ELSEVIER

Biosorption of nickel and copper onto treated alga (*Undaria pinnatifida*): Application of isotherm and kinetic models

Zhen Chen, Wei Ma*, Mei Han

Department of Chemistry, Dalian University of Technology, Dalian 116024, PR China

Abstract

Biosorption of nickel and copper ions from aqueous solution onto treated alga biomass *Undaria pinnatifida* has been studied and the Langmuir, Freundlich and Temkine equilibrium isotherms, pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic model were determined respectively. Within the test range (initial concentration 5–50 mg/L, biosorption doze 0.1–0.5 g, pH 3–7), biosorption performance for metal ions showed an increase in specific metal uptake capacity with an increasing in initial ions concentration and decreasing in biosorbent doze. The optimized condition of pH value for nickel and copper is 4.7 and 4.0, respectively, while contact time is about 100 min. At equilibrium, the maximum total uptake by *U. pinnatifida* was 24.71 mg/g for nickel and 38.82 mg/g for copper. The results for nickel and copper fit well to the Langmuir and the Temkin isotherm, respectively. Pseudo-second-order model described well the sorption kinetic of nickel and copper ions in comparison to pseudo-first-order and intra-particle diffusion kinetic model.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Biosorption; Heavy metal; Treated alga; Kinetic; Isotherm

1. Introduction

Water pollution is one of the most debatable as almost all inorganic or organic wastes are discharged through aquatic route either in water soluble or insoluble forms [1]. Among the wastes, mobile and soluble heavy metal species are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Heavy metal contamination exists in aqueous waste streams of many industries such as metal plating facilities, mining operations, and tanneries [2]. Nickel and copper is the common heavy metal in waste stream of many industries. A water sample which contained 28 mg/L nickel and 5 mg/L copper was taken from a metallurgy factory in Liaoning, China.

Treatment processes for metals contaminated include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and coprecipitation/adsorption [3–7]; nevertheless, it is not very available for these methods that high capital investment for membrane filtration, expensive running cost for ion exchange, active carbon adsorption and rewaste for chemical precipitation and coprecipiation/adsorption. Therefore, there is an urgent need for development of innovative but low cost processes, where metal ions can be removed economically. That is biosorption. It is a proven technology for the removal of heavy metal ions from synthetic and real industrial effluents. Several researchers investigated numerous biomass types and proposed excellent metal biosorbents including bacteria, fungi, and algae [8–11]. Biosorption technology has been shown to be a feasible alternative for removing heavy metals from waste water. Naturally abundant biomass which has been identified for its high sorption capacity to metal ions can be utilized. It is apparent that natural biomass must be different in cite and cannot be copied effectively. Artificial biomass such as *Undaria pinnatifida* can avoid this limitation.

Marine alga, *U. pinnatifida* has been artificially cultured for nearly two decades in China such as at Liaoning and Shandong Province, etc. For high-productivity and low cost, this biomass can be well as biosorbent to absorb heavy metal. The macro-

* Corresponding author.
  E-mail address: chmawv@yahoo.com (W. Ma).

scopic structures of the alga offer a convenient basis for the production of biosorbent particles suitable for sorption process application [12]. The potential of alga biosorption is beginning to be recognized both for the recovery of valuable metals and also for reducing the pollution [13–15].

Considering this, the objective of present study was to access the ability of treated *U. pinnatifida* to remove nickel and copper ions from low initial concentration aqueous solution and use models in non-linear form to describe the sorption data.

2. Materials and methods

2.1. Reagents

All reagents used in present study were of analytical grade. For adjusting the initial pH of the medium 0.1 M solutions of NaOH and HCl were used.

2.2. Biosorbent U. pinnatifida collection

The raw biomass of *U. pinnatifida* was harvested from a aquafarm in Dalian, China. The biomass were washed with deionized water and dried at 105 °C for 24 h.

2.3. Preparation of biomass

U. pinnatifida was soaked in the solution of 0.2 M $CaCl_2$ for 24 h. After treatment the biomass was washed with deionized water. Then the biomass was dried at 105 °C for 24 h in a drying oven. The dried biomass was cut, and then sieved to obtain biosorbent with homogenous known particle size of <0.86 mm.

2.4. Batch sorption experiments

All the sorption experiments were performed at 25 °C and 150 rpm on an orbital shaker for 2 h with biomass in a 125 mL flask containing 100 mL of copper or nickel solution prepared using the metal nitrate. At the end of the experiments, the flasks were removed from the shaker and the samples were centrifuged at 3000 rpm for 10 min and the supernatant liquid was used to determine metal ions concentration. The solutions prepared using deionized water had an initial metal concentration of 1000 mg/L. Known amounts of biomass were contacted with each metal solution. The effects of following parameters such as pH, biomass doze, initial metal ion concentration and contact time were studied. Biosorption experiments were carried out in duplicate.

2.5. Metal analysis

Metal concentrations were measured using an atomic absorption spectrophotometer (solan 969 USA). The wavelength used for the analysis of the metal in this study was 232 nm for nickel and 324.8 nm for copper.

