Copper biosorption by *Myriophyllum spicatum*: Effects of temperature and pH

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Abstract−Using submerged aquatic plants is a cheap and clean technique to remediate heavy metal water pollution at low concentrations. Biosorption of Cu(II) ions by fresh tissues of *Myriophyllum spicatum*, a submerged aquatic plant, was characterized in an artificial solution system under different values of contact time, temperature and pH in this paper. Cu(II) biosorption was fast and equilibrium was attained within 20 min. The equilibrium biosorption data were analyzed using three widely applied isotherm models: Langmuir, Freundlich and Redlich-Peterson isotherm. Langmuir isotherm parameters obtained from the three Langmuir linear equations by using linear method were dissimilar, except when the non-linear method was used. Best fits were yielded with Langmuir and Redlich-Peterson isotherms (R^2=0.961-0.992 and 0.990-0.998, respectively). The saturated monolayer biosorption capacity of *M. spicatum* for Cu(II) at 298 K was calculated to be 0.19 mmol/g. The biosorption capacity of *M. spicatum* for Cu(II) increased with increasing pH, and the resulting isotherms were well described by Langmuir and extended Langmuir models (R^2=0.931-0.993 and 0.961, respectively). The comparison of calculated q_e and experimental q_e values showed that the extended Langmuir model had a better simulation for Cu(II) biosorption by *M. spicatum* than the Langmuir isotherm model. FT-IR was used to characterize the interaction between *M. spicatum* and Cu(II), with the results indicating that carboxyl groups played an important role in Cu(II) binding.

Key words: Aquatic Plant, Copper, Biosorption, Langmuir Isotherm Forms, pH

INTRODUCTION

The main sources of copper in industrial wastewaters include electroplating, metal cleaning plating baths, mining, fertilizers, and petroleum industries [1]. Because heavy metals pose serious environmental problems and are dangerous to human health, considerable attention has been paid to methods for their removal from industrial wastewaters. In conventional practice, precipitation is the most common technology for metals removal, but chemical precipitation of heavy metals produces a large amount of sludge and is ineffective, especially when metals ion concentration in aqueous solution is as low as 100 mg/*l* [2]. Sorption is another well established technique for heavy metal removal, and activated carbon is the most widely used sorbent [3], However, the use of activated carbon can be expensive, so there has been considerable interest in the use of other sorbent materials, particularly biosorbents [4,5] such as marine algae [6], tobacco dust [7], wheat shell [8], stalk waste [9], soybean hull [10] and agricultural by-products [11]. Sorption by biomass is now recognized as an alternative method for the treatment of wastewaters containing heavy metals [12-16].

The use of algae and other biomass for the removal of toxic heavy metals has been discussed in many reviews [17-19]. Kratochvil and Volesky [20] studied the applications of potentially low-cost sorbents including biomass for heavy metals removal. The cell walls of a biomass such as microalgae consist mainly of polysaccharides, proteins and lipids, and the biosorption of heavy metals from aqueous solutions involves four major steps: (1) entrapment by cellular components, (2) active transport across the cell membrane, (3) cation exchange or complexation, and (4) sorption [21]. The first two mechanisms are associated with living cells, and the latter two can only occur with dead cells.

It has been long known 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 gained high interest [22]. 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 very common in these drainage systems and can be found throughout the year.

M. spicatum is a submerged aquatic perennial plant that reproduces primarily by vegetative fragmentation. These fragments are produced during much of the year with the roots often developing on a fragment before it is released by the plant. It is rooted to the bottom and grows to the surface. When the surface is reached, the plant branches profusely to form a dense canopy. Flowering and seed production are common. However, the seeds exhibit prolonged dormancy and their germination is erratic. From one point of view, therefore, it can be thought of as a waste product.

The objective of the present work is to investigate the biosorption potential of *M. spicatum* biomass in the removal of Cu(Π) ions from aqueous solution. Optimum biosorption conditions were determined as a function of contact time, temperature and pH, and thermodynamic and kinetic parameters were also determined. The temperature effect on the equilibrium biosorption of copper onto *M.*

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spicatum was examined and the resulting isotherms compared using the linear and non-linear regression method; three widely used isotherms, including Langmuir (three different linear forms), Freundlich, and Redlich-Peterson, were also examined.

EXPERIMENTAL

1. Preparation of the Plant Biomass and Chemicals

Submerged aquatic plant biomass (*Myriophyllum 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 a fresh and uniform part 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 being used.

