

Biosorption of Cu(II), Ni(II), Zn(II) and Pb(II) ions from aqueous solution by *Sophora japonica* pods powder

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Received: 30 June 2014 / Accepted: 22 December 2014 / Published online: 21 January 2015
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Abstract

Background Biosorption of Cu (II), Ni(II), Zn(II) and Pb(II) ions from aqueous solutions onto *Sophora japonica* pods powder has been studied using batch adsorption technique. The biosorption studies were determined as a function of pH, contact time, initial metal ion concentration, biosorbent dosage and temperature.

Results The kinetic study showed that the biosorption of the Cu(II), Ni(II), Zn(II) and Pb(II) ions followed pseudo-second-order kinetic model. Experimental data obtained were analyzed with Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm models and in each case the Langmuir model appears to have better regression coefficients. Thermodynamic parameters: ΔG° , ΔH° and ΔS° were calculated indicating that the biosorption of Cu(II), Ni(II), Zn(II) and Pb(II) ions is spontaneous and endothermic process.

Conclusions The results of the study showed that *Sophora japonica* pods powder can be efficiently used as a low-cost alternative for the removal of Cu(II), Ni(II), Zn(II) and Pb(II) ions from aqueous solutions.

Keywords Biosorption · *Sophora japonica* pods · Metal ions · Kinetic · Thermodynamics

Background

Metal ion contamination of drinking water and wastewater, with metal ions is a serious and ongoing problem. Heavy

metals are toxic at high concentrations and are high-frequency pollutants seen in municipalities and specific industries. Since contaminated wastewater can easily find its way into both surface water and ground water, this problem should be of great concern to anyone who obtains their drinking water from these sources. Different methods of treating effluent containing Cu(II), Ni(II), Zn(II) and Pb(II) ions have been developed over years which include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, filtration, evaporation recovery and ion exchange [1–3]. However, most of these techniques have some disadvantages such as complicated treatment process and high cost. Another major disadvantage is the production of toxic chemical sludge. The search for novel technologies has recently been directed to the application of biosorption, which constitutes an attractive to commonly applied physical–chemical methods. The advantages of biosorption lie in the good performance in metal removal, cost-effectiveness and eco-friendly to environment. In recent years, the searches for low-cost agricultural by-products have been widely studied for metal ion removal from water and wastewater. These include *Citrus reticulata* [4], maize cob [5], *Tectona grandis* leaves [6], neem biomass [7], *Eucalyptus camaldulensis* leaves [8], rice straw [9], rice husk [10], *Eucalyptus* bark, mango bark and pine apple fruit peel [11], *Moringa oleifera* bark [12], hazelnut, almond and walnut shells [13], *Pinus gerardiana* leaves [14], *Cynodon dactylon*, *Psidium guajava*, *Azadirachta indica*, *Cassia tora* and *Cassia angustifolia* leaves [15], coconut leaves [16], *Ashoka* leaf [17], *Ceratonia siliqua* bark [18] and *Eriobotrya japonica* bark [19]. This paper presents the study of biosorption characteristics of *Sophora japonica* pods powder (Sjp) for the removal of Cu(II), Ni(II), Zn(II) and Pb(II) ions from aqueous solution in batch process.

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Methods

Preparation of the biosorbent

Sophora japonica pods (Sjp) were collected from trees planted at the campus of Royal Scientific Society, Jordan (Fig. 1). The pods were thoroughly rinsed with distilled water to remove dust and left dry at room temperature. The dried pods were crushed and grounded to a fine powder in a grinding mill (Retsch RM 100) and sieved to get size fraction <math><44\ \mu\text{m}</math>. *Sophora japonica* pods powder (Sjp) was dried in an oven at 60 °C for 24 h and stored in a desiccator to prevent water adsorption before its use for the batch experiments.

Chemicals and equipment

All reagents used were of AR grade. Deionized distilled water was used throughout the experimental studies. Stock solutions (1,000 mg/L) were prepared by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$. Desired test solutions of metal ions were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of metal ions prepared from standard solution varies between 5 and 100 mg/L. ACS reagent grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) (E. Merck) were used to adjust the solution pH. The concentrations of Cu(II), Ni(II), Zn(II), and Pb(II) ions in the solutions before and after equilibrium were determined by AAS6300 atomic absorption spectrometer (Shimadzu). The pH of the solution was measured with a WTW pH meter using a combined glass electrode. Fourier transform infrared spectroscopy, FT-IR (IR Prestige-21, Shimadzu) was used to identify the different chemical functional groups present in the Sjp. FT-IR analyses also used to determine the functional groups are responsible for the metal binding with Sjp. The analysis was carried out using KBr and the spectral range varying from 4,000 to $400\ \text{cm}^{-1}$.

