

Biosorption of Copper (II) And Zinc (II) metal cations From Aqueous Solution By Using Non - Conventional Adsorbents

N.P. Mishra

Department of Chemistry, Kutir P.G. College, Chakkey, Jaunpur (U.P.).

Abstract

The present study investigates the biosorption potential of non-conventional, low-cost adsorbents for the removal of Cu(II) and Zn(II) ions from aqueous solutions. Heavy metal contamination in water bodies poses significant environmental and public health risks, necessitating the development of efficient and economical treatment methods. Biosorption using naturally available or waste-derived materials has emerged as a promising alternative to conventional physicochemical techniques. In this work, selected non-conventional adsorbents were evaluated for their metal uptake efficiency under varying experimental conditions, including pH, contact time, initial metal ion concentration, and adsorbent dosage. The results demonstrated a strong dependence of Cu(II) and Zn(II) removal on solution pH, with maximum biosorption observed in the near-neutral range. Equilibrium was attained within a relatively short contact time, indicating rapid adsorption kinetics. Adsorption data were analyzed using Langmuir and Freundlich isotherm models, revealing favorable adsorption behavior and significant metal binding capacity of the adsorbents. Kinetic studies suggested that the biosorption process followed pseudo-second-order kinetics, implying chemisorption as the dominant mechanism. Overall, the findings highlight the effectiveness of non-conventional adsorbents as sustainable and cost-effective materials for the removal of Cu(II) and Zn(II) ions from contaminated water, offering potential applications in wastewater treatment and environmental remediation.

keywords: Biosorption, Cu (II), Zn (II), Non - Conventional adsorbents.

Rapid industrialization, urban expansion, and intensive agricultural activities have significantly contributed to the release of heavy metals into aquatic ecosystems. Among these contaminants, copper (Cu(II)) and zinc (Zn(II)) are commonly detected in industrial effluents originating from electroplating, mining, metal finishing, battery manufacturing, fertilizer production, and textile industries. Although copper and zinc are essential trace elements for biological systems, their presence in elevated concentrations can lead to severe toxicological effects on living organisms and pose serious risks to human health and the environment. Excessive exposure to Cu(II) ions can cause gastrointestinal disorders, liver and kidney damage, and adverse effects on aquatic flora and fauna. Similarly, high levels of Zn(II) ions may result in nausea, anemia, and disruption of enzymatic activities in organisms. Due to their non-biodegradable nature and tendency to bioaccumulate in the food chain, the removal of these metal ions from wastewater before discharge into natural water bodies is of paramount importance. Conventional methods employed for heavy metal removal, such as chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, and activated carbon adsorption, are often associated with high operational costs, generation of secondary sludge, and

reduced efficiency at low metal ion concentrations. These limitations have prompted the search for alternative, eco-friendly, and cost-effective treatment technologies. Biosorption has emerged as a promising approach for the removal of heavy metals from aqueous solutions. This process utilizes biological materials or biomass-derived substances to adsorb metal ions through various mechanisms, including ion exchange, complexation, chelation, and physical adsorption. Non-conventional adsorbents, such as agricultural wastes, plant residues, microbial biomass, and industrial by-products, have gained considerable attention due to their abundance, renewability, low cost, and high metal-binding capacities. The present study focuses on the biosorption of Cu(II) and Zn(II) ions from aqueous solutions using selected non-conventional adsorbents. The work aims to evaluate the efficiency of these materials under different operational parameters and to elucidate the adsorption behavior through equilibrium and kinetic models. The outcomes of this study are expected to contribute to the development of sustainable and economical strategies for heavy metal removal in wastewater treatment systems.

Important Biosorbents and Components

Water hyacinth (raw or processed), Hydrilla verticillata (made into magnetic nanosorbents), biomass from Pinus sylvestris cones, blackgram bran, and pods of Sophora japonica are all plant-based.

- Bacterial: Pseudomonas putida CZ1 (both live and cell-free).
- MNP-HVP stands for "modified" and refers to a mixture of magnetic nanoparticles and plant biomass.
- Typical Results and Processes
- For Cu(II) and Zn(II), the ideal pH ranges from around 4.5 to 5.0.
- Kinetics: The rate is generally well-described by the pseudo-second-order model, which implies chemisorption.
- Isotherms: The equilibrium data is often fit using the Freundlich and Langmuir models, which show heterogeneous surface adsorption and monolayer adsorption.