Analytical grade copper(II) sulfate was used as the metal source and stock solution of this metal ions was prepared in deionized water (Milli-Q, 18.2 MΩ/cm).

2. Kinetics Study

The sorption tests were conducted at a constant temperature (298 K) in conical flasks (250 ml) using an orbital shaker. The agitation velocity was 200 rpm and the plant biomass was about 2 g wet weight. The initial copper concentration of solution (150 ml) was 0.16 mmol/*l*, and the contact time ranged from 5 to 150 min.

3. Sorption Equilibrium Experiments

In effect of the temperature study, the data used to derive the three widely used isotherms were obtained using plant biomass (about 2 g wet weight) and solution (150 ml) at initial copper concentrations of 0.03, 0.06, 0.13, 0.25, 0.38, 0.57 and 1.13 mmol/*l*. The initial pH value was adjusted to around 5.5 during this batch experiment, as required with 1 M HNO₃ (analytical grade) using a precision pH meter (PHS-3C) before the addition of plant biomass. Plant biomass was added to each flask and placed on the orbital shaker with the temperature 278, 288 and 298 K, respectively. The contact time was 120 min. After contacting, the contents of the flask were filtered to separate the biomass from the solution; the filtrates were then analyzed with an atomic sorption spectrophotometer (Model SolaarM, Thermo Electron, USA) to determine the metal concentration in the samples.

In effect of the pH study, the temperature was controlled of 298 K, the initial pH value was adjusted to the desired value (3.0, 4.0, 5.0 and 6.0); no effects were made to maintain the solution pH while metal was being sorbed. The equilibrium pH was measured at the end of the experiments.

Control experiments were performed for Cu(II) to measure any sorption onto the glassware; neither precipitation nor sorption onto the wall of the flasks was observed. The results of metal analysis were used to calculate specific sorption (mmol metal sorbed per g of biomass, dry weight). All the experiments were done in triplicate and the results presented as mean values; the variation was less than five percent in all cases.

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

$$q = \frac{V \cdot (C_0 - C_f)}{W} \qquad (1)$$

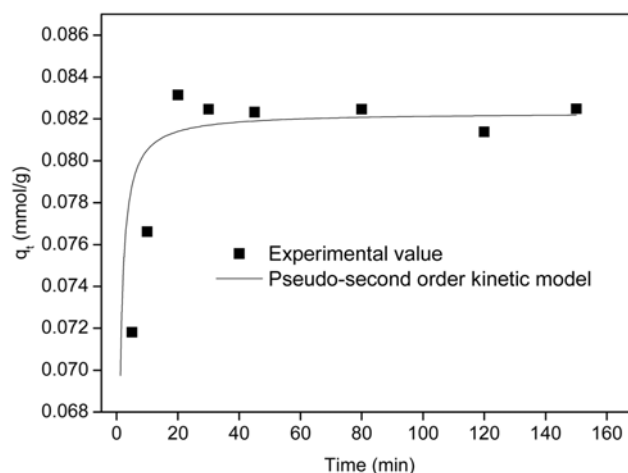where q is the sorption values (mmol/g), C_0 and C_f the initial and

Fig. 1. Pseudo-second order kinetics of the biosorption of copper onto *M. spicatum* (T=298 K; pH_{eq}=4.8-5.5; Initial concentration=0.16 mmol/*l*; Wet weight of biomass=2 g; Agitation velocity=200 rpm).

final concentrations (mmol/*l*), V the volume of solution (*l*) and W the dry weight of biosorbent (g).

RESULTS AND DISCUSSION

1. Biosorption of Copper Ions and Biosorption Kinetics

Contact time is one of the important parameters for successful use of the biosorbents for practical application, and rapid sorption is among the desirable parameters [23]. The rate of copper biosorption onto plant biomass was examined using solutions with initial metal concentration of 0.16 mmol/*l* at initial pH around 5.5. The sorption of Cu(II) seemed to increase with time, reaching equilibrium at about 20 min as shown in Fig. 1.

