



## Competitive effect of Cu(II) and Zn(II) on the biosorption of lead(II) by *Myriophyllum spicatum*

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### ABSTRACT

Batch experiments were conducted to assess the effects of Cu(II) and Zn(II) on the biosorption of Pb(II) ions by fresh tissues of *Myriophyllum spicatum*. The biosorption of Pb(II) was examined for single, binary and ternary solutions at different initial concentrations and different pH values. The experimental results showed that the biosorption capacity increased with increasing pH from 2.0 to 6.0. Both Cu(II) and Zn(II) ions were found to have an adverse effect on the biosorption of Pb(II). The biosorption equilibrium data for single-metal solution were fitted to three isotherm models: Langmuir, Freundlich and Sips, and the Sips isotherm model gave the best fit for the experimental data. The maximum biosorption of Pb(II) in Pb–Cu binary system decreased with increasing concentration of copper ions, and the biosorption equilibrium data for the binary metal solution fitted the Langmuir competitive model well. Comparison between biosorption of Pb(II) and Cu(II) by *M. spicatum* in the binary solution could lead to the conclusion that the biosorbent (*M. spicatum*) has no preference of Pb(II) over Cu(II). Fourier transform infrared (FT-IR) spectroscopy was used to characterize the interaction between *M. spicatum* and Pb(II) ions. The results revealed that the carboxyl, hydroxyl and carbonyl groups are the main binding sites for Pb(II).

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### 1. Introduction

The contamination of the aquatic systems with toxic heavy metal ions is a problem of global concern. In addition to their toxic effects even at low concentrations, heavy metals can accumulate along the food chain which leads to serious ecological and health hazards as a result of their solubility and mobility. Lead, for example, has both acute and chronic effects in humans. It may cause anemia, headache, chills, diarrhea and reduction in hemoglobin formation. Lead poisoning causes severe damage to kidneys, nervous system, reproductive system, liver and brain [1].

Over the past decade there has been increasing concern over the development of methods for recovery or treatment of heavy metals to meet the changing environmental regulations worldwide. The most commonly used techniques for removing heavy metals from wastewater include coagulation–precipitation, ion exchange, electrolytic extraction, filtration, complexation, reverse osmosis, evaporation and sorption. However, many of these techniques have certain shortcomings including high operational cost, high energy requirements, incomplete removal and generating very large amount of sludge that requires disposal. For these reasons,

there is a need to develop low-cost processes where metal ions can be removed economically.

Biosorption is the most widely used and low-cost alternative technology for heavy metal removal. In recent years there has been considerable interest in the use of sorbent materials, particularly biosorbents [2] such as wheat straw [3], sonicated activated sludge [4], tobacco dust [5], wheat shell [6], stalk waste [7], bael leaves [8], agricultural by-products [9] and microbes [10]. Sorption by biomass is now recognized as an alternative method for the treatment of wastewaters containing heavy metals [11–15].

It has long been recognized that aquatic plants, both living and dead, are heavy metal accumulators and, therefore, the use of aquatic plants for the removal of heavy metals from wastewater has gained a lot of attentions [16]. Some submerged aquatic plants are invasive and can be seen generally in aquatic environments like streams, littoral zones of the lakes, drainage systems and wetlands. In China, agricultural areas are very large and drainage channel systems are common around the fields for irrigation. *Myriophyllum spicatum* is a very common species in these drainage systems and can be found throughout the year. Metal accumulation in *M. spicatum* [17,18] indicated that the species may be considered as useful vehicles for the removal and recovery of heavy metal ions from aqueous solutions.

Under most conditions, wastewater streams contain not one but several kinds of metal ions. For instance, lead(II) and copper(II), both of which have been reported to be serious environmental pollutants are frequently existed in wastewaters from chemical,

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plumbing, fertilizer and battery manufacturing industries [19]. Although much research information is available on the single-metal biosorption, relatively less attention has been paid to the biosorption of multi-metal-ion systems [20–26], and no general trend 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 lead ion from aqueous solution by using *M. spicatum* was studied by a set of experiments at various conditions, including contact time, solution pH, and effect of copper(II) and zinc(II) ions. The prime objective of this study was (i) to examine the competitive interference effect of metal ions on the biosorption of lead(II) by *M. spicatum* and (ii) to identify the main functional groups implicated in the interaction between *M. spicatum* and lead(II) by using Fourier transform infrared (FT-IR) spectroscopy.

## 2. Materials and methods

### 2.1. Preparation of the plant biomass and chemicals

Submerged aquatic plant biomass (*M. spicatum*) was collected locally, and was cultivated in a greenhouse for two weeks before experiments. The apical part was cut out from the plant to obtain fresh and uniform surface area of the plant for sorption experiments. The selected plant biomass was washed with diluted HCl solution (3%) and then deionized water for three times in the laboratory before used.

Stocks of 1000 mg/L metal solutions were prepared using  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (analytical grade) in deionized water. Nitrate was chosen as the counter ion because of its low tendency to form metal complexes. The solutions were then diluted to the desired concentrations and analyzed.

### 2.2. Fourier transform infrared spectroscopy

FT-IR spectroscopy was used to detect vibration frequency changes in *M. spicatum* biomass before and after Pb(II) biosorption. The spectra within the range of  $4000\text{--}400\text{ cm}^{-1}$  were collected by a PerkinElmer spectrometer (Nicolet IS10, USA). The plant biomass was oven-dried at  $75^\circ\text{C}$  for 72 h. Specimens were first mixed with KBr and then ground in an agate mortar at an approximate ratio of 1/200 for the preparation of pellets. The resulting mixture was pressed with a pressure of 10 ton for 2 min. The background was automatically subtracted from the sample spectra.

