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Biosorption of Cu(II) and Zn(II) ions from aqueous solution by a new sorbent prepared from *Hydrilla verticillata* and Fe_3O_4 nanoparticles: one-component and binary systems

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ABSTRACT

The biosorption characteristics of Cu(II) and Zn(II) ions from aqueous solution by a magnetic nanosorbent (MNP–*Hydrilla verticillata* powder (HVP)) prepared from HVP and Fe_3O_4 nanoparticles were investigated from single and binary component systems. Optimum biosorption conditions were determined as a function of pH, contact time, and temperature. The results showed that the pH for optimum sorption was 5.0 for Cu(II) and Zn(II) ions. Equilibrium sorption isotherms were measured for the single component system, and the experimental data were analyzed using Langmuir, Freundlich, Dubinin–Radushkevich, Brunauer–Emmett–Teller, and Tempkin models. The Langmuir isotherm described the biosorption of Cu(II) and Zn(II) ions onto MNP–HVP biomass ($R^2 = 0.982$ and 0.980) better than the other four isotherms. The maximum biosorption capacity of MNP–HVP biomass was 66.67 mg/g for Cu(II) ion and 72.20 mg/g for Zn(II) ion. Biosorption equilibrium for binary systems showed that MNP–HVP had easier access for Cu(II) biosorption than Zn(II). Competitive Langmuir, partial competitive Langmuir, and Langmuir–Freundlich isotherms were tested for the equilibrium data of the binary system. The chi-square (χ^2) values indicated that the Langmuir–Freundlich isotherm model showed the best fit to the binary sorption data. The calculated thermodynamic parameters, ΔG°, ΔH°, and ΔS°, showed that the biosorption of Cu(II) and Zn(II) ions onto MNP–HVP biomass was feasible, spontaneous, and endothermic. The kinetics for Cu(II) and Zn(II) sorption was in good agreement with pseudo-second-order kinetic equation. Fourier transform infrared spectrum analysis revealed that Cu(II) and Zn(II) sorption was mainly ascribed to hydroxyl, carboxyl, and C–OH groups in MNP–HVP biomass.

Keywords: Competitive biosorption; *Hydrilla verticillata*; Magnetic sorbent; Equilibrium isotherms; Heavy metals; Kinetic model

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1. Introduction

Along with increasing industrial activity, wastewater from multiple industries such as mining, metal finishing, electroplating, textile, and storage batteries industries, etc., which contains toxic heavy metals that are non-biodegradable and tend to accumulate in living organisms, cause various diseases and disorders [1]. Even the presence of low concentrations of toxic metals in water can cause severe neurological and physiological damage to human body. Metals such as copper (Cu) and zinc (Zn) are known to be essential to plants, humans, and animals, but they can also have adverse effects if their availability in water exceeds threshold values. The World Health Organization recommended a maximum acceptable concentration of Cu(II) and Zn(II) in drinking water of 1.5 and 5.0 mg/L [2], respectively.

Various techniques have been employed to treat wastewater that contains these heavy metals. However, most of these techniques may be ineffective or extremely expensive [3]. During the past two decades, considerable interest has been focused on the use of sorbent materials [4], particularly biosorbents such as wheat straw [5], green alga [6], macro alga [7,8], bacterium [9], gelatin [10], *Nostoc commune* [11], *Ceiba pentandra* hull powder [12], bael leaves [13], pine cone shell [14], and sisal fiber [15]. Sorption by biomass is recognized as an alternative method for the treatment of wastewaters containing heavy metals [16,17].

Although naturally available biosorbents exhibited good sorption ability, separating powdered biosorbents from aqueous solutions is difficult because of small particle sizes. Thus, the separation of these particles from aqueous solutions requires tedious processes such as filtration and centrifugation, thereby limiting their practical application in wastewater treatment [18]. To overcome these problems, recent research have been focused on preparing magnetic nanosorbents by inducing magnetic nanoparticles into biosorbents [19,20]. Magnetic biosorbents can be easily separated from the aqueous solution using an external magnetic field [21,22]. In addition, nanoparticles exhibit good sorption efficiency, especially because of higher surface area and greater active sites for interaction with metallic species, and can easily be synthesized. The application of magnetic nanoparticles in the field of wastewater treatment is becoming a compelling area of research.

In this work, a novel magnetic nanosorbent (MNP–*Hydrilla verticillata* powder (HVP)) was developed by the surface modification of magnetic Fe_3O_4 nanoparticles (MNP) with HVP with the aim of exploring its feasibility as sorbent for the removal of Cu(II) and Zn(II) ions. *H. verticillata*, a submerged aquatic perennial plant that primarily reproduces through vegetative fragmentation, grows at a rapid rate and is commonly found in streams, littoral zones of lakes, drainage systems, and wetlands. This angiosperm is distributed worldwide and produces almost throughout the year, with roots often developing on a fragment before it is released by the plant. This low-cost, non-toxic biosorbent material, which contains active functional groups of hydroxyl and carboxyl present in cellulose, hemicellulose, and pectin components, is selected for its better application and management for wastewater remediation.

At most conditions, wastewater streams contain not one but several kinds of metal ions. For instance, Cu(II) and Zn(II), both of which have been reported to be serious environmental pollutants, frequently exist in wastewaters from chemical, plumbing, fertilizer, and battery manufacturing industries [23]. Although considerable research information on single metal biosorption is available, relatively less attention has been paid to the biosorption of multi-metal-ion systems [24], and no general trend for magnetic sorbents was observed. Examining the effects of divalent cations in various combinations is more representative of the actual environmental problems faced by organisms than the studies of a single metal.

In this study, the sorption behavior of Cu(II) and Zn(II) from aqueous solutions using the new sorbent (MNP–HVP) prepared from *H. verticillata* and Fe_3O_4 nanoparticles was studied through a set of experiments at various conditions, including contact time, solution pH, temperature, and effect of divalent ions. The primary objectives of this study are as follows: (i) to synthesize the new sorbent MNP–HVP by co-precipitation method; (ii) to investigate the biosorption potential of the new biosorbent MNP–HVP in removing Cu(II) and Zn(II) ions from aqueous solutions; (iii) to test the application of the selected multi-component isotherms on modeling competitive biosorption for the new biosorbent MNP–HVP.