Fig. 1 Photograph shows the *Sophora japonica* tree and its pods



Batch biosorption study

Batch biosorption experiments were conducted by mixing biosorbent with Cu(II), Ni(II), Zn(II), and Pb(II) ions solution with desired concentration in 250 mL glass flask. The glass flasks were stoppered during the equilibration period and placed on a temperature controlled shaker at a speed 120 rpm/min. The effect of pH on the equilibrium biosorption of metal ions was investigated by mixing. The amount of biosorption was calculated based on the difference between the initial (C_o , mg/L) and final concentration (C_e , mg/L) in every flask as follows:

$$q_e = \frac{C_o - C_e}{M} \times V, \quad (1)$$

where q_e is the metal uptake capacity (mg/g), V the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g). Percent removal (% R) of metal ions was calculated from the following equation:

$$\% R = \frac{C_o - C_e}{C_o} \times 100. \quad (2)$$

Results and discussion

Effect of pH on metal ion biosorption

The pH has been identified as one of the most important parameter that is effective on metal sorption. It is directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface. The effect of pH on the biosorption of Cu(II), Ni(II), Zn(II), and Pb(II) ions onto Sjp was studied at pH 1.0–8.0, Fig. 2. The maximum biosorption was observed at pH 6.0–7.0 for metal ions. Therefore, the remaining all biosorption experiments were carried out at this pH value. The biosorption mechanisms on the Sjp surface reflect the nature of the physico-chemical interaction of the solution. At highly acidic pH, the overall surface charge on the active sites became

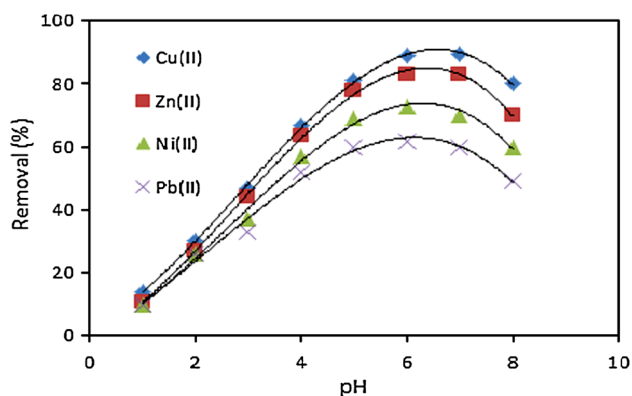


Fig. 2 Effect of pH on the removal of metal ions onto Sjp powder

positive and metal cations and protons compete for binding sites on Sjp, which results in lower uptake of metal. The biosorbent surface was more negatively charged as the pH solution increased from 6.0 to 7.0. The functional groups of the Sjp were more deprotonated and thus available for the metal ions. Decrease in biosorption yield at higher pH ($\text{pH} > 7$) is not only related to the formation of soluble hydroxylated complexes of the metal ions, but also to the ionized nature of the Sjp of the biosorbent under the studied pH. Previous studies also reported that the maximum biosorption efficiency of Cu(II), Ni(II), Zn(II), and Pb(II) ions on biomass was observed at pH 6.0–7.0.

Effect of biosorbent dose

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for Cu(II), Ni(II), Zn(II) and pb(II) ions as a function of biosorbent dosage was investigated. The percentage of the metal biosorption steeply increases with the biosorbent loading up to 0.5 g/0.1 L. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction, whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. The maximum biosorption was attained at biosorbent dosage, 0.5 g/0.1 L. Therefore, the optimum biosorbent dosage was taken as 0.5 g/0.1 L for further experiments. This can be explained by when the biosorbent ratio is small, the active sites for binding metal ions on the surface of Sjp is less, so the biosorption efficiency is low. As the biosorbent dose increased, more active sites to bind metal ions, thus it results an increase in the biosorption efficiency until saturation.

Effect of contact time

The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact

time on the biosorption of Cu(II), Ni(II), Zn(II), and Pb(II) ions by Sjp was investigated. The biosorption of metal ions increased considerably until the contact time 120 min.