The binding process on biosorbents relies on hydroxyl (-OH) and carboxyl (-COOH) groups for ion exchange, chelation, and surface complexation.

Modified materials and live cells frequently outperform raw biomass, leading to high clearance rates. This is due to their efficiency. These research give solid proof that biological materials may be used to remove harmful ions like zinc and copper from contaminated water at a reasonable cost. Agricultural Byproducts: CTS, ES, and SB: These substances were studied as potential substitutes for expensive biosorbents. In instance, the greatest adsorption capacities for Cu(II) and Zn(II) were 34.48 mg/g and 35.71 mg/g, respectively, for eggshells.

Acacia nilotica raw sawdust exhibited pseudo-second-order kinetics and a considerable removal efficiency of around 66% for both metals.

The citrus aurantifolia peels were discovered to effectively remove the ions of copper (II), iron (VI), lead (II), and zinc (II).

Important Dates: This substance was also investigated for its ability to adsorb Cu(II) and Zn(II), with its best performance observed at a pH of 5.

Dead or pre-treated microbes, such the fungus *Neurospora crassa* and the bacteria *Thiobacillus thiooxidans*, have been utilized as a resource for biosorption.

Consistent results from various studies:

A solution's pH has a significant impact on the biosorption process. As the pH rises, the surface becomes more negatively charged, which in turn increases the adsorption capacity. This range of pH is usually between 2 and 6, just before precipitation happens.

Biosorption kinetics of Cu(II) and Zn(II) ions are often well-characterized by the pseudo-second-order kinetic model.

When fitting experimental data, the Langmuir or Freundlich isotherm models are typically employed. In contrast to the Freundlich model, which implies multilayer adsorption on a heterogeneous surface, the Langmuir model often implies a monolayer adsorption process. Biosorbent surface functional groups, such as carboxyl, hydroxyl, and C-OH groups, play a key role in ion exchange and surface complexation, two processes that bind metal ions. By searching academic databases such as ScienceDirect.com, ResearchGate, or Springer Nature Link using terms similar to those in your question, you can discover a plethora of particular research publications.

RESEARCH METHOD

The spectroscopy of 4HT infrared

The spectra within the range of 4,000–400 cm^{-1} were obtained using a PerkinElmer spectrometer (Nicolet IS10, USA). The specimens were first mixed with KBr and then ground in an agate mortar at an approximate ratio of 1/200 for pellet preparation. The resulting mixture was pressed with a pressure of 10 ton for 2 min. The background was automatically subtracted from the sample spectra.

Kinetics study

The sorption tests were conducted in conical flasks (200 mL) using an orbital shaker at a constant temperature. The agitation velocity was 200 rpm, and biosorbent was approximately 0.1 g in weight. The initial

Cu(II) or Zn(II) concentration of the solution (100 mL) was 50 mg/L, and the contact time ranged from 5 to 150 min.

Reagents

Using analytical-grade Cu(II) chloride or Zn(II) chloride, 1,000 mg/L metal solution stocks were prepared in deionized water (Milli-Q, 18.2 Mfi/cm). The low propensity of chloride to form metal complexes led to its selection as the counter ion. We evaluated the solutions after diluting them to the required concentration.

Making the MNP-HVP Biosorbent

In order to prepare for the trials, we gathered biomass from submerged aquatic plants (*H. verticillata*) in the area and grew them in a greenhouse for fourteen days. Fresh samples with equal surface areas for sorbent materials were obtained by cutting away the apical section of the plant. After rinsing with water, the chosen *H. verticillata* parts were dried in a convection oven set at 343 K for 72 hours. Afterwards, the pieces were ground into smaller pieces that were around 0.1 to 0.2 mm in size. Particles having a uniform composition and small size dispersion were then prepared using the chemical precipitation process. In terms of efficiency and prevalence, this method is likely to top the list for obtaining magnetic particles. Under inert conditions, a complete precipitation of Fe₃O₄ was accomplished at an alkaline state while keeping the Fe²⁺ to Fe³⁺ molar ratio of 1:2. An inert atmosphere was used to dissolve 2.1 g of FeSO₄·7H₂O and 3.1 g of FeCl₃·6H₂O in 80 mL of double distilled water while vigorously stirring. The result was 2 g of magnetic particles. Ten milliliters of a 25% ammonium hydroxide solution was added as the solution was being heated to 353 K. After that, 10 g of HVP was added to the solution, and the reaction was stirred constantly at 353 K for 30 minutes to guarantee that the nanoparticle crystals had grown to their full potential (we had already established the adsorbent ratio in our earlier tests). After bringing the mixture to room temperature, it was rinsed many times with double distilled water to extract any compounds that had not yet reacted.