2. Materials and methods

2.1. Reagents

Stocks of 1,000 mg/L metal solutions were prepared in deionized water (Milli-Q, 18.2 MΩ/cm) using Cu(II) chloride (analytical grade) or Zn(II) chloride (analytical grade). Chloride was selected as the counter ion because of its low tendency to form metal complexes. The solutions were then diluted to the desired concentration and analyzed.

2.2. Preparation of MNP–HVP biosorbent

Submerged aquatic plant (*H. verticillata*) biomass was collected locally and cultivated in a greenhouse for 14 d before the experiments. The apical part was cut out from the plant to obtain fresh samples with uniform surface areas for sorbent materials. The selected *H. verticillata* sections were washed with water and dried in a convection oven at 343 K for 72 h. The sections were then crushed into smaller particles of approximate size between 0.1 and 0.2 mm. Chemical precipitation technique was then used to prepare particles with homogeneous composition and narrow size distribution. This technique is probably the most common and efficient method to obtain magnetic particles. Complete precipitation of Fe_3O_4 was achieved at alkaline condition while maintaining Fe^{2+} to Fe^{3+} molar ratio of 1:2 in an inert environment. To obtain 2 g of magnetic particles, 2.1 g of $FeSO_4{\cdot}7H_2O$ and 3.1 g of $FeCl_3{\cdot}6H_2O$ were dissolved with vigorous stirring in an inert atmosphere in 80 mL of double distilled water. While the solution was being heated to 353 K, 10 mL of ammonium hydroxide solution (25%) was added. To ensure the complete growth of nanoparticle crystals, the solution was then added to 10 g of HVP, and the reaction was carried out for 30 min at 353 K with constant stirring (the adsorbent ratio was determined by our previous experiments). The resulting suspension was cooled down to room temperature and then repeatedly washed with double distilled water to remove unreacted chemicals.

2.3. Fourier transform infrared spectroscopy

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.

2.4. 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.

2.5. Sorption equilibrium experiments for single component

In studying the effect of pH, data were obtained using biosorbent (0.1 g) and solutions (100 mL) at an initial concentration of 50 mg/L. The temperature was controlled at 298 K, and the initial pH values were adjusted to the desired values (i.e. 2.0–6.0) as required with 0.1 M HNO_3 or 0.1 M NaOH (analytical grade) using a precision pH meter (PHS-3C) before adding the biosorbent. The data used to derive the five extensively used isotherms were obtained using the biosorbent (0.1 g) and the solution (100 mL) at initial Cu(II) or Zn(II) concentrations of 20, 40, 60, 80, 100, and 120 mg/L. The biosorbent was added to each flask, which was then placed on an orbital shaker at a temperature of 298 K. The contact time was 120 min. After the reaction, the contents of the flask were filtered to separate the biomass from the solution. The filtrates were then analyzed using an atomic adsorption spectrophotometer (Model SolaarM, Thermo Electron, USA) to determine the Cu(II) or Zn(II) concentration in the samples.

The amount of metal ions sorbed onto MNP–HVP was computed using the following equation:

$$q = \frac{V \cdot (C_i - C_f)}{W} \tag{1}$$

The biosorption percentage of Cu(II) or Zn(II) ions was calculated using the following equation:

$$\text{Biosorption Percentage}\,(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

where q is the amount of Cu(II) or Zn(II) biosorbed onto MNP–HVP (mg/g), C_i and C_f are the initial and final concentrations of Cu(II) or Zn(II) ions in the solution (mg/L), respectively, V is the volume of the solution (L), and W is the weight of the biosorbent (g).

All experiments were performed in triplicate, and the results were presented as mean values with standard deviations. Control experiments for Cu(II) or Zn(II) ions were performed to measure any sorption onto the glassware. The final concentration of Cu(II) or Zn(II) ions in each flask after 120 min of agitation without MNP–HVP biomass was highly consistent with the initial concentration. This result indicated that neither precipitation nor sorption onto the flask walls was observed.

2.6. Biosorption equilibrium for binary system

The experiment was carried out at room temperature (298 K) with an initial pH of 5.0 for the following four metal solutions: Cu(II) with varied concentration of Zn(II) at 20 and 40 mg/L, and Zn(II) with varied concentration of Cu(II) at 20 and 40 mg/L. In all cases, the initial metal concentration was varied from 20 to 120 mg/L, and the samples were placed on the shaker for a period of 120 min.

3. Results and discussion

3.1. Fourier transform infrared spectrum analysis

The Fourier transform infrared (FT-IR) spectra of dried unloaded biomass, and Cu(II) or Zn(II) loaded biomass were recorded to obtain information on the nature of possible interactions between the functional groups of MNP–HVP biomass and the metal ions. These spectra are presented in Fig. 1.

The broad and strong bands at 3,402–3,500 cm^{-1} were due to the bound hydroxyl group (–OH). The peaks at 1,621–1,635 cm^{-1} were attributed to the stretching vibration of the carboxyl group (–C=O). The bands at 1,404–1,419 cm^{-1} can be attributed to carboxylate ions. The bands observed at 1,024–1,053 cm^{-1} were assigned to C–OH stretching of alcohols and carboxylic acids. The stretching vibration of the –OH group was shifted from 3,402 cm^{-1} to 3,421 cm^{-1} in the case of Cu(II) loaded biomass and to 3,500 cm^{-1} in the case of Zn(II) loaded biomass. These results revealed that chemical interactions between metal ions and hydroxyl groups occurred on the biomass surface. The carboxyl peak was observed at 1,626 and 1,622 cm^{-1} for Cu(II) and Zn(II) loaded biomass samples, respectively. The peak at 1,053 cm^{-1} shifted to 1,024 and 1,028 cm^{-1} for Cu(II) and Zn(II) loaded biomass samples, respectively. These results indicated that the functional groups mentioned (hydroxyl, carboxyl, and C–OH) were mainly involved in the biosorption of Cu(II) and Zn(II) onto MNP–HVP biomass.