Effect of initial metal ion concentration

Cu(II), Ni(II), Zn(II), and Pb(II) ions biosorption by Sjp was studied in batch experiments using different initial metal concentrations of 5, 20, 40, 60, 80, 100 mg/L. The equilibrium uptake of the biosorbent was observed increasing gradually with an increasing initial concentration of metal ions. The increase of biosorption yield with the increase in metal ion concentration is probably due to higher interaction between the metal ions and sequestering sites of the biosorbent.

Biosorption isotherms

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Cu(II), Ni(II), Zn(II) and Pb(II) ions onto Sjp was modeled using four adsorption isotherms: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms.

Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as [20]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e, \quad (3)$$

where K_L is the Langmuir constant related to the energy of adsorption and q_{\max} is the maximum adsorption capacity (mg/g). Values of Langmuir parameters, q_{\max} and K_L were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e as shown in Fig. 3. Values of q_{\max} , K_L and regression coefficient R^2 are listed in Table 1. These values for Sjp biosorbent indicated that Langmuir model describes the biosorption phenomena as favorable. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L , expressed as in the following Eq. [4]:

$$R_L = \frac{1}{(1 + K_L C_o)}, \quad (4)$$

where K_L is the Langmuir constant and C_o is the maximum initial concentration of Cu(II), Ni(II), Zn(II) and Pb(II)

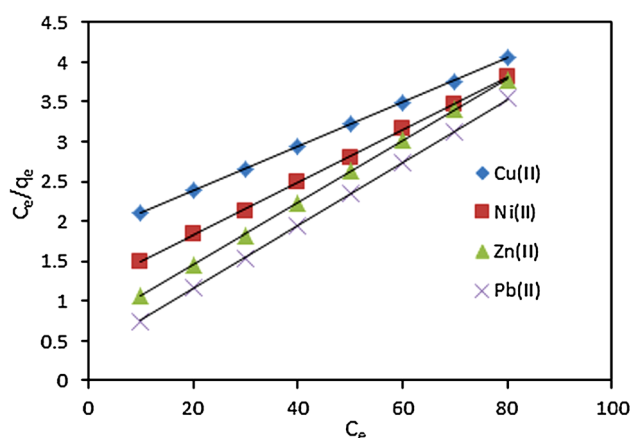


Fig. 3 Langmuir isotherm for metal ions onto Sjp

Table 1 Langmuir isotherm constants

Metal	q_e (mg/g)	K_L (L/mg)	R^2
Cu(II)	35.84	0.0149	0.9999
Ni(II)	30.30	0.0283	0.9997
Zn(II)	25.71	0.0579	0.9999
Pb(II)	25.13	0.1125	0.9998

ions. The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L for Cu(II), Zn(II), Ni(II) and Pb(II) ions biosorption by Sjp was found to be 0.31–0.86 for concentration of 5–100 mg/L of metal ions. They are in the range of 0–1 which indicates the favorable biosorption.

Freundlich isotherm

Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [21]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (5)$$

where K_F is the Freundlich constant related to the bonding energy. $1/n$ is the heterogeneity factor and n (g/L) is a

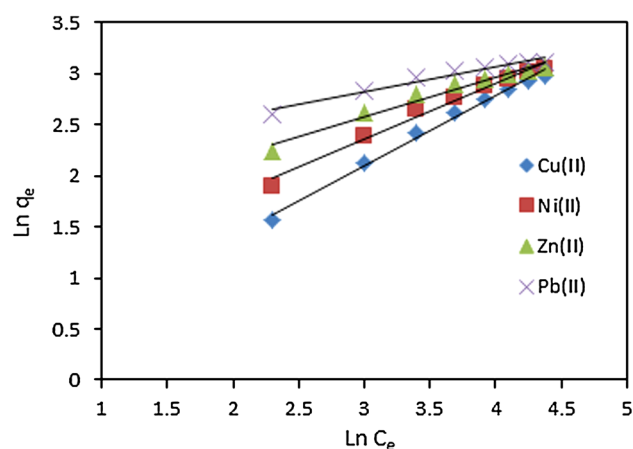


Fig. 4 Freundlich isotherm for metal ions onto Sjp

Table 2 Freundlich isotherm constants

Metal	n (g/L)	K_F (mg/g)	R^2
Cu(II)	1.47	1.06	0.9911
Ni(II)	2.62	4.19	0.9624
Zn(II)	1.83	2.04	0.9809
Pb(II)	4.08	8.06	0.9601

measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of $\ln q_e$ versus $\ln C_e$, Fig. 4. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.47, 2.62, 1.83, and 4.08 for Cu(II), Ni(II), Zn(II) and Pb(II) ions, respectively, Table 2. Since n lie between 1 and 10, this indicates the physical biosorption of metal ions onto Sjp. The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm models.