The biosorption kinetics was analyzed by applying the pseudo-second order Lagergren rate equation, where the copper binding capacity was assumed to be proportional to the number of active sites occupied on the sorbent. The equation is given by:

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

where k is the equilibrium rate constant of pseudo-second order sorption kinetics (g/(mmol·min)), q_e the equilibrium uptake (mmol/g), q_t the amount of sorbate on sorbent at time t (mmol/g). Eq. (2) can be integrated and rearranged to give:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k} \qquad (3)$$

where the term $q_e^2 k$ represents the initial sorption rate. The coefficient of determination (R^2) of 0.9999 clearly indicated that biosorption of copper by *M. spicatum* followed pseudo-second order kinetics. The values of q_e (0.082 mmol/g) and k (54.81 g/(mmol·min)) were

Table 1. Parameters of pseudo-second order kinetic model

k (g/(mmol·min))	q_e (mmol/g)	R^2
54.81	0.082	0.9999

Table 2. Isotherms and their linear forms

Isotherm	Linear form	Plot
Langmuir-1	$q_e = \dfrac{q_m K_a C_e}{1 + K_a C_e}$ $\dfrac{C_e}{q_e} = \dfrac{1}{q_m} C_e + \dfrac{1}{K_a q_m}$	$\dfrac{C_e}{q_e}$ vs C_e
Langmuir-2	$\dfrac{1}{q_e} = \left(\dfrac{1}{K_a q_m}\right)\dfrac{1}{C_e} + \dfrac{1}{q_m}$	$\dfrac{1}{q_e}$ vs $\dfrac{1}{C_e}$
Langmuir-3	$\dfrac{q_e}{C_e} = K_a q_m - K_a q_e$	$\dfrac{q_e}{C_e}$ vs q_e
Freundlich	$q_e = K_f C_e^{1/n}$ $\log(q_e) = \log(K_f) + 1/n \log(C_e)$	$\log(q_e)$ vs $\log(C_e)$
Redlich-Peterson	$q_e = \dfrac{AC_e}{1 + BC_e^g}$ $\ln\left(A\dfrac{C_e}{Q_e} - 1\right) = g\ln(C_e) + \ln(B)$	$\ln\left(A\dfrac{C_e}{Q_e} - 1\right)$ vs $\ln(C_e)$

calculated from the slope and intercept of the straight line. The value of the calculated q_e (Table 1) was in excellent agreement with that obtained experimentally (0.082 mmol/g).

2. Effect of Temperature on Equilibrium Biosorption

At constant temperature, Cu(II) held onto *M. spicatum* would be in equilibrium with copper ions in bulk solution. The linear regression was used to determine the best-fitting isotherm. The Langmuir isotherm could be linearized into three different forms (Table 2), and simple linear regression resulted in different parameter estimates. The values of the Langmuir constant, the saturation capacity, q_m, and the biosorption equilibrium constant, K_a, are shown in Table 3 for the biosorption of Cu(II) onto *M. spicatum* at 278, 288 and 298 K. The values of the coefficient of determination, R^2, obtained for Langmuir-1 and Langmuir-2, were closer to 1.000 than the other linear form of the Langmuir equation. This indicated that there is strong positive evidence that the biosorption of Cu(II) onto *M. spicatum* follows monolayer coverage of Cu(II) on the biomass surface and that the interaction between two copper molecules is negligible. The monolayer biosorption capacity, q_m, for Langmuir-1

using linear regression was found to increase from 0.15 to 0.20 mol/g and for Langmuir-2 was found to increase from 0.10 to 0.15 mmol/g for an increase in solution temperatures from 278 to 298 K. The biosorption constant, K_a, increased from 22.86 to 36.20 l/mmol, using Langmuir-1 form and from 60.96 to 100.97 l/mmol, using Langmuir-2 form as temperatures varied from 278 to 298 K. The results revealed that the heat of biosorption largely determined the magnitude of the Langmuir constant, K_a. The increase in K_a values with temperature indicated a higher heat of biosorption with increasing temperature. This meant that stronger bonds were formed at higher temperature supporting the fact that biosorption was endothermic.

The Redlich-Peterson isotherm constants and the coefficient of determination (R^2) for the biosorption of Cu(II) onto *M. spicatum* using the linear regression are shown in Table 3. It can be seen that the values of g are close to unity, which means that the isotherms are approaching the Langmuir form but not the Freundlich isotherm. The biosorption of Cu(II) onto *M. spicatum* was less likely to be a multilayer biosorption. The biosorption constant, B, increased from 45.53 to 93.33 (l/mmol)^g as temperatures varied from 278 to 298 K, indicating a higher sorption capacity with increasing temperature.