RESULTS AND DISCUSSION

Examining the FTIR spectra and their analysis

In order to learn more about the potential interactions between the functional groups of MNP-HVP biomass and the metal ions, the Fourier transform infrared (FT-IR) spectra of dried, unloaded biomass and biomass loaded with Cu(II) or Zn(II) were recorded. Spectra like this can be seen in Figure 1. The attached hydroxyl group (-OH) was responsible for the wide and robust bands seen at 3,402-3,500 cm⁻¹. The stretching vibration of the carboxyl group (-C=O) was deemed to be responsible for the peaks observed at 1,621-1,635 cm⁻¹. Carboxylate ions are responsible for the bands seen at 1,404-1,419 cm⁻¹. Alcohols and carboxylic acids were identified as the source of the bands seen at 1,024-1,053 cm⁻¹. In the case of Cu(II) loaded biomass, the stretching vibration of the -OH group was moved from 3,402 cm⁻¹ to 3,421 cm⁻¹, and in the case of Zn(II) loaded biomass, it was moved to 3,500 cm⁻¹. Metal ions and hydroxyl groups interacted chemically on the biomass surface, as shown by these data. For biomass samples enriched with Cu(II) and

Zn(II), the carboxyl peak was seen at 1,626 cm⁻¹ and 1,622 cm⁻¹, respectively. For biomass samples enriched with Cu(II) and Zn(II), the peak at 1,053 cm⁻¹ moved to 1,024 and 1,028 cm⁻¹, respectively. The biosorption of Cu(II) and Zn(II) onto MNP-HVP biomass was shown to be mostly influenced by the functional groups specified, namely hydroxyl, carboxyl, and C-OH.

Biosorption velocities in ion-free solutions

The quantity of Cu(II) and Zn(II) biosorbed onto MNP-HVP is affected by the contact time, as shown in Fig. 2. At first, the sorption rate was steep; after only 10 minutes, almost 49.95% of the total Cu(II) or 72.30% of the total Zn(II) had been removed. After 30 minutes of contact time, Cu(II) and Zn(II) biosorption yields skyrocketed. It seems that heavy metal ions reached the biosorption equilibrium within around 30 minutes of contact with the sorbent, suggesting that the biosorption stages were quick. To learn more about how Cu(II) and Zn(II) biosorb onto MNP-HVP, a kinetic study was performed. The experimental data was analyzed using pseudo-second-order and intraparticle diffusion models to shed light on the biosorption kinetics of Cu(II) and Zn(II) ions onto MNP-HVP. Here we can see the pseudo-first-order rate equation in its linear form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

in where q_e and q_t are the concentrations of metal ions adsorbed at equilibrium and time t , respectively, and k_1 is the rate constant of the equation, expressed in units of min⁻¹. Experimental determination of the sorption rate constants (k_1) can be accomplished by graphing $\ln(q_e - q_t)$ vs. t .

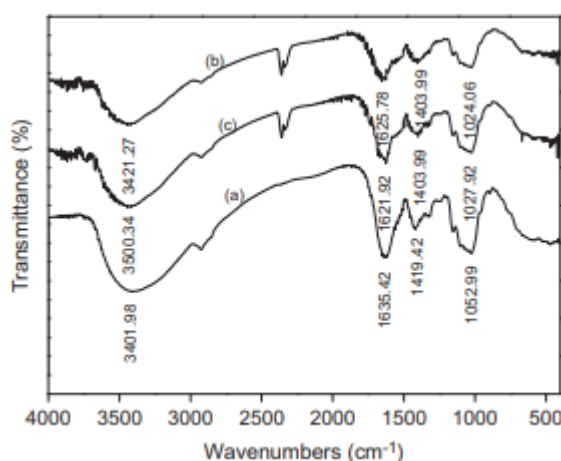


Fig. 1. FT-IR absorption spectrum of MNP-HVP: (a) native, (b) Cu(II) treated, and (c) Zn(II) treated.