### 2.3. Batch experiments for single-ion situation

Experiments were carried out for single-metal solution, Pb(II). For the fresh tissue of *M. spicatum*, a known amount (about 0.18 g, dry weight) of plant biomass was mixed with 100 mL of metal solution in a 200 mL flask and placed on an orbital shaker (200 rpm) at  $25 \pm 1^\circ\text{C}$ . The batch sorption studies were conducted as follows:

Sorption kinetics study: Samples with initial Pb(II) concentration of 100 mg/L were taken at different time intervals, from 5 to 150 min. The initial pH was about 5.0.

The effect of pH: Each solution at initial Pb(II) concentrations of 100 mg/L with *M. spicatum* biomass (about 0.18 g, dry weight) was shaken for 120 min. The initial pH value was adjusted to a desired value, from 2.0 to 6.0, with 0.1 M  $\text{HNO}_3$  or 0.1 M NaOH (analytical grade) using a precision pH meter (PHS-3C) before the addition of plant biomass.

Sorption isotherms experiment: Each solution (100 mL) at initial lead(II) concentrations of 10, 50, 100, 150, 200 and 250 mg/L with

*M. spicatum* biomass (about 0.18 g, dry weight) was shaken for 120 min.

Clear solutions were then separated from the biomass by using  $0.45\ \mu\text{m}$  membrane filters and analyzed using an atomic adsorption spectrophotometer (Model SolaarM, Thermo Electron, USA).

### 2.4. Effect of competitive interference

Isotherm experiments were carried out at room temperature ( $25 \pm 1^\circ\text{C}$ ) with initial pH of 5.0 for five metal solutions: Pb(II) alone; Pb(II) with a constant concentration of Zn(II), 30 mg/L; Pb(II) with a constant concentration of Cu(II), 30 mg/L; Pb(II) with constant concentrations of both Cu(II) and Zn(II), 30 mg/L and Pb(II) with variable concentration of Cu(II), 10–250 mg/L. In all cases, the concentration of Pb(II) was varied from 10 to 250 mg/L and the samples were placed on the shaker for a period of 120 min.

In order to characterize the interference by the Langmuir competitive model, another experiment was carried out at room temperature ( $25 \pm 1^\circ\text{C}$ ) with initial pH of 5.0 for three metal solutions: Pb(II) with varies concentration of Cu(II), 10, 30 and 50 mg/L, respectively. In all cases, the Pb(II) concentration was varied from 10 to 250 mg/L and the samples were placed on the shaker for a period of 120 min.

### 2.5. Preferring sorption study

A 100 mL solution containing 100 mg/L of one of the metals ions, Cu(II) or Pb(II), with about 0.18 g (dry weight) fresh tissue of *M. spicatum* was placed on the shaker for 120 min. The solution was then given enough time (120 min) to settle, after which a 50 mL of the clear solution was removed and replaced with 50 mL of 200 mg/L of the other metal (the second metal ion). The new solution mixture was shaken for another 120 min and clear solutions were then taken for AAS analysis for both ions.

### 2.6. Analysis of experimental data

Biosorption values were calculated from the changes in solution concentration using the equation:

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

The percent removal (%) of metal ions was calculated using the following equation:

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

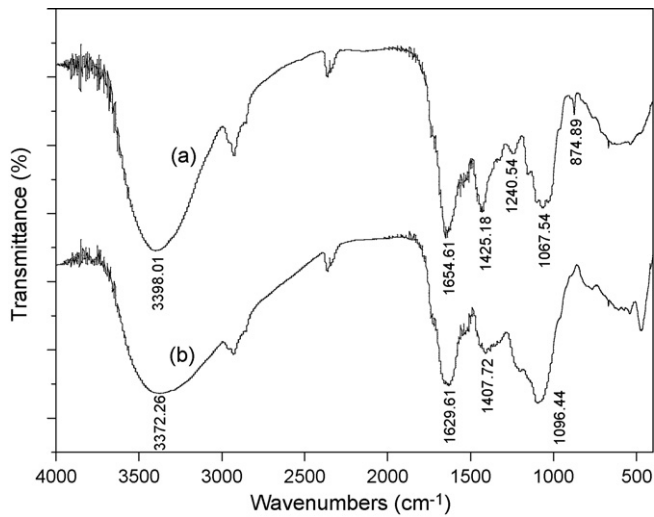
where  $q$  is the sorption values (mg/g),  $C_i$  and  $C_f$  the initial and final concentrations (mg/L),  $V$  the volume of solution (L) and  $W$  the dry weight of biosorbent (g).

All experiments were done in triplicate and the results presented as mean values with standard deviations. Control experiments were performed for metal ions to measure any sorption onto the glassware. Neither precipitation nor sorption onto the wall of the flasks was observed.

## 3. Results and discussion

### 3.1. FT-IR spectrum analysis

FT-IR was used to identify *M. spicatum*'s surface functional groups responsible for binding Pb(II). The FT-IR spectra of Pb(II) unloaded and loaded forms of the biosorbent in the range of  $4000\text{--}400\text{ cm}^{-1}$  were taken and presented in Fig. 1. It could be seen that the FT-IR spectra displays a number of absorption peaks, indicating the complex nature of the biomass examined [27].



**Fig. 1.** Fourier transform infrared absorption spectrum of *M. spicatum*: (a) native and (b) Pb(II) treated (Pb: 100 mg/L).