Temkin isotherm

Temkin isotherm equation [22] assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin isotherm has been used in the linear form as follows:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e. \quad (6)$$

A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants b_T and A_T from the slope and the

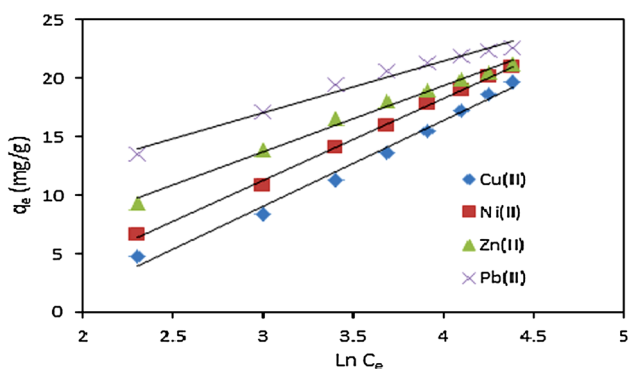


Fig. 5 Temkin isotherm for metal ions onto Sjp

Table 3 Temkin isotherm constants

Metal	b_T (J/mol)	K_T (L/g)	R^2
Cu(II)	353.88	0.16	0.9881
Ni(II)	370.47	0.25	0.9983
Zn(II)	459.11	0.56	0.9933
Pb(II)	590.43	0.42	0.9811

intercept, Fig. 5. Where A_T (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy and constant b_T is related to the heat of biosorption, Table 3.

Dubinin–Radushkevich (D–R) isotherm

The Dubinin–Radushkevich isotherm [23] describes the biosorption nature of the sorbate on the biosorbent and to calculate the mean free energy of biosorption.

$$\ln q_e = \ln q_{max} - \beta \varepsilon^2, \tag{7}$$

where ε can be correlated

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right), \tag{8}$$

where R is the gas constant (8.314 J/mol K). T is the absolute temperature (K). The D–R isotherm constants β and q_{max} were obtained from the slope and intercept of the plot of $\ln q_e$ against ε^2 , Fig. 6. The calculated values are listed in Table 4. The mean free energy of biosorption, E , defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution and calculated from the β value from:

$$E = \frac{1}{\sqrt{2\beta}}. \tag{9}$$

If the magnitude of E is between 8 and 16 kJ/mol, then the sorption process is supposed to proceed via chemisorption reaction, while for values of E is <8 kJ/mol, the

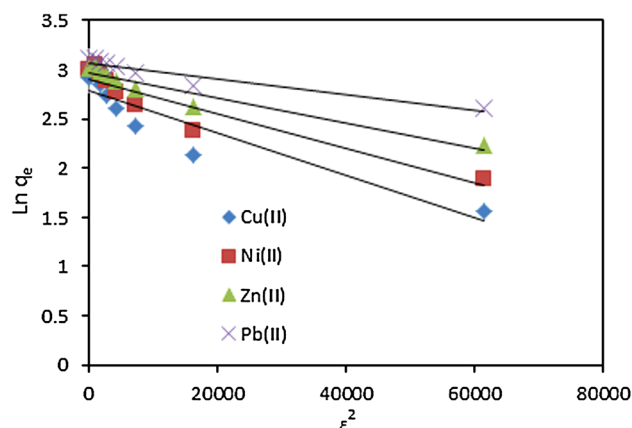


Fig. 6 D–R isotherm for metal ions onto Sjp

Table 4 Dubinin–Radushkevich (D–R) isotherm constants

Metal	β	q_{max} (mg/g)	R^2
Cu(II)	8.00E–06	21.62	0.9098
Ni(II)	1.00E–05	19.55	0.9152
Zn(II)	2.00E–05	18.33	0.8791
Pb(II)	2.00E–05	16.21	0.8516

sorption process is of physical nature. The value of E calculated from for the biosorption of metal ions by Sjp is 0.11 kJ/mol. This indicates that the biosorption process is of physical nature.