3.2. Biosorption kinetics for single-ion solutions

The effect of contact time on the amount of Cu(II) and Zn(II) biosorbed onto MNP–HVP is shown in Fig. 2. The sorption rate was initially fast, and approximately 49.95% of the total Cu(II) or 72.30% of the total Zn(II) was removed within 10 min. The biosorption yield of Cu(II) and Zn(II) increased considerably until the contact time reached 30 min. Heavy metal ions appeared to reach the biosorption equilibrium within approximately 30 min of being in contact with the sorbent, which implies fast biosorption steps.

A kinetic investigation was conducted to further investigate the biosorption mechanism of Cu(II) and Zn(II) onto MNP–HVP. Pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to analyze the experimental data to clarify the biosorption kinetics of Cu(II) and Zn(II) ions onto MNP–HVP.

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

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

where q_e and q_t (mg/g) are the amounts of metal ions sorbed at equilibrium and time t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}). The sorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ vs. t.

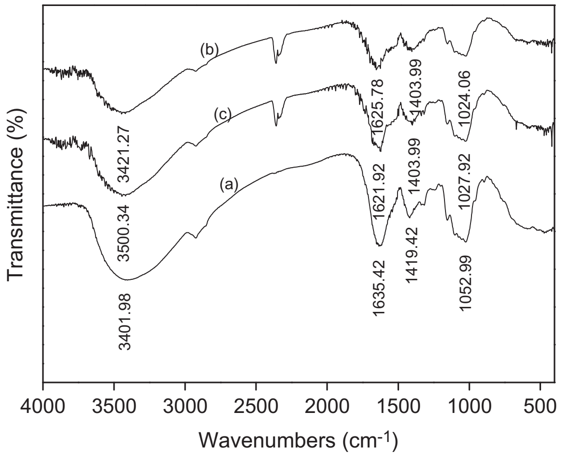

Fig. 1. FT-IR absorption spectrum of MNP–HVP: (a) native, (b) Cu(II) treated, and (c) Zn(II) treated.

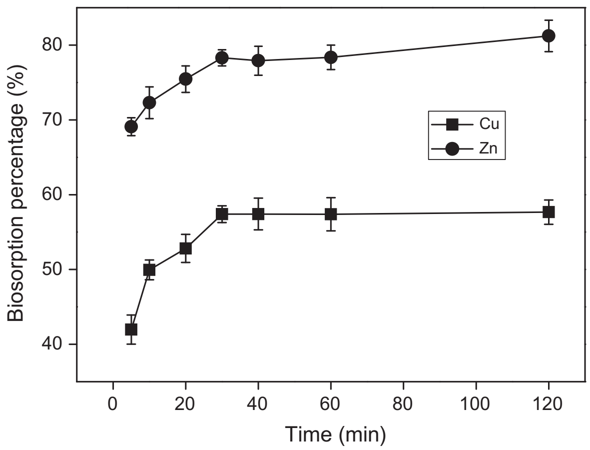

Fig. 2. Effect of contact time on Cu(II) and Zn(II) biosorption percentage.

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the rate constant for pseudo-second-order sorption [g/(mg min)], q_t (mg/g) is the amount of biosorption at time t (min), and q_e is the amount of biosorption at equilibrium (mg/g). A straight line of t/q_t vs. t would indicate the applicability of pseudo-second-order kinetics, where the q_e and k_2 values were determined from the slope and intercept of the plot, respectively.

The intraparticle diffusion equation is expressed as follows:

$$q_t = k_3 t^{0.5} + C \tag{5}$$

where q_t is the amount sorbed (mg/g) at time t (min), k_3 is the rate constant of intraparticle diffusion [mg/(gmin$^{0.5}$)], and C is the value of the intercept (mg/g), which provides insight about the boundary layer thickness.

The values of rate constants and coefficients of determination for each model are shown in Table 1. Compared with pseudo-first-order and intraparticle diffusion models, the pseudo-second-order model can satisfactorily explain the biosorption kinetic behaviors of heavy metals onto MNP–HVP with a coefficient of determination of 0.999 for Cu(II) and Zn(II). The calculated q_e value (Table 1) was in excellent agreement with that obtained experimentally. The low coefficient of determination of the pseudo-first-order and intraparticle diffusion models indicated that sorption did not occur exclusively onto one site in each ion, and intraparticle diffusion was not only the rate-determining factor for Cu(II) or Zn(II) binding onto MNP–HVP. In accordance with the pseudo-second reaction mechanism, the overall rate of Cu(II) or Zn(II) sorption processes appeared to be controlled by electrostatic attractions and chemical processes. In other words, the overall rate is controlled through the sharing of electrons between biosorbent and sorbate and the exchange of electrons between particles involved.

3.3. Effect of pH

Solution pH is an important parameter in the biosorption process. These pH values affect the surface charge of sorbent, degree of ionization, and speciation of sorbate during sorption [25]. The effect of H^+ ion concentration in aqueous solutions on the removal efficiency of Cu(II) and Zn(II) ions was studied at different pH values ranging from 2.0 to 6.0. From Fig. 3, Cu(II) and Zn(II) biosorption increases with increasing solution pH. The pH dependency of biosorption efficiency could be explained by functional groups involved in metal uptake and metal chemistry. At low pH values, H^+ ions occupy most of the biosorption sites on the MNP–HVP surface, and less Cu(II) or Zn (II) ions could be sorbed because of electric repulsion with H^+ ions on the MNP–HVP surface. With increasing pH value, the MNP–HVP surface became more negatively charged, and the biosorption of heavy metal ions increased and reached equilibrium at pH 5.0. The decrease in biosorption efficiency at higher pH (>5.0) was due to the formation of soluble hydroxyl complexes of Cu(II) and Zn(II) ions and their competition with the active sites.

3.4. Biosorption isotherm for single ions

Sorption data can be analyzed using well-known equilibrium isotherms to obtain insights about the surface properties and affinity of the sorbent as well as the sorption mechanism. Five of the most common isotherm models (Langmuir, Freundlich, Dubinin–Radushkevich (D–R), Brunauer–Emmett–Teller (BET), and Tempkin) were used to analyze the experimental results.