Table 3. Isotherm parameters obtained using the linear method for the biosorption of copper onto *M. spicatum* at different temperature

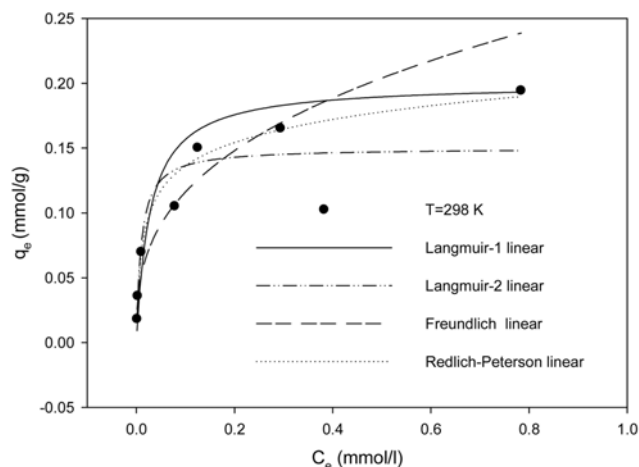| Isotherm	Parameter	278 K	288 K	298 K
Langmuir-1	q_{max}, mmol/g	0.15	0.16	0.20
	K_a, l/mmol	22.86	30.48	36.20
	R^2	0.998	0.998	0.995
Langmuir-2	q_{max}, mmol/g	0.10	0.13	0.15
	K_a, l/mmol	60.96	79.38	100.97
	R^2	0.951	0.998	0.994
Langmuir-3	q_{max}, mmol/g	0.14	0.15	0.17
	K_a, l/mmol	34.93	68.58	81.28
	R^2	0.823	0.965	0.869
Freundlich	$1/n$	0.91	0.34	0.35
	K_F, (mmol/g)(l/mmol)$^{1/n}$	0.024	0.21	0.26
	R^2	0.940	0.913	0.938
Redlich-Peterson	g	0.93	0.93	0.87
	B, (l/mmol)^g	45.53	72.31	93.33
	A, l/mol	6.25	11.32	18.25
	R^2	0.951	1.000	0.994

Fig. 2. Isotherms obtained using the linear method for the biosorption of copper onto *M. spicatum* at a temperature 298 K (pH$_{eq}$=4.8-5.5; Contact time=120 min; Wet weight of biomass=2 g; Agitation velocity=200 rpm).

Fig. 2 shows the plots comparing the theoretical Langmuir, empirical Freundlich, and the Redlich-Peterson isotherm with the experimental data for the biosorption of Cu(II) onto *M. spicatum* at a temperature of 298 K. The values of the coefficient of determination for the Redlich-Peterson and the Langmuir-1 isotherm form were the same, but the fit of both isotherms to experimental data was different. The use of coefficient of determination of linear regression analysis for comparing the best fit of different linear isotherms was found not to be appropriate [24]. Therefore, a further analysis was attempted. Sigmaplot version 10.0 was used for non-linear regression.

Table 4 shows isotherm parameters obtained by using non-linear method. In the case of Langmuir isotherm, by using non-linear method there was no problem with transformation of the non-linear isotherm equation to linear forms, and also they had the same error structures. In the case of Redlich-Peterson, the values of g were close to unity, which was the same as the results from linear method; this meant that the isotherms were approaching the Langmuir but not Freundlich isotherm. The Langmuir constants obtained from the non-linear and linear methods differed even when compared with results of Langmuir-1, which had the highest coefficient of deter-

mination for any Langmuir isotherm (Tables 3 and 4). It seems that the best fit was obtained by Langmuir-1 as compared with other Langmuir equations because it had the highest coefficient of determination and the Langmuir constants K_a and q_m were both closer to those obtained using the non-linear method. Fig. 3 shows that the Redlich-Peterson and Langmuir isotherms seem to be the best-fitting models for the experimental results with the same values of coefficient of determination (Table 4). The Langmuir isotherm is a special case of the Redlich-Peterson isotherm when constant g is unity. In addition, it was reported that the Freundlich isotherm is a special case of the Redlich-Peterson isotherm when constants A and B are much greater than unity [24]. Unlike the linear analysis, different isotherm forms would affect R^2 significantly, and impact the final determination of parameters while non-linear methods would prevent such errors.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L [25,26] given by Eq. (4):

$$R_L = \frac{1}{1+K_a \cdot C_0} \qquad (4)$$

where C_0 (mmol/l) is the highest initial concentration of sorbate and K_a (l/mmol) is the Langmuir constant. The parameter R_L indicates the nature of the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). For the sorption of Cu(II) by *M. spicatum* at different temperature, R_L values obtained were 0.036 at temperature 278 K, 0.028 at 288 K, and 0.020 at 298 K, respectively. The values of R_L in the range of 0.036-0.020 for three different temperatures indicated that biosorption of Cu(II) onto *M. spicatum* is a favorable process.