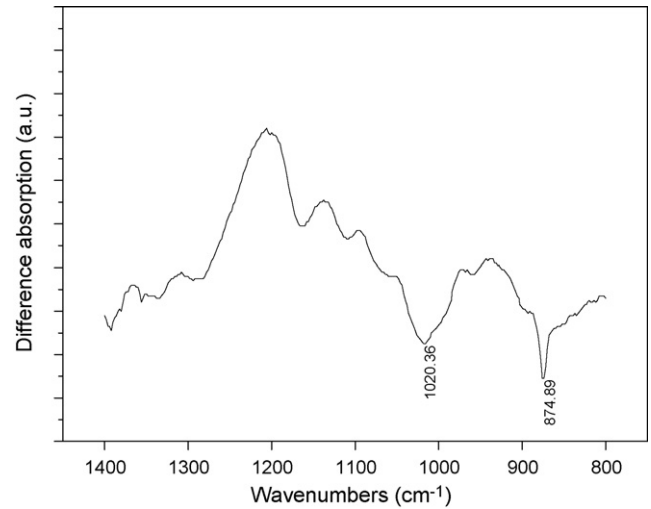
The FT-IR spectra of unloaded biomass showed sharp absorption at  $3398\text{ cm}^{-1}$  (indicative of  $-\text{OH}$  and  $-\text{NH}_2$  groups),  $2926\text{ cm}^{-1}$  (indicative of  $\text{C}-\text{H}$  group). The absorption bands at  $1654\text{ cm}^{-1}$  (mainly  $\text{C}=\text{O}$  stretch) indicative of the stretching band of the carbonyl double bond ( $\text{C}=\text{O}$  stretching band). The bands at  $1425\text{ cm}^{-1}$  can be attributed to carboxylate ions. The strong band around  $1100\text{--}1000\text{ cm}^{-1}$  is due to the  $\text{C}-\text{OH}$  bond, which is a characteristic peak for polysaccharides [28].

The absorption spectrum of Pb-loaded biomass was compared with that of the pristine biomass. The FT-IR spectrum for Pb-loaded biosorbent showed the wave number and intensity of some peaks were shifted or substantially lower than those before biosorption, suggesting the functional groups play a significant role in the binding of lead. Fig. 1 showed that the Pb-loaded *M. spicatum* exhibited spectra with clear shifts of the carboxyl (bands at  $1407.72\text{ cm}^{-1}$ ), carbonyl (bands at  $1629.61\text{ cm}^{-1}$ ) and hydroxyl (bands at  $3372.26\text{ cm}^{-1}$ ) stretching band to lower frequency. This shift is typical for the complexation of the groups by coordination with metal ions [28].

In order to further validate our spectroscopic observations concerning the changes occurred after the treatment of plant biomass with lead, we have calculated difference IR spectra between 800 and  $1400\text{ cm}^{-1}$  by the method suggested by Merroun [29] (FT-IR spectrum of untreated plant biomass minus spectrum of biomass exposed to lead). The results shown in Fig. 2 indicated the presence of two absorption peaks. The peaks at  $1020.36$  and  $874.89\text{ cm}^{-1}$  are attributed to the  $\text{C}-\text{OH}$  stretching and aromatic  $\text{C}-\text{H}$  bending vibrations, respectively. On the basis of variations of the bands, it was reasonable to assume that the Pb(II) ions biosorption onto *M. spicatum* should be chelated with the carboxyl, hydroxyl and carbonyl groups. In addition, the disappearance of the band at  $874.89\text{ cm}^{-1}$  indicated that there was also clear possibly belonging to aromatic protons of the biosorbent indicating possibly the involvement of aromatic fatty acids in the biosorption of Pb(II). Similar FT-IR findings had been reported for the biosorption of lead(II) onto green algae [30] and chestnut shell [31].

### 3.2. Biosorption kinetics for single-ion solution

Kinetic studies are necessary to determine the equilibration time for biosorption. Batch experiments have been carried out to determine the rate of lead biosorption by *M. spicatum*. It can be observed from Fig. 3 that the sorption rate is very fast initially, and



**Fig. 2.** FT-IR spectra of *M. spicatum* unexposed to lead minus spectra of exposed *M. spicatum* (difference IR spectra).

about 66% of total lead is removed within 10 min. The biosorption capacity reaches 85% of the equilibrium biosorption capacity within 10 min and the biosorption of lead reaches plateau value within 20 min. In order to ensure sorption equilibrium, contact time for lead biosorption was chosen at 120 min in this study.

The biosorption kinetics was analyzed by applying the pseudo-second order Lagergren rate equation, where the lead binding capacity was assumed to be proportional to the number of active sites occupied on the sorbent. The equation was given by Ho and McKay [32]:

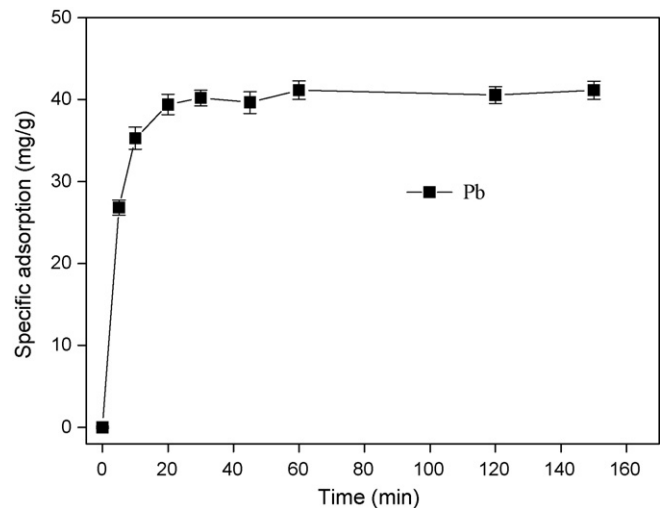
$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (3)$$

where  $k$  is the equilibrium rate constant of pseudo-second order sorption kinetics ( $\text{g}/\text{mg min}$ ),  $q_e$  the equilibrium biosorption ( $\text{mg}/\text{g}$ ),  $q_t$  the amount of sorbate on sorbent at time  $t$  ( $\text{mg}/\text{g}$ ).