The theoretical Langmuir sorption isotherm is based on three assumptions, namely that sorption cannot proceed beyond monolayer coverage, all surface

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

		Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
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/(gmin$^{0.5}$)]	R^2
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

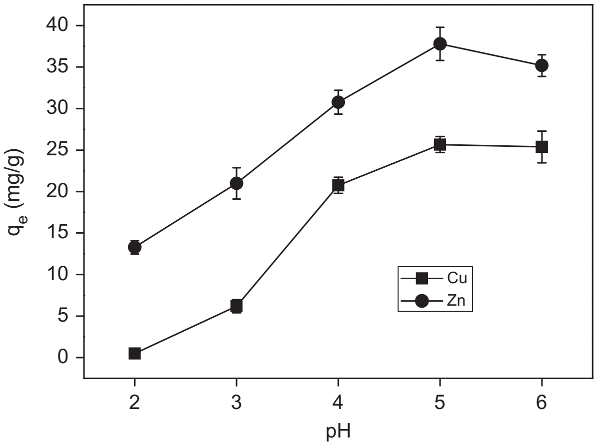

Fig. 3. Effect of pH on Cu(II) and Zn(II) biosorption onto MNP–HVP.

sites are equivalent and can accommodate at most one sorbed atom, and the ability of a molecule to adsorb at a given site is independent of the occupation of the neighboring sites. 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:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

where q_e is the amount of metal sorbed per specific amount of sorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), K_L is the Langmuir constant (L/mg), and q_m is the maximum amount of metal ions required to form a monolayer (mg/g).

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, which can be expressed in the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \tag{7}$$

where K_L is the Langmuir constant (L/mg) and C_i is the initial concentration (mg/L). R_L indicates the shape of the isotherm ($R_L > 1$ unfavorable; $R_L = 1$ linear; $0 < R_L < 1$ favorable, and $R_L = 0$ irreversible).

The Freundlich isotherm assumes a heterogeneous surface with a non-uniform distribution of heat over the surface, which is commonly described by the following equation:

$$q_e = K_F C_e^{1/n} \tag{8}$$

where K_F and $1/n$ are the Freundlich constants related to sorption capacity and sorption intensity, respectively.

The D–R isotherm proposed an equation for the analysis of the isotherm to determine whether the sorption process occurred via a physical or chemical process. The D–R equation is more general than the Langmuir model because the former does not assume a homogeneous surface, a constant sorption potential, nor the absence of steric hindrance between sorbed and incoming particles [26]. The D–R equation is shown as below:

$$q_e = q_m \exp\left(-\beta\left[RT\ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \tag{9}$$

where q_e is the biosorption capacity (mg/g), β is activity coefficient constant related to biosorption energy (mol^2/kJ^2), q_m is the maximum biosorption capacity to form a monolayer (mg/g), T is absolute temperature (K), and R is a gas constant [8.314 J/(mol K)]. The sorption free energy E (kJ/mol) could be calculated by the following equation:

$$E = \frac{1}{\sqrt{2\beta}} \tag{10}$$

The BET model is an extension of the Langmuir model for multi-layer biosorption. This model is based on the assumption that each sorbate in the first biosorbed layer functions as a biosorption site for the second layer and beyond. The general BET isotherm is given in Eq. (11)

$$q_e = \frac{q_m C_{BET} C_e}{(C_s - C_e)\left[1 + (C_{BET} - 1)\left(\frac{C_e}{C_s}\right)\right]} \tag{11}$$

where C_{BET} is the constant relating to the energy of interaction with the surface (L/mg), C_s is the saturation concentration of the solute (mg/L), C_e is the concentration of solute remaining in the solution at equilibrium (mg/L), q_e is the amount of solute sorbed per unit weight of sorbent (mg/g), and q_m is the maximum specific uptake corresponding to monolayer saturation (mg/g). Linearization of Eq. (11) would yield the C_{BET} and q_m values, which can be calculated from the slope and the intercept, respectively.

The Tempkin isotherm model assumes that the sorption energy decreases linearly with the surface coverage because of sorbent–sorbate interactions. The linear form of the Tempkin isotherm model is defined below [27]:

$$q_e = RT \ln K_T + \frac{RT}{b_T} \ln C_e \tag{12}$$

where b_T is the Tempkin constant related to heat of sorption (J/mol), and K_T is the Tempkin isotherm constant (L/g). These constants were obtained from plotting q_e vs. ln C_e.

The sorption isotherm parameters are summarized in Table 2. The Langmuir isotherm model fitted well with the Cu(II) and Zn(II) removal data by MNP–HVP with R^2 values of 0.982 and 0.980, respectively. For the Langmuir isotherm, q_e is lower than the predicted maximum uptake value (q_m). This result indicates that Cu(II) and Zn(II) removal by MNP–HVP proceeds at higher Cu(II) and Zn(II) concentrations. The constant K_L values of 0.066 and 0.0106 indicate significant binding strength affinity of Cu(II) and Zn(II) toward MNP–HVP. The values of R_L in the range of 0.112–0.431 for Cu(II) or 0.440–0.825 for Zn(II) indicate that the biosorption of Cu(II) or Zn(II) onto MNP–HVP is a favorable process. The Freundlich isotherm model also provided a good fit to the experimental Cu(II) and Zn (II) removal data with R^2 values of 0.906 and 0.973, respectively. n values of 1.745 and 2.890 for Cu(II) and Zn(II) removal data (which is within the n of 1–10 intervals) indicate that the biosorption of Cu(II) and Zn(II) using MNP–HVP is favorable at the experimental condition used. The D–R and BET isotherms fitted well with the experimental data, with high R^2 values, but the values of q_m were considerably smaller than that of the experimental data, thereby suggesting the unlikely occurrence of multilayer sorption. The mean free energy (E) of >8 kJ/mol suggests that ion exchange may occur during the biosorption process along with the primary chemical binding. The Tempkin isotherm fitted well with the experimental data with R^2 of 0.959 and 0.949 for Cu(II) and Zn(II), respectively. These results indicated that sorption energy decreases linearly with surface coverage. Considering the values of R^2 and isotherms constants, the Langmuir, Freundlich, and Tempkin models evidently fit the experimental data reasonably well, but the Langmuir isotherm model best fits the data.