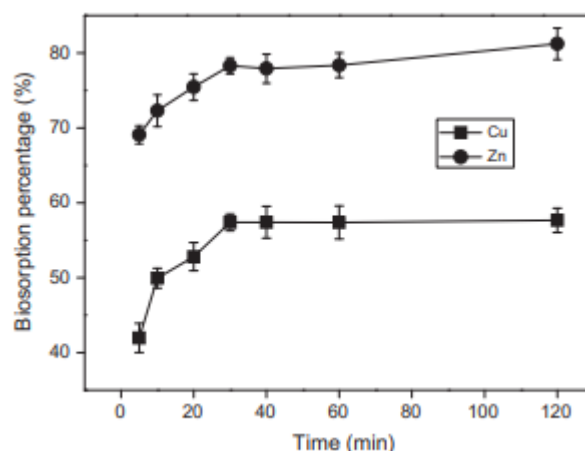


Fig. 2. Effect of contact time on Cu(II) and Zn(II) biosorption percentage

The linear form of the pseudo-second-order rate equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

the quantity of biosorption at time t (min) is represented by q_t (mg/g), the amount of biosorption at equilibrium (mg/g), and k_2 is the rate constant for pseudo-second-order sorption [g/(mg min)]. The use of pseudosecond-order kinetics, in which the values of q_e and k_2 are derived from the slope and intercept of the plot, respectively, would be indicated by a straight line of t/q_t vs. t . Here is the expression for the intraparticle diffusion equation:

$$q_t = k_3 t^{0.5} + C$$

k_3 is the rate constant of intraparticle diffusion, expressed as milligrams per milligram of sample volume at time t (in minutes), and q_t is the quantity sorbed. The thickness of the boundary layer may be inferred from the intercept value, which is C in milligrams per gram. Table 1 displays the calculated rate constants and coefficients of determination for all of the models. With a coefficient of determination of 0.999 for Cu(II) and Zn(II), the pseudo-second-order model more adequately explains the biosorption kinetic behaviors of heavy metals onto MNP-HVP when compared to the pseudo-first-order and intraparticle diffusion models. Table 1 shows that the computed q_e value agreed very well with the empirically determined value. It was found that sorption did not happen entirely onto one site in each ion, and intraparticle diffusion was not the main factor controlling the rate of Cu(II) or Zn(II) binding onto MNP-HVP, as the poor coefficient of determination of the pseudo-first-order and intraparticle diffusion models demonstrated. Chemical and electrostatic processes seemed to regulate the total rate of Cu(II) or Zn(II) sorption, in line with the pseudo-second reaction mechanism. Put simply, the total rate is modulated by means of electron sharing between the biosorbent and the sorbate, as well as electron exchange amongst the particles themselves.

Effect of pH

One critical variable in biosorption is the pH of the solution. The sorbate's speciation, surface charge, and degree of ionization are all impacted by these pH levels [25]. Researchers looked examined the removal efficiency of Cu(II) and Zn(II) ions at pH values ranging from 2.0 to 6.0, and how the concentration of H⁺ ions in aqueous solutions affected this effectiveness. The biosorption of Cu(II) and Zn(II) increases when the pH of the solution rises, as seen in Figure 3. Potentially relevant functional groups in metal absorption and metal chemistry might account for the pH dependence of biosorption effectiveness. Because of electrostatic repulsion, less Cu(II) or Zn (II) ions are able to be adsorbed onto the MNP-HVP surface at low pH levels, and most of the biosorption sites on the surface are occupied by H⁺ ions. The biosorption of heavy metal ions increased as the pH value rose, reaching equilibrium at pH 5.0, as the surface of the MNP-HVP grew more negatively charged. As a result of Cu(II) and Zn(II) ion soluble hydroxyl complex formation and competition with the active sites, biosorption efficiency decreased at higher pH values (>5.0).

Isotherm of biosorption for individual ions

By applying well-known equilibrium isotherms to sorption data, one may learn about the sorption mechanism, the sorbent's surface characteristics and affinity, and more. The experimental findings were analyzed using five of the most prevalent isotherm models: Langmuir, Freundlich, Dubinin- Radushkevich (D-R), Brunauer-Emmett-Teller (BET), and Tempkin. The three assumptions upon which the theoretical Langmuir sorption isotherm is founded are as follows: first, that sorption cannot continue beyond monolayer coverage; second, that each surface site is equal and can only hold one sorbed atom; and third, that a molecule's adsorption capacity at any particular site is unrelated to the occupancy of nearby sites.