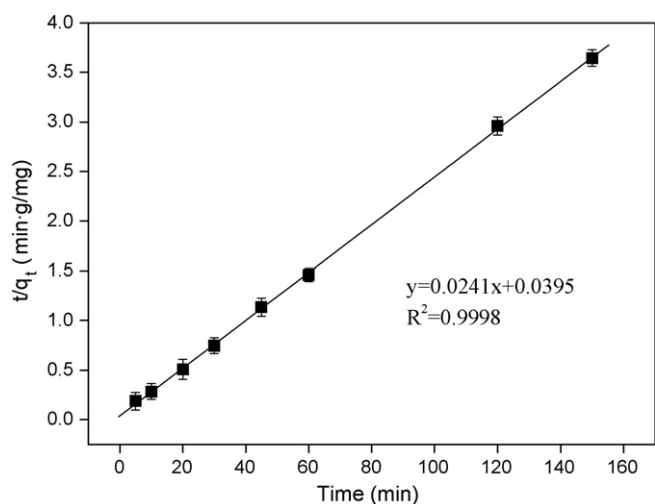
Eq. (3) can be integrated and rearranged to give [33]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k} \quad (4)$$

where the term  $q_e^2 k$  represents the initial sorption rate.



**Fig. 3.** The effect of contact time on the biosorption of Pb(II) onto *M. spicatum*. (Temperature =  $25^\circ\text{C}$ ; pH 5.0; initial concentration =  $100\text{ mg}/\text{L}$ ; dry weight of biomass =  $0.18\text{ g}$ ; and agitation velocity =  $200\text{ rpm}$ .)



**Fig. 4.** Pseudo-second order kinetics of the biosorption of Pb(II) onto *M. spicatum*. (Temperature = 25 °C; pH 5.0; initial concentration = 100 mg/L; dry weight of biomass = 0.18 g; and agitation velocity = 200 rpm.)

A plot of  $t/q_t$  versus time was shown in Fig. 4. It was obvious that the plot was a near perfect straight line with correlation coefficient ( $R^2$ ) of 0.9998. This clearly indicated that biosorption of lead by *M. spicatum* followed the pseudo-second order kinetics equation. The values of  $q_e$  (41.49 mg/g) and  $k$  (0.015 g/mg min) were calculated from the slope and intercept of the straight line. The value of the calculated  $q_e$  was in excellent agreement with that obtained experimentally (41.14 mg/g).

### 3.3. Effect of initial pH on Pb(II) biosorption for single-ion solution

The pH of the metal solution influences significantly the biosorption process. Hydrogen ion affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the sorbate during the reaction. Changes in solution pH can alter the chemical nature of the functional groups on *M. spicatum* and then the metal sorption capacity of the sorbent. Table 1 displayed lead biosorption onto *M. spicatum* as a function of solution pH. The removal efficiency of lead ions was 37% at a solution pH of 2.0, and it increased when solution pH increased from 2.0 to 5.0. At pH 5.0, the removal rate was 76%. It showed that the sorption amount of lead rose markedly with increasing solution pH and that the sorption process was pH-dependent. The rise in lead biosorption value with increasing pH can be explained by the presence of a strong relation between biosorption and the number of negatively charged sites, which is highly dependent on the dissociation of functional groups. It is believed that hydrogen ions compete with lead ions for the same sorption sites at low pH as proposed by many researchers [34,35]. At low pH values, protons occupy most of the biosorption sites on the biosorbent surface and less lead ions could be sorbed because of electric repulsion with protons on biosorbent. When the pH values increased, biosorbent surfaces were more negatively charged and the biosorption of metal ions (positive charge) increased. It can be observed from Table 1 that the optimum pH range for lead binding is  $\text{pH} \geq 5.0$ . Although the binding of Pb(II) was slightly higher at higher pH, pH 5.0 was used in the following studies because

**Table 1**  
The effect of solution pH on Pb(II) biosorption onto *M. spicatum*.

Initial pH	2.0	3.0	4.0	5.0	6.0
Specific sorption (mg/g)	19.96 ± 0.85	35.82 ± 0.90	39.58 ± 0.76	41.21 ± 0.87	41.97 ± 0.54

**Table 2**  
Isotherm constants for lead biosorption onto *M. spicatum*.

Isotherm	Parameter		$R^2$
Langmuir	$B$ (L/mg)	0.12	0.989
	$q_m$ (mg/g)	55.12	
Freundlich	$a_F$	13.21	0.936
	$b_F$	0.29	
Sips	$a_{LF}$	0.11	0.994
	$K_{LF}$	10.40	
	$n_{LF}$	0.79	

wastewater containing heavy metals usually shows weak acidity and lead ion hydrolyzes at higher pH.