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	Metal ions	
		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	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
Tempkin	b_T (J/mol)	199.966	201.265
	K_T (L/g)	0.9998	1.005
	R^2	0.959	0.949

3.5. Comparison with other biosorbents

The sorption capacity of MNP–HVP biosorbent for the removal of Cu(II) and Zn(II) ions from aqueous solutions was compared with those of other biosorbents reported in literature. Table 3 shows the biosorption capacity, q_m, based on Langmuir sorption capacity. The maximum Cu(II) and Zn(II) ion biosorption onto MNP–HVP obtained in this study were 66.67 and 72.20 mg/g, respectively. q_m was found to be higher than those of other biosorbents [2,3,5,6,11,14,23,26,28–42]. Furthermore, the facile fabrication method presents additional advantages for MNP–HVP as an effective biosorbent for the removal of Cu(II) and Zn(II) ions from industrial wastewaters.

3.6. Effect of temperature and thermodynamic analysis

In environmental engineering practice, both energy and entropy factors must be considered to determine processes that occur spontaneously. In this study, biosorption experiments were conducted in the temperature range of 278, 288, and 298 K. The effect of temperature on Cu(II) and Zn(II) biosorption can be inferred from Fig. 4. When the temperature was increased from 278 to 298 K, the amount of metal ions sorbed onto MNP–HVP at equilibrium increased from 49.67 to 54.17 mg/g for Cu(II) and from 56.29 to 64.63 mg/g for Zn(II), respectively. The sorption capacity for Cu(II) and Zn(II) slightly increased with increasing temperature. These results suggest that biosorption between MNP–HVP biosorbent and metal ions could involve a combination of chemical interaction and physical adsorption. The advantageous effect of higher temperatures on Cu(II) and Zn(II) biosorption can be attributed to the following: (i) an increase in the number of binding sites on the biosorbent surfaces because of the re-orientation of the cell wall components of the plant biomass; (ii) increased rate of

Table 3
Comparison of the biosorption capacity of different biosorbents

Sorbent	Metal uptake (mg/g)		References
	Zn(II)	Cu(II)	
MNP–HVP	72.20	66.67	This study
Pinus sylvestris L.	26.39	28.83	[2]
Ulva lactuca	22.75	53.96	[6]
Chemically pretreated *Rosa gruss an teplitz*	116.28	84.74	[23]
Gymnogongrus torulosus	44.20	51.84	[26]
Valonia tannin resin	35.51	45.44	[28]
Streptomyces rimosus	27.40	30.00	[29]
Sargassum filipendula	44.66	/	[3]
N. commune	115.41	/	[11]
Dried activated sludge	17.86	/	[30]
Acinetobacter sp.	36.00	/	[31]
Modified corn cob	79.21	/	[32]
Streptomyces ciscaucasicus strain CCNWHX 72-14	54.00	/	[33]
Botrytis cinerea	12.98	/	[34]
Orange waste	43.16	/	[35]
B. cereus AUMC B52	66.60	/	[36]
Wheat straw	/	11.43	[5]
Pine cone shell	/	6.81	[14]
Myriophyllum spicatum	/	12.16	[37]
Coconut shell	/	7.25	[38]
Spider silk	/	3.27	[39]
Maple wood sawdust	/	9.51	[40]
Eichhornia crassipes	/	27.70	[41]
Chemically modified *Moringa oleifera*	/	146.87	[42]

sorbate diffusion across the external boundary layer and in the internal pores of the sorbate particles; (iii) ionization of chemical moieties on the cell wall; (iv) higher affinity of sites for metal ions; and (v) effect on the equilibrium capacity of the sorbate.

The thermodynamic equilibrium constant, K^0, for sorption reactions was determined using the method suggested by Khan and Singh [43]. This method involves plotting ln (q_e/C_e) vs. q_e and extrapolating to zero. The results indicated that the K^0 value increased from 1.231 to 2.223 for Cu(II) and from 1.288 to 3.295 for Zn(II) when the solution temperature was increased from 278 to 298 K (Table 4). The increase in K^0 value with increasing temperature indicated the endothermic nature of biosorption processes.

Thermodynamic parameters, namely ΔG°, ΔH°, and ΔS°, that describe Cu(II) and Zn(II) biosorption onto MNP–HVP were calculated based on Eqs. (13) and (14):

$$\Delta G^\circ = -RT \ln K^0 \tag{13}$$

$$\ln K^0 = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{14}$$

where R is the universal gas constant [8.314 J/(molK)], and T is the temperature in Kelvin.

Plots of ln K^0 vs. $1/T$ for Cu(II) or Zn(II) biosorption by MNP–HVP are linear. ΔH° and ΔS° are determined from the slope and intercept of the plots, respectively. The values of ΔH°, ΔS°, and ΔG° are shown in Table 4. The negative values of ΔG° at different temperatures are due to the fact that the sorption process is spontaneous with a high preference of metal ions for the MNP–HVP sorbent. The magnitude of ΔH° provides information about sorption. The positive value of enthalpy change indicates that biosorption is endothermic in nature. The positive values of ΔS° show increased randomness at the solid/solution interface with specific structural changes in the sorbate (hydrated metal ions) and biosorbent (MNP–HVP).

3.7. Biosorption equilibrium for binary system and competitive isotherms

The competition of Cu(II) and Zn(II) in a binary solution for biosorption sites on MNP–HVP was determined by reacting different concentrations of Cu(II) and Zn(II) in the same solutions and determining their uptake by MNP–HVP. The experimental plots are