Table 1. Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models

Metal ions	q_e, exp (mg/g)	q_e, cal (mg/g)	k_1 (min ⁻¹)	R ²	q_e, cal (mg/g)	k_2 [g/(mg·min)]	R ²	C (mg/g)	k_3 [mg/(g·min ^{0.5})]	R ²
	\multicolumn{4}{\text{Pseudo-first-order}}	\multicolumn{4}{\text{Pseudo-second-order}}	\multicolumn{2}{\text{Intraparticle diffusion}}							
Cu(II)	28.84	2.57	0.042	0.742	29.41	0.0251	0.999	23.14	0.588	0.549
Zn(II)	40.65	7.58	0.041	0.941	41.67	0.0148	0.999	34.80	0.542	0.821

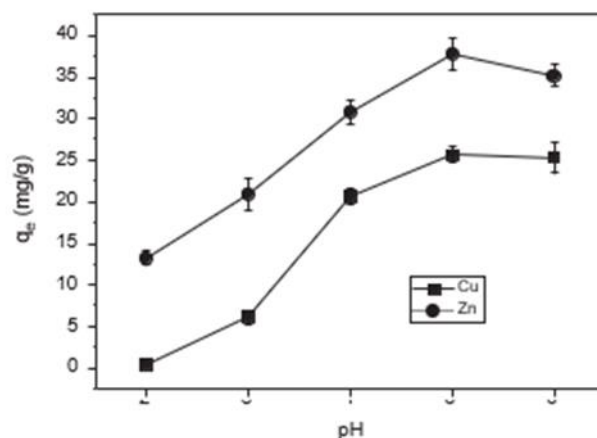


Fig. 3. Effect of pH on Cu(II) and Zn(II) biosorption onto MNP-HVP

This isotherm model is valid for monolayer sorption on a surface containing a finite number of identical sorption sites and can be written in its non-linear form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

This equation states that the maximum quantity of metal ions needed to create a monolayer is q_m , the equilibrium concentration of the solution is C_e , the Langmuir constant is K_L , and the amount of metal sorbed per particular amount of sorbent is q_e , where q_e is measured in mg/g. The following equation expresses the basic properties of the Langmuir isotherm in terms of R_L , a dimensionless constant separation factor:

$$R_L = \frac{1}{1 + K_L C_i}$$

Here, C_i is the starting concentration in milligrams per liter and K_L is the Langmuir constant in milliliters per milligram. A shape of the isotherm is indicated by R_L , where $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $0 < R_L < 1$ is favorable, and $R_L = 0$ is irreversible. The following equation often characterizes the Freundlich isotherm, which takes into account a heterogeneous surface with a non-uniform distribution of heat over the surface:

$$q_e = K_F C_e^{1/n}$$

$$q_e = RT \ln K_T + \frac{RT}{b_T} \ln C_e$$

in where K_T stands for the Tempkin isotherm constant and b_T for the Tempkin constant as it relates to the heat of sorption (in J/mol). By graphing q_e vs. $\ln C_e$, these constants were derived.

Below is a summary of the sorption isotherm characteristics from Table 2. The results on Cu(II) and Zn(II) removal by MNP-HVP were well-fit by the Langmuir isotherm model (R^2 values of 0.982 and 0.980, respectively). The maximum uptake value (q_m) is projected to be higher than q_e for the Langmuir isotherm. According to these findings, MNP-HVP is able to remove Cu(II) and Zn(II) at greater concentrations of the aforementioned metals. The strong binding affinity of Cu(II) and Zn(II) for MNP-HVP is shown by their constant K_L values of 0.066 and 0.0106, respectively. Biosorption of Cu(II) or Zn(II) onto MNP-HVP is a favorable process, as shown by R_L values ranging from 0.112 to 0.431 for Cu(II) or from 0.440 to 0.825 for Zn(II). With R^2 values of 0.906 and 0.973, respectively, the Freundlich isotherm model fitted the experimental data on Cu(II) and Zn(II) elimination well. Using MNP-HVP for Cu(II) and Zn(II) biosorption is advantageous under the experimental conditions, as indicated by n values of 1.745 and 2.890 for Cu(II) and Zn(II) removal data, respectively, which fall within the n of 1-10 ranges. The experimental data was well-fit by the D-R and BET isotherms (with high R^2 values), but the q_m values were much less, indicating that multilayer sorption was not likely to occur. It is possible that ion exchange occurs during biosorption in addition to the main chemical binding, as shown by the mean free energy (E) of >8 kJ/mol. The experimental data were well-fit by the Temp-kin isotherm; for Cu(II) and Zn(II), the R^2 values were 0.959 and 0.949, respectively. According to these findings, the sorption energy drops in a straight line when the surface area

is covered. Taking into account the values of R^2 and isotherms constants, it is clear that the experimental data is relatively well-fit by the Freundlich, Tempkin, and Langmuir models; nevertheless, the Langmuir isotherm model provides the best match.