Biosorption kinetics

Parameters from two kinetic models, pseudo-first-order and pseudo-second-order, were fit to experimental data to examine the biosorption kinetics of Cu(II), Ni(II), Zn(II) and Pb(II) ions uptake onto Sjp.

Pseudo-first-order kinetics

The pseudo-first-order equation of Lagergren [24] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \tag{10}$$

where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg/g), and k_1 is the rate constant of pseudo-first-order sorption (1/min). After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, the integrated form of equation becomes:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t. \tag{11}$$

The equation applicable to experimental results generally differs from a true first-order equation in two ways: the

parameter $k_1(q_e - q_t)$ does not represent the number of available sites; and the parameter $\ln q_e$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\ln(q_e - q_t)$ against t , whereas in a true first-order sorption reaction $\log q_e$ should be equal to the intercept of $\ln(q_e - q_t)$ against t . To fit the equation to experimental data, the equilibrium sorption capacity, q_e , must be known. In many cases is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20–60 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, on treating q_e as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, to analyze the pseudo-first-order model kinetics. The pseudo-first-order rate constant can be obtained from the slope of plot between $\log(q_e - q_t)$ against time (t), Fig. 7. The calculated values and their corresponding linear regression correlation coefficient values are listed in Table 5. R^2 was found to be 0.926, which shows that this model cannot be applied to predict the adsorption kinetic model.

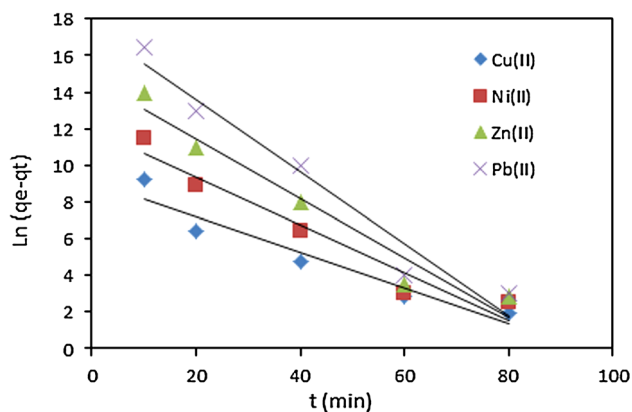


Fig. 7 Pseudo-first-order kinetics for metal ions onto Sjp

Table 5 Pseudo-first-order parameters

Metal ion	k_1 (1/min)	q_e (mg/g)	R^2
Cu(II)	0.458	8.18	0.9828
Ni(II)	0.383	7.93	0.9903
Zn(II)	0.307	7.55	0.8778
Pb(II)	0.232	6.71	0.9901

Pseudo-second-order kinetics

The pseudo-second-order rate expression, which has been applied for analyzing chemisorption kinetics rate, is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \quad (12)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg/g), and k is the rate constant of pseudo-second-order sorption, (g/mg min). For the boundary conditions to $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, the integrated form of Eq. (12) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (13)$$

where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t . If pseudo-second-order kinetics is applicable, the plot of t/q_t versus t of Eq. (13) should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot, Fig. 8. The pseudo-second-order rate constant k_2 , the calculated q_e value and the corresponding linear regression correlation coefficient value are given in Table 6. At all initial metal concentrations, the linear regression correlation coefficient R^2 values were higher. The higher values confirm that the adsorption data are well represented by pseudo-second-order kinetics.

Thermodynamic parameters

To describe thermodynamic behavior of the biosorption of Cu(II), Ni(II), Zn(II) and Pb(II) ions onto Sjp, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_D, \quad (14)$$

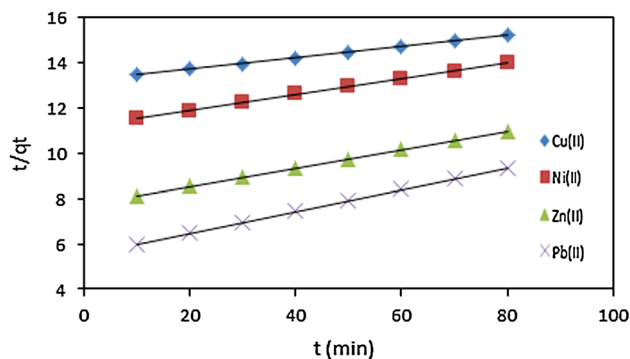


Fig. 8 Pseudo-second-order kinetics for metal ions onto Sjp

Table 6 Pseudo-second-order parameters

Metal ion	k_2 (g/mg min)	q_e (mg/g)	R^2
Cu(II)	5.00E-05	39.53	0.9999
Ni(II)	1.10E-04	28.49	0.9999
Zn(II)	2.10E-04	24.75	0.9998
Pb(II)	4.20E-04	20.75	0.9999