3. Biosorption Thermodynamics

The thermodynamic equilibrium constant, K^o for the sorption reactions was determined by the method suggested by Khan and Singh [27] by plotting $\ln(q_e/C_e)$ versus q_e (Fig. 4) and extrapolating to zero. Results indicated that the K^0 value was increased from 2.02 to 3.09 for an increase in solution temperature from 278 to 298 K. Previ-

Table 4. Isotherm parameters obtained using the non-linear method for the biosorption of copper onto *M. spicatum* at different temperature

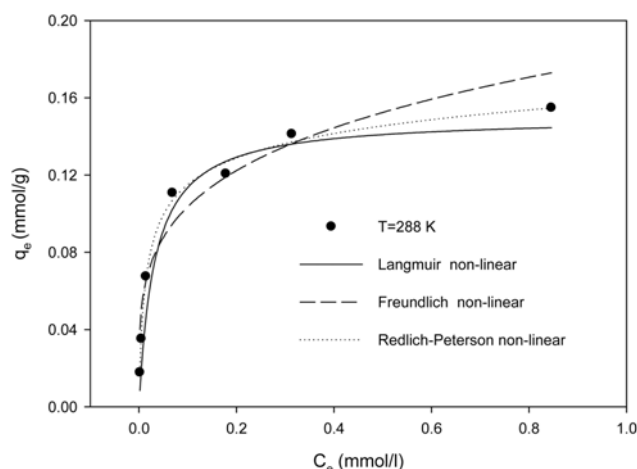| Isotherm	Parameter	278 K	288 K	298 K
Langmuir	q_{max}, mmol/g	0.14	0.15	0.19
	K_a, l/mmol	23.50	31.12	42.55
	R^2	0.992	0.989	0.961
Freundlich	1/n	0.28	0.24	0.27
	K_F, (mmol/g)(l/mmol)$^{1/n}$	0.16	0.18	0.22
	R^2	0.956	0.962	0.976
Redlich-Peterson	g	0.94	0.91	0.89
	B, (l/mmol)^g	27.22	77.82	116.10
	A, l/mol	4.08	12.42	24.12
	R^2	0.994	0.998	0.990

Fig. 3. Isotherms obtained using the non-linear method for the biosorption of copper onto *M. spicatum* at a temperature 288 K (pH$_{eq}$=4.8-5.5; Contact time=120 min; Wet weight of biomass=2 g; Agitation velocity=200 rpm).
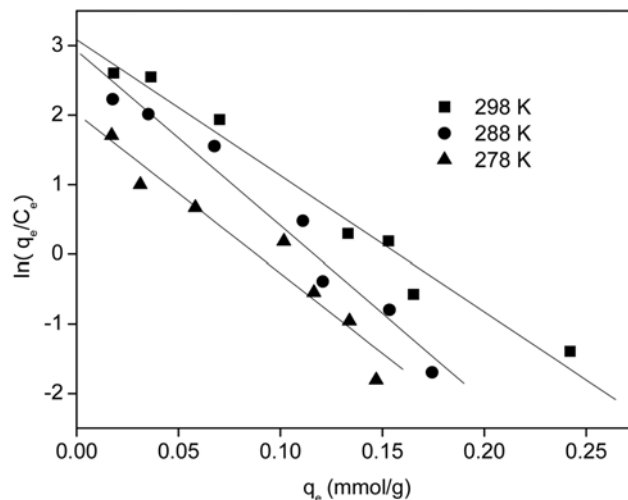

Fig. 4. Plots of ln(q$_e$/C$_e$) versus q$_e$ for *M. spicatum* at various temperatures (pH$_{eq}$=4.8-5.5; Contact time=120 min; Wet weight of biomass=2 g; Agitation velocity=200 rpm).

ous research [11] had showed that for Cr(IV) biosorption onto rice bran, the K^0 value was increased from 1.60 to 7.04 for an increase in temperature from 308 to 328 k. The endothermic nature of biosorption was indicated by the increase in K^o values with a rise in temperature [28]. Thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) for *M. spicatum* were calculated from the variation of the thermodynamic equilibrium constant K^0 at various temperatures according to the following Eqs. (5) and (6):

$$\Delta G^0 = -RT\ln K^0 \tag{5}$$

$$\ln K^0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{6}$$

where R is the universal gas constant (8.314 J/(mol·K)), T the temperature in Kelvin (K).