Table 2. Isotherm constants of Langmuir, Freundlich, D–R, BET and Tempkin models for biosorption of Cu(II) and Zn(II) using MNP–HVP biosorbent

Isotherm	Parameters	Cu(II)	Zn(II)
Langmuir	q_m (mg/g)	66.67	72.20
	K_l (L/mg)	0.066	0.0106
	R^2	0.982	0.980
Freundlich	$1/n$	0.573	0.346
	K^f	8.414	16.24
	R^2	0.906	0.973
D–R (Dubinin–Radushkevich)	q_m (mg/g)	0.17	0.18
	β (mol ² /kJ ²)	4.045×10^{-3}	3.348×10^{-3}
	E (kJ/mol)	11.12	12.22
	R^2	0.990	0.988
BET	C^{BET} (L/mg)	5.01	2.055×10^6
	q_m (mg/g)	18.14	48.66
	R^2	0.959	0.921
Temkin	b_t (J/mol)	199.966	201.265
	K_t (L/g)	0.9998	1.005
	R^2	0.959	0.949

In contrast to competing biosorbents

We compared the sorption capacities of MNP-HVP biosorbent to other biosorbents stated in the literature for the removal of Cu(II) and Zn(II) ions from water solutions. The biosorption capacity, denoted as q_m , according to the Langmuir sorption capacity, is displayed in Table 3. The study found that MNP-HVP could biosorb a maximum of 66.67 and 72.20 mg/g of Cu(II) and Zn(II), respectively. Compared to other biosorbents, this one had a greater q_m [2,3,5,6,11,14,23,26,28-42]. Additional benefits for MNP-HVP as a biosorbent for the removal of Cu(II) and Zn(II) ions from industrial wastewaters are presented by the simple fabrication technique.

A thermodynamic examination of the effects of temperature

The determination of spontaneous processes in environmental engineering practice requires consideration of both entropy and energy. The temperature range of 278, 288, and 298 K was used to conduct biosorption tests in this work. The impact of temperature on the biosorption of Cu(II) and Zn(II) may be assumed from Figure 4. The equilibrium quantity of metal ions adsorbed onto MNP-HVP for Cu(II) rose from 49.67 to 54.17 mg/g and for Zn(II) from 56.29 to 64.63 mg/g as the temperature was raised from 278 to 298 K. As the temperature rose, the sorption capacity of Cu(II) and Zn(II) was marginally higher. These findings point to the possibility of a mixed chemical-physical adsorption process during biosorption of metal ions using MNP-HVP biosorbent. The following factors contribute to the positive impact of higher temperatures on Cu(II) and Zn(II) biosorption: (i) the re-orientation of plant biomass cell wall components leads to an increase in the number of binding sites on biosorbent surfaces; (ii) the rate of sorbate diffusion across the external boundary layer and in the internal pores of the sorbate particles is accelerated; (iii) chemical moieties on the cell wall are ionized; (iv) sites for metal ions are more strongly bound; and (v) the sorbate's equilibrium capacity is affected.

Table 3. Comparison of the biosorption capacity of different biosorbents

Sorbent	Zn(II) uptake (mg/g)	Cu(II) uptake (mg/g)	References
MNP-HVP	72.20	66.67	This study
<i>Pinus sylvestris</i> L.	26.39	28.83	[2]
<i>Ulva lactuca</i>	22.75	53.96	[6]
Chemically pretreated <i>Rosa gruss an teplitz</i>	116.28	84.74	[23]
<i>Gymnogruntus</i> sp.	44.20	51.84	[26]
Valonia tannin resin	35.51	45.44	[28]
<i>Streptomyces rimosus</i>	27.40	30.00	[29]
<i>Sargassum filipendula</i>	44.66	/	[3]
<i>N. commune</i>	115.41	/	[11]
Dried activated sludge	17.86	/	[30]
<i>Acinetobacter</i> sp.	36.00	/	[31]
Modified corn cob	79.21	/	[32]