Table 7 Thermodynamic parameters of metal ions

T/K	K_D	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
Cu(II)				
293	5.45	-4.13	14.55	63.77
303	6.74	-4.81		
313	7.98	-4.23		
Ni(II)				
293	4.33	-3.57	17.34	71.41
303	5.59	-4.34		
313	6.82	-4.99		
Zn(II)				
293	3.09	-2.75	21.45	82.69
303	4.28	-3.66		
313	5.42	-4.39		
Pb(II)				
293	1.74	-1.35	32.58	115.84
303	2.72	-2.52		
313	4.09	-3.67		

where R is the universal gas constant (8.314 J/mol K). T (K) is the temperature. K_D is the distribution coefficient. The thermodynamic equilibrium constant (K_D) of the adsorption is defined as:

$$K_D = \frac{C_a}{C_e}, \quad (15)$$

where C_a is mg of adsorbate adsorbed per liter and C_e is the equilibrium concentration of solution, mg/L. According to thermodynamics, the Gibb's free energy change is also related to the enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the Gibbs–Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (16)$$

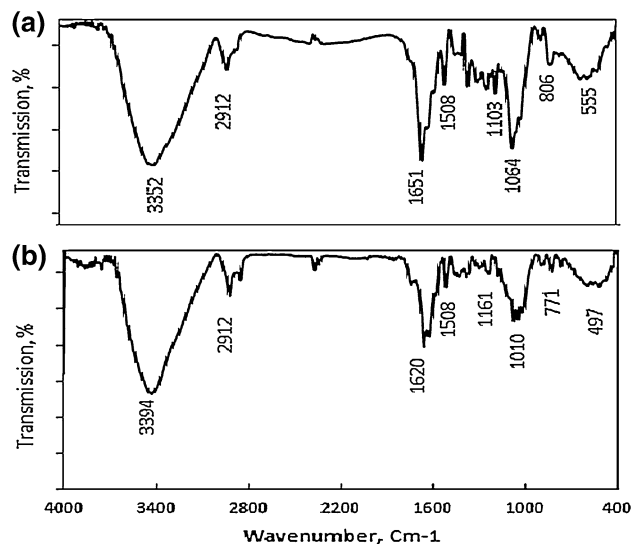
Equations (15) and (16) can be written as:

$$-RT \ln K_D = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

or

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (18)$$

According to Eq. 18, the values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the

**Fig. 9** FT-IR spectra of **a** Sjp, **b** metal-loaded Sjp

slope and intercept of the plot of $\ln K_D$ vs. $1/T$. The calculated values of thermodynamic parameters ΔG° , ΔH° and ΔS° for the biosorption of Cu(II), Ni(II), Zn(II) and Pb(II) ions onto Sjp are reported in Table 7. A negative value of the free energy (ΔG°) indicated the spontaneous nature of the biosorption process. It was also noted that the change in free energy, increases with rise in temperature. This could be possibly because of activation of more sites on the surface of Sjp with increase in temperature or that the energy of biosorption sites has an exponential distribution and a higher temperature enables the energy barrier of biosorption to be overcome. For physical adsorption, the free energy change (ΔG°) ranges from (-20 to 0) kJ/mol and for chemical adsorption it ranges between (-80 and -400) kJ/mol. The ΔG° for Ni(II) and Zn(II) biosorption onto Sjp was in the range of (-2.97 to -5.49) kJ/mol and so the biosorption was predominantly physical biosorption. A positive value of ΔS° as 69.85–80.24 J/mol K showed increased randomness at solid solution interface during the adsorption of Cu(II), Ni(II), Zn(II) and Pb(II) ions onto Sjp.