Plots of $\ln K^o$ versus 1/T for Cu(II) biosorption by *M. spicatum* were linear, ΔH^0 and ΔS^0 were determined from the slope and intercept of the plots. The corresponding numerical values for ΔG^0, ΔH^0 and ΔS^0 are given in Table 5. The negative values of ΔG^0 indicated the feasibility of the process and the spontaneity of sorption reaction. The values of ΔH^0 are positive for *M. spicatum*, showing the sorption process is endothermic in nature. In most cases, the biosorption of heavy metal ions onto plant biomass has been shown to be spontaneous and endothermic [29]. The positive values of ΔS^0 for *M. spicatum* suggested increased randomness at the solid-solution interface during the sorption process.

4. Effect of pH on Biosorption

The pH value of the aqueous solution is an important controlling parameter in the biosorption process. These pH values affect the surface charge of sorbent, the degree of ionization and speciation of sorbate during sorption. The experimental results obtained for Cu(II) biosorption at a constant pH values were fitted to the Langmuir non-linear isotherm equation using the commercial software Sigmaplot version 10.0. Sorption equilibrium parameters are displayed in Table 6 and isotherms in Fig. 5. The results indicated that the Langmuir model was suitable to describe the sorption isotherm of Cu(II) biosorption onto *M. spicatum* at a constant pH_{eq} value ($R^2=$ 0.931-0.993). The biosorption capacity of *M. spicatum* for Cu(II) slightly increased with pH_{eq} value, and reach a maximum value of

Table 5. Thermodynamic parameters for copper biosorption onto *M. spicatum* at various temperatures

Temperature (K)	K^0	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/(mol·K))
278	2.02	−1.74	14.70	59.11
288	2.93	−2.33		
298	3.09	−2.92		

Table 6. Isotherm parameters obtained using the non-linear method for the biosorption of copper onto *M. spicatum* at different pH_{eq} value

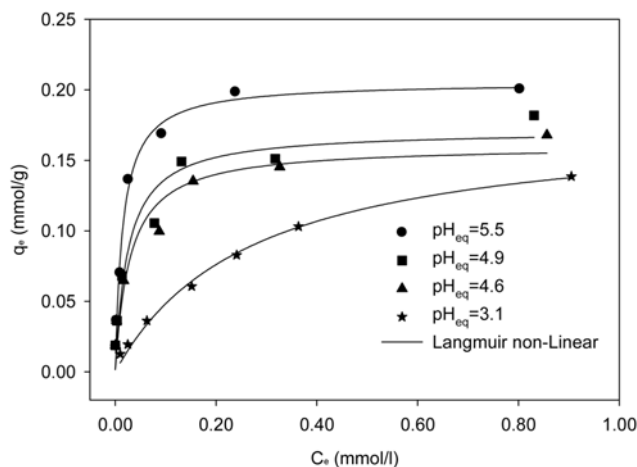| Isotherm	Parameter	pH_{eq}=3.1	pH_{eq}=4.6	pH_{eq}=4.9	pH_{eq}=5.5
Langmuir	q_{max}, mmol/g	0.181	0.186	0.185	0.191
	K_a, l/mmol	4.46	16.51	35.56	37.47
	R^2	0.990	0.931	0.935	0.993

Fig. 5. Equilibrium isotherm for copper biosorption onto *M. spicatum* at different pH (T=298 K; Contact time=120 min; Wet weight of biomass=2 g; Agitation velocity=200 rpm).
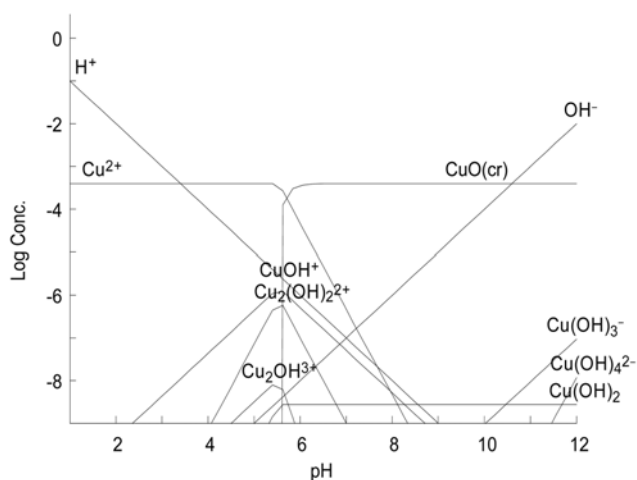

Fig. 6. Concentration diagram of copper species in aqueous solution (Copper concentration: 0.4 mmol/*l*).

about 0.19 mmol/g at a pH_{eq} value of 5.5.