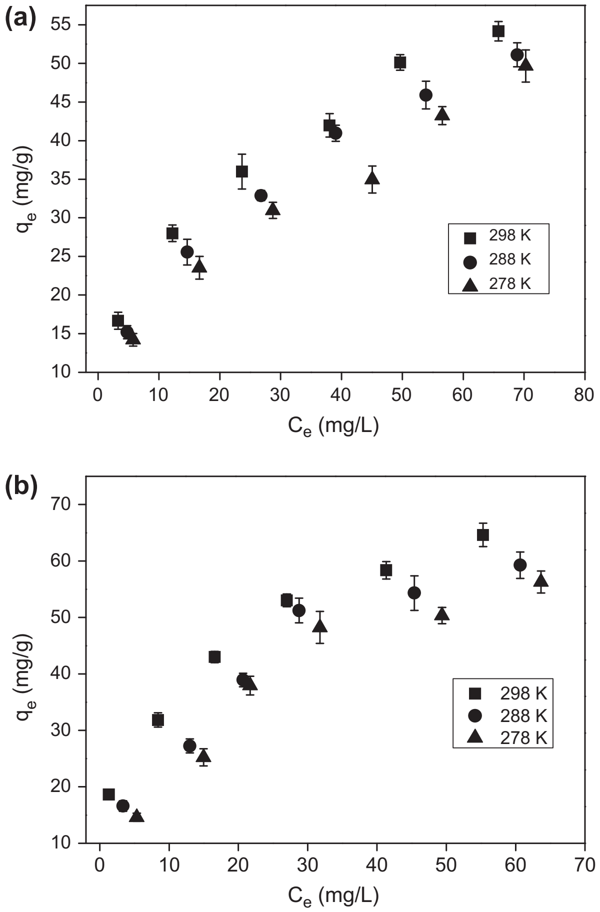

Fig. 4. Effect of temperature on Cu(II) and Zn(II) biosorption onto MNP–HVP: (a) Cu(II) and (b) Zn(II).

shown in Fig. 5. As shown in Fig. 5, Cu(II) biosorption decreased from 54.17 to 23.12 mg/g with the presence of Zn(II), and Zn(II) biosorption decreased from 64.63 to 18.48 mg/g. Zn(II) biosorption was more affected by the presence of Cu(II), indicating that MNP–HVP had easier access for Cu(II) biosorption than Zn(II).

The equilibrium data were analyzed using competitive Langmuir, partial competitive Langmuir, and Langmuir–Freundlich isotherm models.

Competitive Langmuir isotherm based on the Langmuir hypotheses implies the following equilibrium equations between cations and the sorbent sites [44]:

$$M_1 + S \leftrightarrow M_1S \tag{15}$$

$$M_2 + S \leftrightarrow M_2S \tag{16}$$

Thus, the resultant isotherm can be represented by the expression:

$$q_{\mathrm{e,i}} = \frac{Q_0 K_{\mathrm{L,i}} C_{\mathrm{e,i}}}{1 + \sum_{\mathrm{j}=1}^{2} K_{\mathrm{L,j}} C_{\mathrm{e,j}}} \quad \text{for } i = 1,2 \tag{17}$$

Partial competitive Langmuir isotherm considers that a cation can be attached to a free binding site or to a site already occupied by a different cation. In this case, the equilibrium equations represented by Eqs. (15) and (16) are complemented by:

$$M_1 + M_2S \leftrightarrow M_1(M_2S) \tag{18}$$

$$M_2 + M_1S \leftrightarrow M_2(M_1S) \tag{19}$$

These four equilibrium equations yield [44]:

$$q_{\mathrm{e,i}} = Q_0 \left(\frac{K_{\mathrm{L,i}} C_{\mathrm{e,i}} + K_{\mathrm{L,i}} K_{\mathrm{L,ij}} C_{\mathrm{e,i}} C_{\mathrm{e,j}}}{1 + K_{\mathrm{L,i}} C_{\mathrm{e,i}} + K_{\mathrm{L,j}} C_{\mathrm{e,j}} + \left(K_{\mathrm{L,i}} K_{\mathrm{L,ij}} + K_{\mathrm{L,j}} K_{\mathrm{L,ji}} \right) C_{\mathrm{e,i}} C_{\mathrm{e,j}}} \right) \quad \text{for } i,j = 1,2 \text{ with } i \neq j \tag{20}$$

where all parameters are obtained from multi-component sorption data.

The Langmuir–Freundlich isotherm for a binary system is given by Luna et al. [3]:

$$q_{\mathrm{e,i}} = \frac{Q_0 K_{\mathrm{LF,i}} C_{\mathrm{e,i}}^{1/n_{\mathrm{i}}}}{1 + \sum_{\mathrm{j}=1}^{2} K_{\mathrm{LF,j}} C_{\mathrm{e,j}}^{1/n_{\mathrm{j}}}} \quad \text{for } i = 1,2 \tag{21}$$

Table 4
Thermodynamic parameters for Cu(II) and Zn(II) biosorption onto MNP–HVP at constant temperatures

Metal ions	Temperature (K)	K^0	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° [J/(mol·K)]
Cu(II)	278	1.231	−0.469	20.353	74.859
	288	1.636	−1.218		
	298	2.223	−1.967		
Zn(II)	278	1.288	−0.515	33.431	119.8879
	288	1.900	−1.715		
	298	3.295	−2.913		

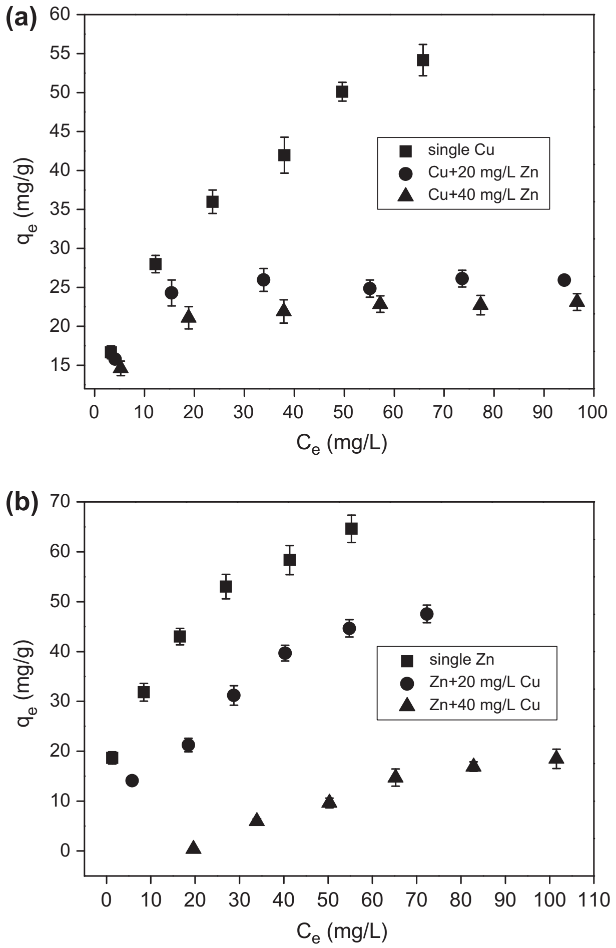

Fig. 5. Effect of cation competition for Cu(II) and Zn(II) biosorption onto MNP–HVP: (a) Cu(II) and (b) Zn(II).

where all parameters are obtained from multi-component sorption data.