FT-IR spectral analysis

An untreated Sjp sample with 20 mg/L Cu(II), Ni(II), Zn(II), and Pb(II) ions solution was analyzed by FT-IR. The Sjp displays a number of absorption peaks, reflecting its complex nature (Fig. 9a). The band at 3,352 cm^{-1} could be ascribed to the stretching absorption band of amino (-NH) and hydroxyl (-OH) groups; this band shifted to 3,394 cm^{-1} (Fig. 9b) in metal-loaded Sjp indicating participation of these functionalities in metal binding. The band at 2,912 cm^{-1} could be assigned to -CH stretching



Table 8 Maximum biosorption capacity, q_e (mg/g) by different biosorbents

Biosorbent	The metal uptake capacity, q_e (mg/g)				Refs.
	Cu(II)	Ni(II)	Zn(II)	Pb(II)	
Rice husk		8.86			[25]
<i>M. oleifera</i> bark		26.84			[12]
Eucalyptus bark			1.688		[11]
Coconut shell		3.68	1.56		[26]
<i>Tectona grandis</i> L.			16.42		[6]
<i>Ceratonia siliqua</i> bark	21.65	42.19	31.35		[18]
Peanut shell	25.39				[27]
orange peel	50.25				[28]
Groundnut hull				31.54	[29]
Banana peel				31.25	[30]
<i>Robinia pseudoacacia</i> pods	35.84	30.3	25.71	25.13	This work

vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ functional groups. The adsorption bands at $1,651\text{ cm}^{-1}$ in native Sjp spectra were assigned to the carboxyl group stretching vibration, which shifted to $1,620\text{ cm}^{-1}$ in metal-loaded Sjp, Fig. 9b. Peaks at $1,508$ – $1,103\text{ cm}^{-1}$ are indicative of the N–H stretching of the primary and secondary amides, and the presence of amide (III) or suffamide band, respectively [12]. The strong bands at $1,064$ and $1,010\text{ cm}^{-1}$ can be assigned to the C–O stretching vibrations of alcohols. Additional peak at 555 cm^{-1} can be assigned to bending modes of aromatic compounds, Fig. 9a was shifted to 497 cm^{-1} , Fig. 9b confirms the participation of this group in metal ion bindings. FT-IR study of Sjp powder indicates that the carboxyl ($-\text{C}=\text{O}$), hydroxyl ($-\text{OH}$) and amine ($-\text{NH}$) groups are mainly involved for binding Cu(II), Ni(II), Zn(II) and Pb(II) ions onto Sjp.

Comparison of *Sophora japonica* pods powder with other biosorbents

A comparative of the maximum biosorption capacity, q_{max} of Sjp with those of some other biosorbents reported in literature is given in Table 8. Differences in q_{max} are due to the nature and properties of each biosorbent such as surface area and the main functional groups in the structure of the biosorbent. A comparison with other adsorbents indicated a high metal ion biosorption capacity of Sjp.

Conclusions

The experimental investigation concluded that Sjp could be used as potential biosorbent for removal of Cu(II), Ni(II), Zn(II) and Pb(II) ions from aqueous solutions. The batch biosorption parameters: pH of solution, biosorbent dose, contact time, initial metal concentration and temperature were found to be effective on the biosorption process. The

kinetic studies revealed that the biosorption process followed the pseudo-second-order kinetic model. Thermodynamic parameters ΔG° , ΔH° and ΔS° showed the endothermic and spontaneous nature of the biosorption of Cu(II), Ni(II), Zn(II) and Pb(II) ions onto *Sophora japonica* pods. Langmuir model showed the best fit for the experimental data. The maximum biosorption capacity of Cu(II), Ni(II), Zn(II) and Pb(II) ions onto Sjp at pH 6.0–7.0 and $30\text{ }^\circ\text{C}$ is 35.84, 30.3, 25.71, and 25.13 mg/g, respectively. Compared to various biosorbents reported in the literature, the Sjp showed good promise for its use in wastewater

Acknowledgments Authors are thankful for Royal Scientific Society and Princess Sumaya University for Technology, El Hassan Science City, Jordan for providing the necessary facilities to carry out this work.

Conflict of interest The authors declare that they have no competing interests.

Author contributions This work was carried out in collaboration between all authors. Author AMA designed the study, wrote the protocol, and the first draft of the manuscript. Author RAA contributed in characterization and analysis. Author MWA carried out the experiments and analysis. All authors read and approved the final manuscript.

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