### 3.4. Biosorption isotherms for single-ion situation

The most appropriate method for assessing biosorbent capacity is the derivation of a whole sorption isotherm. The sorption data can be analyzed using well-known equilibrium isotherms to obtain some insight into the surface properties and affinity of the sorbent as well as the sorption mechanism. Three of the most common isotherm models (Langmuir, Freundlich and Sips isotherm model) were used to analyze the experimental results.

The Langmuir equation is based on the assumption that all sites possess equal affinity for the sorbate and a monolayer is formed when the solid surface reaches saturation [36]. Langmuir equation can be described as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (5)$$

where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  the amount of metal ions sorbed (mg/g),  $q_m$  is  $q_e$  for a complete monolayer (mg/g),  $b$  is a sorption equilibrium constant (L/mg).

The Freundlich model is an empirical equation based on sorption on a heterogenous surface. It is given as:

$$q_e = a_F C_e^{b_F} \quad (6)$$

where  $a_F$  and  $b_F$  are isotherm constants, respectively.

Combining Langmuir and Freundlich isotherms gives the Sips isotherm. At low sorbate concentration, the Sips isotherm assumes the form of the Freundlich model, while at high concentration, it predicts a constant, monolayer sorption behavior similar to that of the Langmuir isotherm [37]. It can be written in the Langmuir–Freundlich forms as follows:

$$q_e = \frac{K_{LF} C_e^{n_{LF}}}{1 + (a_{LF} C_e)^{n_{LF}}} \quad (7)$$

where  $K_{LF}$ ,  $n_{LF}$ , and  $a_{LF}$  are isotherm constants, respectively.

Experimental data for the single-metal solutions were fitted to the three isotherm models, and all parameters were estimated by non-linear regression (Table 2). The value of correlation coefficient ( $R^2 = 0.989$ ) obtained for Langmuir isotherm strongly indicates that the biosorption of Pb(II) onto *M. spicatum* follows monolayer coverage of Pb(II) on the biomass surface and that the interaction between two lead molecules is negligible. The monolayer saturation capacity ( $q_m$ ) is 55.12 mg/g (dry weight). The Sips isotherm gave the best fit for the experimental data with correlation coefficient ( $R^2$ ) of 0.994. The Langmuir and Sips equations represent the better fit of the experimental data than the Freundlich equation.



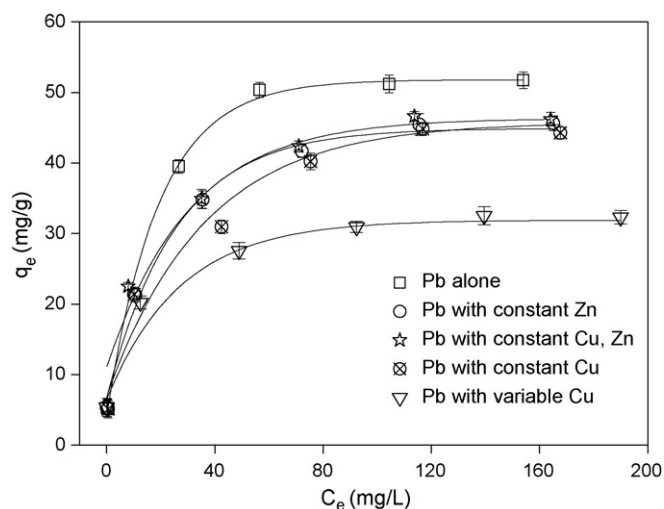


Fig. 5. Equilibrium isotherm data for Pb(II) in single, binary and ternary solutions. (Temperature = 25 °C; pH 5.0; contact time = 120 min; dry weight of biomass = 0.18 g; and agitation velocity = 200 rpm.)

### 3.5. Effect of interference by metal ions

Interference by other ions may have a detrimental effect on the biosorption of lead by *M. spicatum*. One of the major objectives of this work is to examine whether competition among metal ions can hinder the metal binding ability of *M. spicatum*. The experimental data are shown in terms of sorption isotherms in Fig. 5. It is clear from the figure that both Cu(II) and Zn(II) ions have negative effect on the biosorption of Pb(II). In the single-ion situation, the maximum biosorption obtained at initial concentration (250 mg/L) of Pb(II) ions was found to be  $51.72 \pm 1.33$  mg/g, while the biosorption obtained in the binary metal solutions at the same initial concentration of Pb(II) ions and biosorption conditions, was found to be  $46.18 \pm 1.40$  mg/g when concentration of Cu(II) ions was 30 mg/L. The effect of Zn(II) ions on Pb(II) biosorption by *M. spicatum* was similar to that of Cu(II) ions (Fig. 5). The maximum Pb(II) biosorption obtained at the same conditions was found to be  $45.64 \pm 0.68$  mg/g when concentration of Zn(II) ions was 30 mg/L. The competition posed by copper or zinc ions is apparent in binary solutions. However, the biosorption of Pb(II) ions onto *M. spicatum* in ternary solution seems to be the same to that in the binary solutions. It may be attributed to the presence of Zn(II), which competes with copper instead of lead. Copper and zinc are very similar in molecular mass (63.57 and 65.38 g/mol), ionic radius (73 and 74 pm) and electronegativity (1.90 and 1.65 Pauling). These similarities between the two metal ions enhance their competition for the same active sites on the cell walls and consequently lessen the competitive effect of each other on lead. It is a well-known fact that a fixed quantity of biosorbents (*M. spicatum*) could only offer a finite number of surface binding sites which would be expected to be saturated by the competing metal ions, especially at relatively high concentration of them. In addition, it was noteworthy that the phenomenon might not only result from the saturation of *M. spicatum* biomass, but also be partly related to the ability of these metal ions to compete for the biosorption sites [25].