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 (CuOH$^+$, Cu(OH)$_2^0$, Cu(OH)$_3^-$, Cu$_2$(OH)$_2^{2+}$ and Cu^{2+}) can be viewed as potential sorbates in the uptake of copper ions from aqueous solution, the data presented in this study suggest that under experimental conditions (pH_{eq}<5.6) (see Fig. 6) the species responsible for the removal of copper is the predominant one in the species distribution, namely the Cu(II) ions. Thus, sorption can be explained by elucidating the mechanism whereby the Cu(II) ions are accommodated on the *M. spicatum* surface.

An attempt was made to predict the sorption isotherm in binary sorbate systems based on q_{max}, K_m, and K_h values that are directly adopted from single sorbate systems. A simple "one-site" extended Langmuir model is thus tried which is given by [30]:

$$q = \frac{(q_{max}/K_m)C_e}{1+(1/K_m)C_e+(1/K_h)[H^+]} \tag{7}$$

Where C_e is the equilibrium concentration of metal ions (mmol/*l*),

Table 7. Fitting results of the extended Langmuir model for copper biosorption onto *M. spicatum*

Parameter	Value	S.E.	CV%
q_{max}, mmol/g	0.19	0.02	9.64
K_m, mmol/l	0.08	0.04	44.12
K_H, mmol/l	0.94	0.48	50.71
R^2	0.961		

$[H^+]$ the equilibrium concentration of H^+ (mmol/l), q_{max} the maximum amount of sorption (mmol/g), K_m and K_h are equilibrium constants for metal binding (mmol/l), respectively.

The metal biosorption and final solution concentration data determined as described were fitted to Eq. (7) using non-linear regression analysis (Sigmaplot version 10.0). The best-fit values for each variable in the model were determined along with standard errors (S.E.) and coefficients of variation (CV%) (Table 7). For Cu(II) biosorption by *M. spicatum*, a comparison with the Cu(II) biosorption (Fig. 5) showed that the model gave good prediction for the maximum biosorption value q_{max} (0.19 mmol/g); the coefficient of variation (the standard error×100/parameter) was less than 10%, indicating that the biosorption value predicted by the model lay on average within 10% of the experimental value.

Fig. 7 shows the plots comparing the theoretical q_e values calculated by the non-linear Langmuir and the extended Langmuir models with the experimental q_e values for copper biosorption onto *M. spicatum* at a pH_{eq} 3.1. The values of the coefficient of determination, R^2, for the Langmuir and the extended Langmuir models were the same, but the fit of both models to experimental data was also different. At a pH_{eq} 3.1, for the extended Langmuir model, the average relative error between predicted data and experimental q_e values was 5.48%, whereas for the Langmuir model, the value obtained was 21.75%. The comparison of theoretical q_e values calculated by different models and experimental q_e values showed that the extended Langmuir model had a better simulation for copper biosorption by *M. spicatum* than the Langmuir isotherm model.
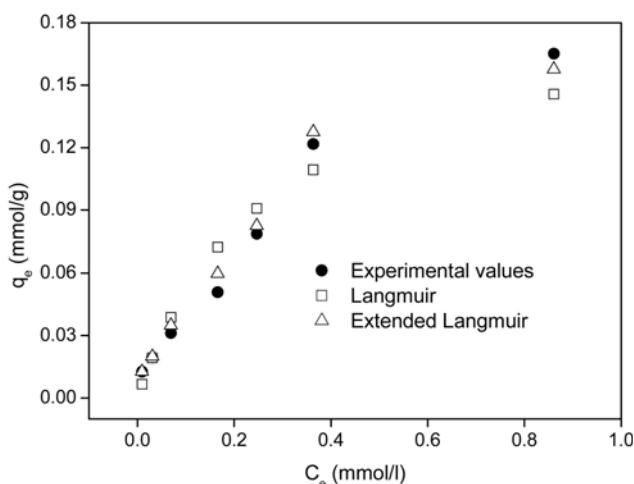

