRef\]](#)
61. Tunali, S.; Akar, T. Zn(II) biosorption properties of *Botrytis cinerea* biomass. *J. Hazard. Mater.* **2006**, *131*, 137–145. [\[CrossRef\]](#)
62. Luna, A.S.; Costa, A.L.H.; Costa, A.C.A.; Henriques, C.A. Competitive biosorption of cadmium(II) and zinc(II) ions from binary systems by *Sargassum filipendula*. *Bioresour. Technol.* **2010**, *101*, 5104–5111. [\[CrossRef\]](#)
63. Miretzky, P.; Saralegui, A.; Fernandezcirelli, A. Simultaneous heavy metal removal mechanism by dead macrophytes. *Chemosphere* **2006**, *62*, 247–254. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Sağ, Y.; Kaya, A.; Kutsal, T. The simultaneous biosorption of Cu and Zn on *Rhizopus arrhizus*: Application of the adsorption models. *Hydrometallurgy* **1998**, *50*, 297–314. [\[CrossRef\]](#)
65. Malkoc, E.; Nuhoglu, Y.; Dundar, M. Adsorption of chromium(VI) on pomace—An olive oil industry waste: Batch and column studies. *J. Hazard. Mater.* **2006**, *138*, 142–151. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Tewari, N.; Vasudevan, P.; Guha, B. Study on biosorption of Cr(VI) by *Mucor hiemalis*. *Biochem. Eng. J.* **2005**, *23*, 185–192. [\[CrossRef\]](#)
67. Tunali, S.; Akar, T.; Özcan, A.S.; Kiran, I. Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by *Cephalosporium aphidicola*. *Sep. Purif. Technol.* **2006**, *47*, 105–112. [\[CrossRef\]](#)
68. Sprynskyy, M. Solid-liquid-solid extraction of heavy metals (Cr, Cu, Cd, Ni and Pb) in aqueous systems of zeolite–sewage sludge. *J. Hazard. Mater.* **2009**, *161*, 1377–1383. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.