The solubility of a metal is an essential property to enable the metal ion to penetrate into the porous structure of *M. spicatum*. Although many species ( $\text{PbOH}^+$ ,  $\text{Pb}_2\text{OH}^{3+}$ ,  $\text{Pb}(\text{OH})_4^{2-}$ ,  $\text{Pb}(\text{OH})_3^-$  and  $\text{Pb}^{2+}$ ) can be viewed as potential sorbates in the biosorption of lead ions from ternary solutions (Pb/Cu/Zn), the data presented in this study suggest that, under experimental conditions ( $\text{pH}_{\text{eq}} < 5.9$ ) (see Fig. 6), the species responsible for the removal of lead ions is the predominant one in the species distribution, namely the Pb(II)

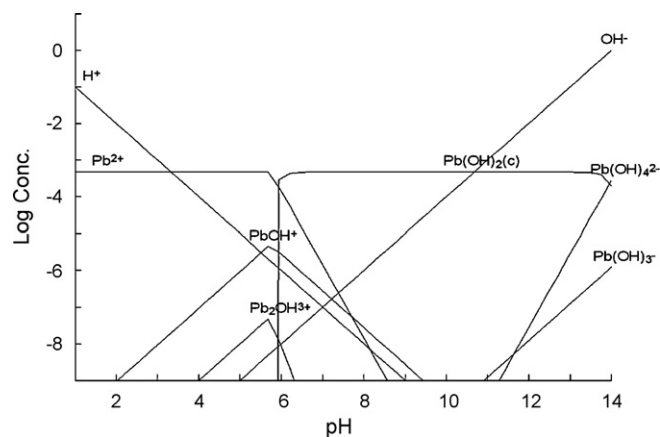


Fig. 6. Concentration diagram of lead species in ternary metal solutions. (Concentration of lead = 100 mg/L; concentration of copper = 30 mg/L; and concentration of zinc = 30 mg/L.)

ions. Thus, sorption can be explained by elucidating the mechanism whereby the Pb(II) ions are accommodated on the *M. spicatum* surface. The negative effect of the presence of Cu(II) and Zn(II) on the biosorption of lead by the plant biomass is due to the competitive effect of these ions, but not to the low solubility of lead in these ternary metal solutions.

It is obvious from Fig. 5 that for a binary solution with variable Cu(II) concentrations, the lead binding capacity of *M. spicatum* decreased to almost two third as compared to that of a solution with a constant Cu(II) concentrations. This aspect was examined further by conducted a set of experiments for a binary solution containing constant Pb(II) concentration (100 mg/L) and variable concentrations (10–150 mg/L) of Cu(II) or Zn(II). The results again indicated that although Cu(II) or Zn(II) ions had an adverse effect on the biosorption of Pb(II) in binary solutions, the effect of Cu(II) is much more than that of Zn(II) (Fig. 7).

It is generally complicated to find a common rule to identify how metal properties affect competitive sorption. The factors that affect the binding of metal ions on materials largely depend on physicochemical properties of metals. It has been reported that in general, the greater the atomic weight, electronegativity, electrode potential and ionic size, the greater will be the affinity for sorption [38,39]. Thus, in bimetallic or trimetallic combination, sorption of

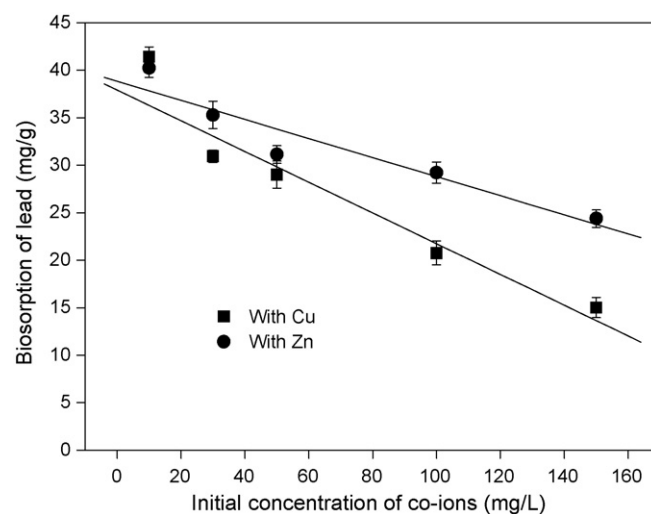
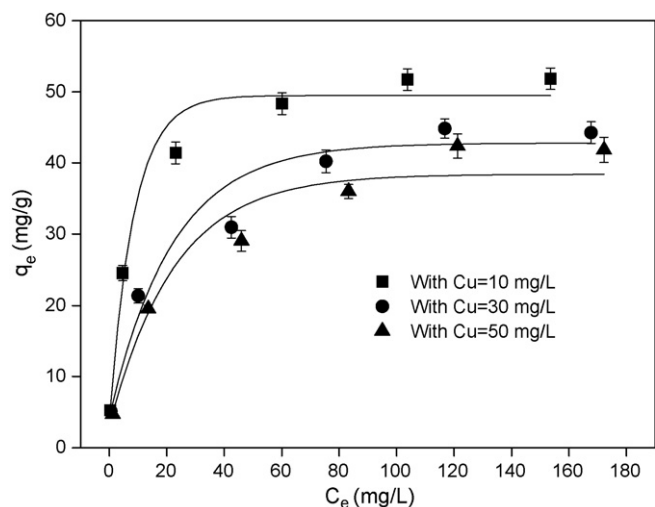


Fig. 7. Effect of other ions on the biosorption of Pb(II) in a binary solution. (Initial Pb(II) concentration = 100 mg/L; temperature = 25 °C; pH 5.0; contact time = 120 min; dry weight of biomass = 0.18 g; and agitation velocity = 200 rpm.)