Fig. 7. Comparison between the theoretical q_e values calculated by different models and the experimental q_e values at a pH_{eq} 3.1 (T=298 K; Contact time=120 min; Wet weight of biomass=2 g; Agitation velocity=200 rpm).
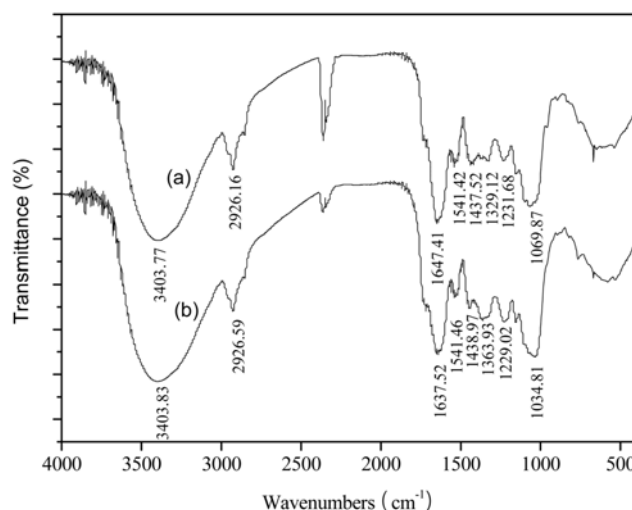
Fig. 8. Fourier transform infrared absorption spectrum of *M. spicatum*: (a) native and (b) Cu(II) treated (Copper concentration: 0.78 mmol/l).

5. FT-IR Spectrum Analysis

M. spicatum was characterized with respect to its surface functional groups using FT-IR (Fourier Transform Infrared) spectroscopy. FT-IR was also used to identify functional groups responsible for binding Cu(II). The FT-IR spectra of metal unloaded and loaded forms of the biosorbent in the range of 4,000-400 cm^{-1} were taken and presented in Fig. 8. It can be seen that the FT-IR spectra display a number of absorption peaks, indicating the complex nature of the biomass examined [31].

The FT-IR spectra of unloaded biomass show sharp absorption at 3,403 cm^{-1} (indicative of -OH and -NH$_2$ groups), and 2,926 cm^{-1} (indicative of C-H group). The absorption bands at 1,647 cm^{-1} (mainly C=O stretching) and 1,541 cm^{-1} (mainly -NH, -CN stretching) can be attributed to the amide I and amide II bands of amide bond due to the protein-peptide bond. A band at 1,231 cm^{-1}, representing amide III stretching, is observed in the spectra. The bond at 1,069 cm^{-1} could be attributed to the C-OH stretch of sugar. The absorption spectrum of Cu-loaded biomass was compared with that of native biomass. The FT-IR spectrum for Cu-loaded biosorbent showed wavenumber and intensity of some peaks were shifted or substantially lower than those before biosorption, suggesting the functional groups in the binding of copper. Fig. 8 shows that the Cu-loaded *M. spicatum* exhibited spectra with clear shifts of the carboxyl stretching band to lower frequency. This shift is typical for the complexation of the carboxyl groups by coordination with metal ions [32]. Fig. 8 also shows that there was a substantial decrease in the absorption intensity of C=O bands at 1,437 cm^{-1} and amide III stretching bands at 1,231 cm^{-1}; the C=O stretching band and amide III bands of amide bonds were involved in copper binding by *M. spicatum*. On the basis of variations of the bands, it was reasonable to assume that the peak values suggested the chelating character of Cu(II) biosorption onto carboxyl groups.

CONCLUSIONS

From the work presented here, the submerged aquatic plant (*Myrio-*

phyllum spicatum) can be effective as a biosorbent for the removal of copper ions. Batch sorption studies showed that the overall sorption rate was well described by the pseudo-second order model, with correlation of determination (R^2) of 0.9999. Biosorption of Cu(II) from aqueous solution by *M. spicatum* is a spontaneous and endothermic process. Both two-parameter Langmuir and three-parameter Redlich-Peterson isotherms were the best-fitting models for the biosorption of Cu(II) onto *M. spicatum*. The saturated monolayer biosorption capacity of *M. spicatum* for Cu(II) at 298 K was calculated to be 0.19 mmol/g. Non-linear method of error analysis could be a better way to compare isotherm fitting. The biosorption capacity of Cu(II) onto *M. spicatum* slightly increased with pH value, and reached a maximum value of about 0.19 mmol/g at a pH$_{eq}$ value of 5.5. The comparison of theoretical q$_e$ values calculated by two different models and experimental q$_e$ values showed that the extended Langmuir model had a better simulation for copper biosorption by *M. spicatum* than the Langmuir isotherm model. FT-IR spectrum analysis indicated the chelating character of Cu(II) biosorption onto carboxyl groups.

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