The experimental data of simultaneous sorption of Cu(II) and Zn(II) were employed for the parameter estimation of competitive isotherms using the same numerical method of the single metal systems investigation. The results are presented in Table 5, in which the optimal set of parameters for each isotherm and the corresponding values of the determination efficient are shown. To allow the comparison of fitting quality in relation to model complexity, and the number of parameters in each alternative is also included.

To evaluate the best fit of isotherm models to experimental equilibrium data, an error function is required to enable the optimization procedure. Chi-square (χ^2) test was carried out to discover the best fit among the competitive sorption isotherm models used. The chi-square test statistic involves the sum of the squares of differences between experimental data and the data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The mathematical statement for χ^2 analysis can be written as [42]

$$\chi^2 = \sum \frac{(q_{\mathrm{e}} - q_{\mathrm{e,m}})^2}{q_{\mathrm{e,m}}} \tag{22}$$

where $q_{\mathrm{e,m}}$ is the equilibrium capacity obtained by calculating from the model (mg/g), and q_{e} is the experimental data on the equilibrium capacity (mg/g).

The χ^2 values are presented in Table 5. If data from the model are similar to the experimental data, χ^2 will be a low number, whereas different values yield χ^2 of a higher number. Therefore, analyzing the data-set using the non-linear chi-square test is important to confirm the best fit isotherm for the biosorption system. The χ^2 values of the three isotherms used are comparable; hence, the sorption of metal ions follows

Table 5
Isotherm models for binary sorption of Cu^{2+} and Zn^{2+}

	Isotherm models		
Metal ions	Competitive Langmuir (3 parameters)	Partial competitive Langmuir (5 parameters)	Langmuir–Freundlich (5 parameters)
Cu(II)	$Q_0 = 25.4322$, $K_{L,1} = 0.4867$, $K_{L,2} = 0.0319$ $R^2 = 0.7515$ $\chi^2 = 18.142$	$Q_0 = 65.9432$, $K_{L,1} = 25.9095$, $K_{L,12} = 0.1264$, $K_{L,2} = 54.5801$, $K_{L,21} = 0.1174$ $R^2 = 0.9310$ $\chi^2 = 13.7444$	$Q_0 = 25.57$, $1/n_1 = 1.16$, $K_{LF,1} = 2.5358 \times 10^{-4}$, $1/n_2 = 0.595$, $K_{LF,2} = 2.1888 \times 10^{-4}$ $R^2 = 0.9397$ $\chi^2 = 11.5441$
Zn(II)	$Q_0 = 202.2257$, $K_{L,1} = 1.4678 \times 10^{-8}$, $K_{L,2} = 4.5662 \times 10^{-6}$ $R^2 = 0.949$ $\chi^2 = 33.9125$	$Q_0 = 176.5683$, $K_{L,1} = 100.0244$, $K_{L,12} = 4.1817 \times 10^{-4}$, $K_{L,2} = 2.562 \times 10^3$, $K_{L,21} = 2.0729 \times 10^{-4}$ $R^2 = 0.9503$ $\chi^2 = 38.089$	$Q_0 = 53.2695$, $K_{LF,1} = 5.0861$, $1/n_1 = 2.2983$, $1/n_2 = 2.4072$, $K_{LF,2} = 100.2182$ $R^2 = 0.9697$ $\chi^2 = 30.577$

the three isotherms. Furthermore, the data better fits the Langmuir–Freundlich model because its χ^2 values are less than those of other isotherm models.

By analyzing the results from isotherms with only parameters based on experimental binary data, we can observe that the adherence of model predictions to the experimental data increases with the number of parameters, and the best fit was provided by the Langmuir–Freundlich model. Compared with competitive Langmuir and partial competitive Langmuir models, the Langmuir–Freundlich model can more satisfactorily explain the binary biosorption behaviors of heavy metals onto MNP–HVP, with coefficients of determination of 0.9397 for Cu(II) and 0.9697 for Zn(II). The relationship between Langmuir–Freundlich model prediction and experimental sorption data for Cu(II) and Zn(II) are presented in Fig. 6. Evidently, the values of q_e calculated by the Langmuir–Freundlich model were consistent with those obtained experimentally (the calculated data approximate the experimental data with deviations less than 10%, except for seven and nine data points for Cu(II) and Zn(II), respectively). These results suggested that the Langmuir–Freundlich model was suitable to predict the sorption isotherm for heavy metal biosorption onto MNP–HVP in binary sorbate system.