**Fig. 8.** Equilibrium isotherm data for Pb(II) in Pb–Cu binary solutions. (Temperature = 25 °C; pH 5.0; contact time = 120 min; dry weight of biomass = 0.18 g; and agitation velocity = 200 rpm.)

metals is a competitive process between ions in solution and those sorbed onto the biomass surface.

### 3.6. Langmuir competitive model

In order to take into account the interference of copper ions on lead biosorption by *M. spicatum*, sorption isotherm data for Pb(II) in Pb–Cu binary solutions are presented in Fig. 8. It is shown that the lead biosorption capacity for *M. spicatum* decreased with an increasing concentration of copper ions.

A simple “one-site” Langmuir competitive model was tried to predict the sorption isotherm in binary sorbate system which is given by [40]:

$$q_e = \frac{(q_{\max}/K_1)C_{e1}}{1 + (1/K_1)C_{e1} + (1/K_2)C_{e2}} \quad (8)$$

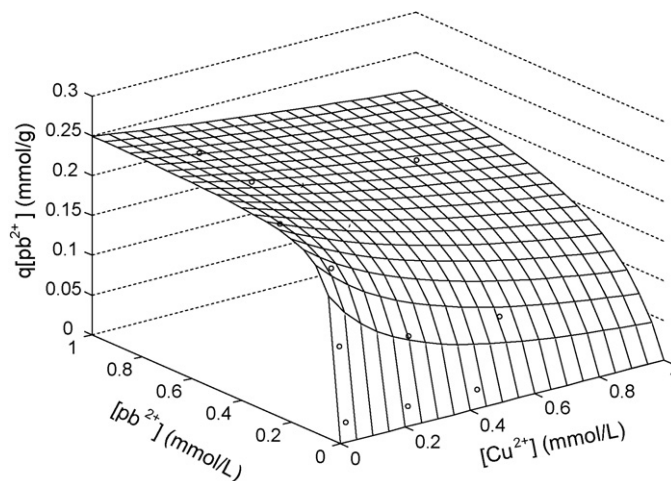
where  $K_1$ ,  $K_2$  are the isotherm parameters (mmol/L),  $C_{e1}$ ,  $C_{e2}$  are the equilibrium concentrations of metal ions (mmol/L).

The results of the non-linear regression analysis for copper competitive interference on lead biosorption onto *M. spicatum* were summarized in Table 3. Comparison with the lead biosorption in single-ion situation, it was shown that the Langmuir competitive model had good simulations with experimental data with correlation coefficients ( $R^2$ ) of 0.984. The model gave good prediction for  $q_{\max}$  (0.26 mmol/g, namely 53.87 mg/g) with standard error (S.E.) of  $9.06 \times 10^{-3}$ . The coefficient of variation (C.V.) was less than 5%, indicating that biosorption value predicted by the model was within 5% of the average experimental value. The coefficients of variation of  $K_1$  and  $K_2$  were relatively high, this may attribute to the low values of  $K_1$  and  $K_2$  which indicated that the plant biomass has great biosorption capacity for metal ions. The results were also plotted in three-dimensional format using Matlab version 7.1 and the resulting biosorption surface was shown in Fig. 9. Reasonable fit was evident in this case.

**Table 3**

Fit results of the Langmuir competitive model for Pb–Cu binary system.

Parameter	Value	S.E.	C.V.
$q_{\max}$ (mmol/g)	0.26	$9.06 \times 10^{-3}$	3.48e–2
$K_1$ (mmol/L)	$2.09 \times 10^{-2}$	$5.49 \times 10^{-3}$	2.63e–1
$K_2$ (mmol/L)	$8.66 \times 10^{-2}$	$2.75 \times 10^{-2}$	3.18e–1
$R^2$	0.984		

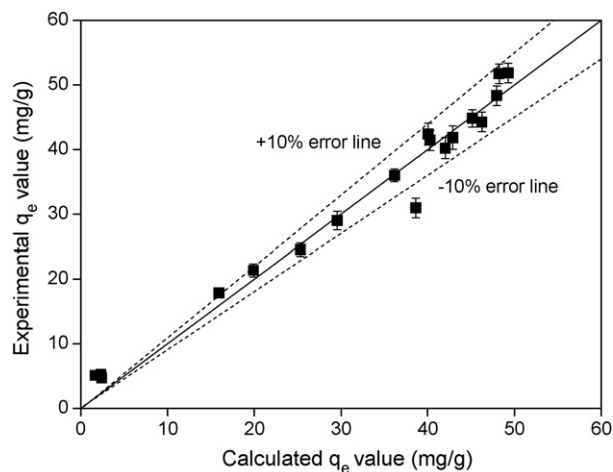


**Fig. 9.** Three-dimensional biosorption surface showing model prediction (continuous surface) and experimental data points. (Temperature = 25 °C; pH 5.0; contact time = 120 min; dry weight of biomass = 0.18 g; and agitation velocity = 200 rpm.)

In order to further examine the model accuracy, comparison of theoretical predictions with experimental values of Pb(II) biosorption was shown in Fig. 10. It was obvious that the values of  $q_e$  calculated by the Langmuir competitive model were in excellent consistent with those obtained experimentally (except for four data points, the other calculated data are very close to the experimental data with deviations less than 10%). The results suggested that the Langmuir competitive model was suitable to predict the sorption isotherm in Pb–Cu binary sorbate system.