<i>Streptomyces ciscaucasicus</i> strain CCNWHX 72-14	54.00	/	[33]
<i>Botrytis cinerea</i>	12.98	/	[34]
Orange waste	43.16	/	[35]
<i>B. cereus</i> AUMC B52	66.60	/	[36]
Wheat straw	/	11.43	[5]
Pine cone shell	/	6.81	[14]
<i>Myriophyllum spicatum</i>	/	12.16	[37]
Coconut shell	/	7.25	[38]
Spider silk	/	3.27	[39]
Maple wood sawdust	/	9.51	[40]
<i>Eichhornia crassipes</i>	/	27.70	[41]
Chemically modified <i>Moringa oleifera</i>	/	146.87	[42]

Following the procedure proposed the K_0 thermodynamic equilibrium constant for sorption processes was calculated. This technique entails obtaining a zero value by projecting the graph of $\ln(q_e/C_e)$ against q_e . According to Table 4, when the solution temperature was raised from 278 to 298 K, the K_0 value for Cu(II) increased from 1.231 to 2.223 and for Zn(II) from 1.288 to 3.295. The fact that the K_0 value increased as the temperature rose showed that biosorption processes are endothermic. Equations were used to compute the thermodynamic parameters ΔG° , ΔH° , and ΔS° , which represent the biosorption of Cu(II) and Zn(II) onto MNP-HVP.

$$\Delta G^\circ = -RT \ln K^\circ$$

$$\ln K^\circ = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

the temperature in Kelvin, and the universal gas constant, R , is defined as 8.314 J/(molK). An MNP-HVP biosorption plot of $\ln K_0$ vs $1/T$ for Cu(II) or Zn(II) is linear. The slope and intercept of the plots are used to determine ΔH° and ΔS° , respectively. Table 4 displays the values of H° , S° , and G° . The reason why the values of ΔG° at different temperatures are negative is because the sorption process is spontaneous and the MNP-HVP sorbent has a strong predilection for metal ions. The amount of information concerning sorption is given by the size of ΔH° . Biosorption is endothermic because the enthalpy change value is positive. The sorbate (hydrated metal ions) and biosorbent (MNP-HVP) undergo unique structural modifications, leading to enhanced unpredictability at the solid/solution interface, as shown by the positive values of ΔS° .

CONCLUSION

This study aimed to evaluate the effectiveness of a new MNP-HVP sorbent for Cu(II) and Zn(II) ions, which was created from a powdered aquatic plant found in the area. The absorption of Cu(II) and Zn(II) was

investigated in relation to operational factors including solution pH, contact duration, temperature, and cation competition. The Freundlich model was shown to be inadequate in describing biosorption equilibrium data for single ions when compared to the Langmuir isotherm model. The highest monolayer biosorption capacities of Cu(II) and Zn(II) for MNP-HVP biomass were 66.67 mg/g and 72.20 mg/g, respectively. When it comes to modeling the binary system's equilibrium data, the Langmuir-Friendlich isotherm model provides the best match, according to the sum of squares errors. Compared to Zn(II), Cu(II) biosorption was easier with MNP-HVP. Thermodynamic characteristics revealed that the biosorption process was feasible, endothermic, and spontaneous. The pseudosecond-order kinetic model was well followed by the biosorption of Cu(II) and Zn(II) ions onto MNP-HVP biomass, according to the kinetic data. All things considered, MNP-HVP is a highly effective advanced sorbent for cleaning up polluted environments.