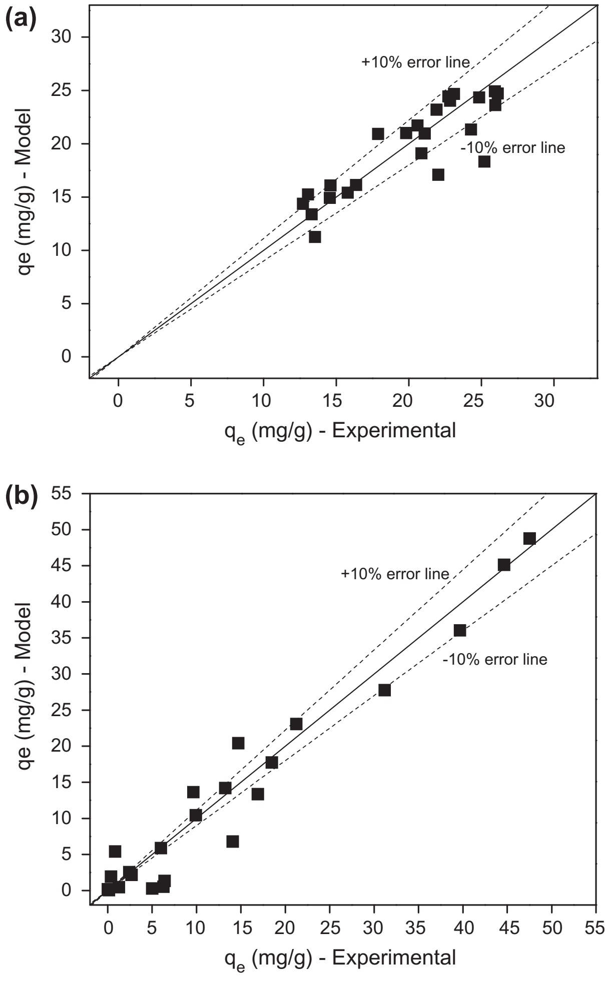

Fig. 6. Predicted and experimental sorption data for Cu(II) and Zn(II) in the binary system—Langmuir–Freundlich model: (a) Cu(II) and (b) Zn(II).

3.8. Desorption

To maintain a low processing cost down and to open the possibility of recovering the metals extracted from the solid phase, regenerating the biosorbent material is preferred. A strong desorption agent, that is, HCl acid, is conventionally used to recover quantities of metals from metal loaded biosorbents. Desorption experiments were carried out through various concentrations of HCl (0.1–0.6 M), respectively (Fig. 7). The desorption efficiency was increased with increasing HCl concentration and remained almost the same when the HCl concentration was higher than 0.4 M. The highest desorption efficiency for Cu(II) and Zn(II) sorbed on MNP–HVP biomass could reach approximately 90%. Hence, 0.4 M HCl solution was a suitable concentration for the regeneration of metal ions. This property of MNP–HVP may be utilized in small-scale commercial units to remove Cu(II) and Zn(II) from their discharging effluents in an economical and efficient manner.

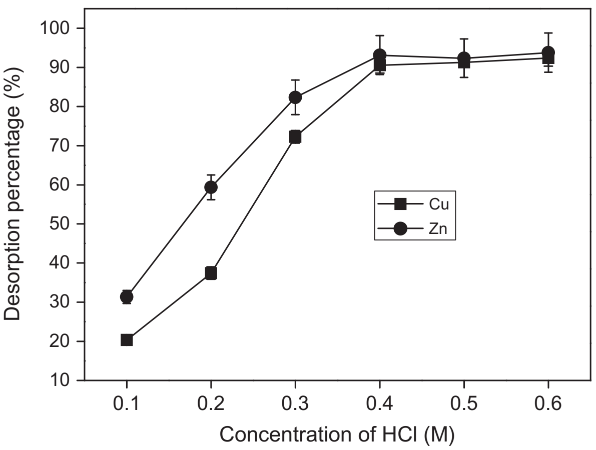

Fig. 7. Effect of HCl concentration on Cu(II) and Zn(II) desorption percentage.

4. Conclusions

This study focused on assessing the adsorption efficiency of a novel MNP–HVP sorbent developed from a local submerged aquatic plant powder for Cu(II) and Zn(II) ions. The effect of operating parameters, such as pH of solution, contact time, temperature, and cation competition, was studied on the uptake of Cu(II) and Zn(II). Biosorption equilibrium data for single ions were better described by the Langmuir isotherm model than the Freundlich model. The maximum monolayer biosorption capacities of MNP–HVP biomass were 66.67 mg/g for Cu(II) and 72.20 mg/g for Zn(II). For the equilibrium data modeling of the binary system, the sum of squares errors indicates that the Langmuir–Freundlich isotherm model gives the best fit to the binary sorption data. MNP–HVP had more easy access for Cu(II) biosorption than Zn(II). The thermodynamic parameters indicated the feasibility, endothermic, and spontaneous nature of the biosorption process. Kinetic data showed that the biosorption of Cu(II) and Zn(II) ions onto MNP–HVP biomass followed the pseudo-second-order kinetic model well. Based on all results, MNP–HVP is a promising advanced sorbent in environmental pollution cleanup.

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Symbols

b_T — Tempkin constant related to heat of sorption (J/mol)
C — intraparticle diffusion constant (mg/g)
C_{BET} — BET isotherm constant (L/mg)
C_e — metal ion concentration in the solution at equilibrium (mg/L)
$C_{e,i}$ — metal ion concentration for each component in the solution at equilibrium (mg/L)
C_i — initial metal ion concentration in the solution (mg/L)
C_s — saturation concentration of solute (mg/L)
C_t — metal concentration in the solution at a given time (mg/L)
E — sorption free energy (kJ/mol)
k_1 — rate constant of the pseudo-first-order kinetics (min^{-1})
k_2 — rate constant of the pseudo-second-order kinetics [g/(mg min)]
k_3 — rate constant of intraparticle diffusion [mg/(g min$^{0.5}$)]
K_F — Freundlich biosorption constant
K_L — Langmuir biosorption constant (L/mg)
$K_{L,i}$ — competitive Langmuir isotherm constants (L/mg)
$K_{L,ij}$ — partial competitive Langmuir isotherm constant (L/mg)
$K_{LF,\ i}$, $n_{i,}$ — Langmuir–Freundlich isotherm constants
K_T — Tempkin isotherm constant (L/g)
n — Freundlich isotherm constant
q_e — amount of metal sorbed at equilibrium (mg/g)
$q_{e,i}$ — amount of each component sorbed at equilibrium (mg/g)
$q_{e,m}$ — biosorption capacity obtained by calculating from models (mg/g)
q_t — metal ion sorbed on biosorbent at a given time t (mg/g)
q_m — maximum biosorption capacity to form monolayer (mg/g)
Q_0 — biosorption capacity for one component in binary systems (mg/g)
R — universal gas constant [8.314 J/(mol K)]
R_L — separation factor
t — contact time (min)
T — temperature in Kelvin (K)
V — value of metal ions solution (L)
W — weight of the biosorbent (g)
β — activity coefficient constant related to biosorption energy (mol^2/kJ^2)

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