### 3.7. Preferring sorption

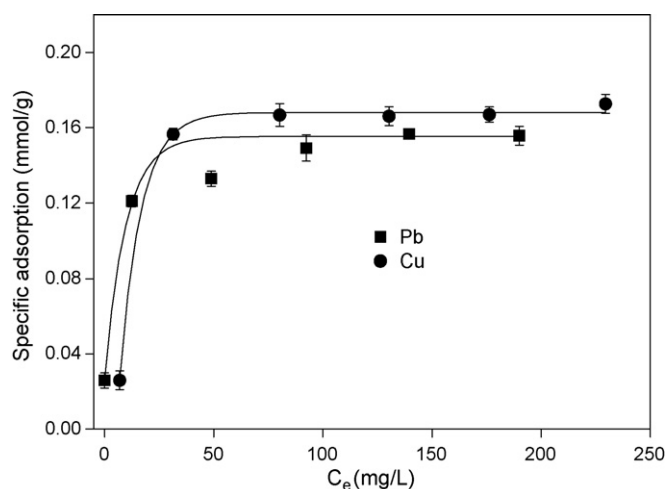
An important aspect of biosorption in binary metal solutions is the preference by the biosorbent of one metal ion over another. Due to the addition of the second metal ions, the firstly sorbed ions would be replaced by the second metal ions from the binding sites. Sorption and desorption of heavy metal ions by the plant biomass were found to occurred rapidly, and the equilibrium could be reached within 20 min. The sorption and desorption data for binary solution was shown in Table 4. The results showed that the amount of initial sorption was almost the same ( $0.036 \pm 0.005$  and  $0.035 \pm 0.002$  mmol). At the same time, the amount desorbed due to



**Fig. 10.** Comparison of model predictions with experimental values of Pb(II) biosorption. (Temperature = 25 °C; pH 5.0; contact time = 120 min; dry weight of biomass = 0.18 g; and agitation velocity = 200 rpm.)

**Table 4**  
Sorption and desorption data for a binary solution, Cu(II) and Pb(II).

	Cu(II)	Pb(II)
Initial amount (mmol)	0.157 ± 0.01	0.048 ± 0.001
Initial sorption (mmol)	0.036 ± 0.005	0.035 ± 0.002
Amount desorbed (mmol)	0.014 ± 0.004	0.013 ± 0.001
Amount sorbed from other metal (mmol)	0.031 ± 0.002	0.027 ± 0.001



**Fig. 11.** Equilibrium isotherm data for Pb(II) and Cu(II) at 25 °C in a binary solution with equal initial concentration. (Temperature = 25 °C; pH 5.0; contact time = 120 min; dry weight of biomass = 0.18 g; and agitation velocity = 200 rpm.)

the addition of the second metal ions was almost the same for the two cases ( $0.014 \pm 0.004$  and  $0.013 \pm 0.001$  mmol). However, the amount sorbed from another metal was just slightly higher than the amount desorbed. The difference between the desorbed and adsorbed amounts could be attributed to the fact that the second metal ion had a higher initial concentration and consequently the driving force for sorption is higher. These findings obviously indicated that the biosorbent has no preference for Cu(II) and Pb(II) in spite of the differences in physicochemical property of metal ions.

Analysis of the equilibrium isotherm data for a binary solution containing equal initial concentration of Cu(II) and Pb(II) was shown in Fig. 11. The isotherm showed that *M. spicatum* only had a slightly higher sorption capacity for copper ions. The preference of the sorbent for one of the two ions may be expressed by the separation factor  $\alpha_B^A$ , which is defined by [41]:

$$\alpha_B^A = \frac{q_A C_B}{q_B C_A} \quad (9)$$

If the ion A is preferred, the factor  $\alpha_B^A$  is larger than unity, and if B is preferred, the factor is less than unity. The separation factor  $\alpha_{Cu}^{Pb}$  was calculated from equilibrium data at a pH of 5.0 and  $C_e \approx 0.5$  mmol/L. The value was found to be unity, which proved again that the biosorbent (*M. spicatum*) has no preference of one ion over the other.

#### 4. Conclusions

Several batch experiments were carried out to examine the competitive effect of Cu(II) and Zn(II) on the biosorption of lead(II) by fresh tissues of *M. spicatum*. The experimental results showed that the biosorption of lead was adversely affected by low acidic pH values and the presence of high concentrations of other metal ions. Equilibrium data of single-ions were fitted to three isotherm models, and the Sips isotherm model gave the best fit of the exper-

imental data with correlation coefficient ( $R^2$ ) of 0.994. The lead biosorption capacity for *M. spicatum* decreased with increasing concentration of copper ions, and a simple Langmuir competitive model has been shown to fit the experimental data well, with correlation coefficient ( $R^2$ ) of 0.984. Comparison of theoretical and experimental values of  $q_e$  showed that the Langmuir competitive model fit well with the experimental data. The interactions between lead(II) and the functional groups on the biosorbent surface were examined by FT-IR analysis, and the possible functional groups responsible for the lead(II) binding were carboxyl, carbonyl and hydroxyl groups. Overall, this study suggested that biosorption of Pb(II) ions by *M. spicatum* can be an inexpensive and effective way of metal-ion treatment. Current work in our laboratory is to address the competition effects of metal co-ions on biosorption process and to extend a mathematical model for biosorption of binary metal systems.

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