REFERENCE

- [1] T.A. Saleh, V.K. Gupta, Column with CNT/magnesium oxide composite for lead(II) removal from water, *Environ. Sci. Pollut. Res.* 19 (2012) 1224–1228.
- [2] H. Uzun, O. Aksakal, E. Yildiz, Copper(II) and zinc(II) biosorption on *Pinus sylvestris* L., *J. Hazard. Mater.* 161 (2009) 1040–1045.
- [3] A.S. Luna, A.L.H. Costa, A.C.A. da Costa, C.A. Henriques, Competitive biosorption of cadmium(II) and zinc(II) ions from binary systems by *Sargassum filipendula*, *Bioresour. Technol.* 101 (2010) 5104–5111.
- [4] V.K. Gupta, A. Suhas, A. Nayak, S. Agarwal, M. Chaudhary, Removal of Ni (II) ions from water using scrap tire, *J. Mol. Liq.* 190 (2014) 215–222.
- [5] V.B.H. Dang, H.D. Doan, T. Dang-Vu, A. Lohi, Equilibrium and kinetics of biosorption of cadmium(II) and copper(II) ions by wheat straw, *Bioresour. Technol.* 100 (2009) 211–219.
- [6] M.M. Areco, S. Hanel, J. Duran, M. dos Santos Afonso, Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga *Ulva lactuca* and the development of a sustainable matrix for adsorption implementation, *J. Hazard. Mater.* 213–214 (2012) 123–132.
- [7] A. Rathinam, B. Maharshi, S.K. Janardhanan, R.R. Jonnalagadda, B.U. Nair, Biosorption of cadmium metal ion from simulated wastewaters using *Hypnea valentiae* biomass: A kinetic and thermodynamic study, *Bioresour. Technol.* 101 (2010) 1466–1470.
- [8] A.A. Al-Homaidan, H.J. Al-Houri, A.A. Al-Hazzani, G. Elgaaly, N.M.S. Moubayed, Biosorption of copper ions from aqueous solutions by *Spirulina platensis* biomass, *Arab. J. Chem.* 7 (2014) 57–62.

- [9] W. Huang, Z. Liu, Biosorption of Cd(II)/Pb(II) from aqueous solution by biosurfactant-producing bacteria: Isotherm kinetic characteristic and mechanism studies, *Colloids Surf., B* 105 (2013) 113–119.
- [10] M.E. Mahmoud, R.H.A. Mohamed, Biosorption and removal of Cr(VI)–Cr(III) from water by eco-friendly gelatin biosorbent, *J. Environ. Chem. Eng.* 2 (2014) 715–722.
- [11] F.M. Morsy, S.H.A. Hassan, M. Koutb, Biosorption of Cd(II) and Zn(II) by *Nostoc commune*: Isotherm and kinetics studies, *CLEAN—Soil, Air, Water* 39 (2011) 680–687.
- [12] D.K.V. Ramana, D.H.K. Reddy, B.N. Kumar, Y. Harinath, K. Seshaiiah, Removal of nickel from aqueous solutions by citric acid modified *Ceiba pentandra* hulls: Equilibrium and kinetic studies, *Can. J. Chem. Eng.* 90 (2012) 111–119.
- [13] S. Chakravarty, A. Mohanty, T.N. Sudha, A.K. Upadhyay, J. Konar, J.K. Sircar, A. Madhukar, K.K. Gupta, Removal of Pb(II) ions from aqueous solution by adsorption using bael leaves (*Aegle marmelos*), *J. Hazard. Mater.* 173 (2010) 502–509.
- [14] G. Bla'zquez, M.A. Marti'n-Lara, E. Dionisio-Ruiz, G. Tenorio, M. Calero, Copper biosorption by pine cone shell and thermal decomposition study of the exhausted biosorbent, *J. Ind. Eng. Chem.* 18 (2012) 1741–1750.
- [15] W.N.L. dos Santos, D.D. Cavalcante, E.G.P. da Silva, C.F. das Virgens, F.S. Dias, Biosorption of Pb(II) and Cd(II) ions by *Agave sisalana* (sisal fiber), *Microchem. J.* 97 (2011) 269–273.
- [16] J. He, J.P. Chen, A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modeling simulation tools, *Bioresour. Technol.* 160 (2014) 67–78.
- [17] M. Fomina, G.M. Gadd, Biosorption: Current perspectives on concept, definition and application, *Bioresour. Technol.* 160 (2014) 3–14.
- [18] D. Harikishore Kumar Reddy, S.M. Lee, Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal, *Colloids Surf., A* 454 (2014) 96–103.
- [19] P.S. Haddad, T.M. Martins, L. D'Souza-Li, L.M. Li, K. Metze, R.L. Adam, M. Knobel, D. Zanchet, Structural and morphological investigation of magnetic nanoparticles based on iron oxides for biomedical applications, *Mater. Sci. Eng., C* 28 (2008) 489–494.
- [20] D. Hritcu, M.I. Popa, N. Popa, V. Badescu, V. Balan, Preparation and characterization of magnetic chitosan nanospheres, *Turk. J. Chem.* 33 (2009) 785–796