2.6. Calculations

The metal concentration in the liquid phase was determined at beginning (C_i) and equilibration (C_e) in mg/L. The following equation was used to compute biosorbent uptake capacity at equilibrium q_e (mg/g):

$$q_e = (C_i - C_e) \times \frac{V}{1000w} \tag{1}$$

where V is the volume of solution in mL and w is the mass of biosorbent in g.

Average and standard deviation values from triplicates were calculated using Microsoft Office XP. The figures, the coefficient (R^2) values of the non-linear form of pseudo-first-order and pseudo-second-order models were determined using statistical functions of Origin 7.5.

2.7. Non-linear regression analysis

In this study all the model parameters were evaluated by non-linear regression. The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data. Not only the correlation coefficient (R^2) but also the residual root mean square error (RMSE) and the Chi-square test were used to measure the goodness-of-fit. RMSE [8] can be represented as follows:

$$RMSE = \sqrt{\frac{1}{m-2}\sum_{i=1}^{m}(Q_i - q_i)^2} \tag{2}$$

where Q_i is the observation from the batch experiment, q_i is the estimate from the isotherm for corresponding Q_i and m is the number of observations in the experimental isotherm. The smaller RMSE value indicates the better curve fitting.

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and values obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models [16]. It can be defined as

$$\varepsilon^2 = \sum_{i=1}^{m}\frac{(Q_i - q_i)^2}{q_i} \tag{3}$$

If data from model are similar to the experimental data, ε^2 will be a small number.

3. Results and discussion

3.1. Effect of treatment and initial concentrations

The capacities of treated *U. pinnatifida* and untreated *U. pinnatifida* for metal ion were compared at the different concentrations respectively in Fig. 1. It was noted that the treatment of $CaCl_2$ had greatly enhanced the adsorption capacity. At the sorption of nickel, the adsorption capacity for untreated *U. pinnatifida* increased from 0.98 to 11.33 mg/g with the increasing of the initial concentration in 5–50 mg/L. The same direction
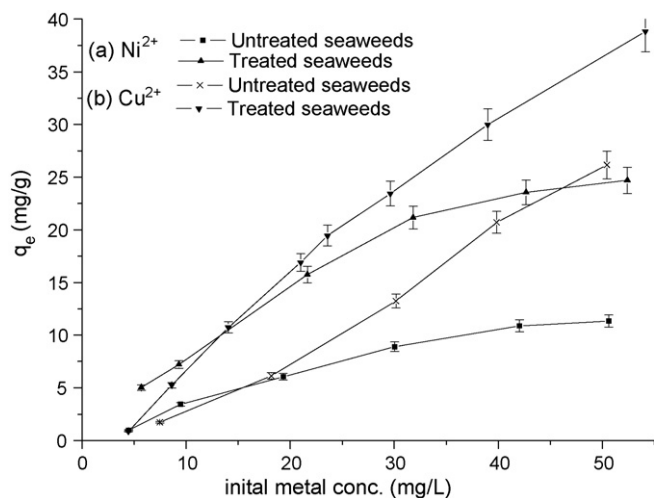
Fig. 1. Effect of initial metal concentration and treatment on biosorption of (a) nickel and (b) copper (0.1 g biomass in 100 ml metal solution for 120 min with pH 4.7for nickel and pH 4 for copper).

Fig. 2. Effect of pH on biosorption of (a) nickel and (b) copper (0.1 g biomass in 100 ml of 30 mg/L metal solution for 120 min).

was found from the sorption by treated *U. pinnatifida*, and the capacity was about 10 mg/g higher than the data of untreated *U. pinnatifida* biosorption at most initial concentration, respectively. The biosorption of copper was similar to the direction of nickel sorption. The capacity of treated *U. pinnatifida* increased from 0.88 to 38.82 mg/g with the increasing of initial concentration. The maximum capacity by treated *U. pinnatifida* is 24.71 and 38.82 mg/g for nickel and copper, respectively.

Fig. 1 also clarifies the relation between capacities and the metal ion concentration which shows that the adsorption concentrations increased with the increasing of the initial metal ion concentration. This was most probably due to increase in the initial ion concentrations which provided more chance for the biosorbent.

The effect of the HCl and NaOH solution also had been experimented, which adsorption capacity was not apparent. So the highest metal uptake nickel and copper ions was obtained by CaCl$_2$ solution treated *U. pinnatifida* which was then used for further study.

3.2. pH profiles study for metal ion binding

The effect of the biosorbent on metal sorption was experimented with not keeping constant during the sorption process, and the result is shown in Fig. 2. In nickel sorption, the sorption capacity increased significantly and reached 21.16 mg/g at pH 4.7, then decreased with increasing solution pH. The effect of pH on copper sorption shows a similar increase in sorption capacity. A sorption capacity of 29.43 mg/g was achieved at pH 4.

The low metal biosorption at pH below 3 may be explained on the basis of active sites being protonated, resulting in a competition between H$^+$ and M^{2+} for occupancy of the binding sites [17]. At pH above 7.0 the metal occurs as calculated mathematically by ion product equation, the precipitation seemed to be apparent for the sorption of the metal ions.
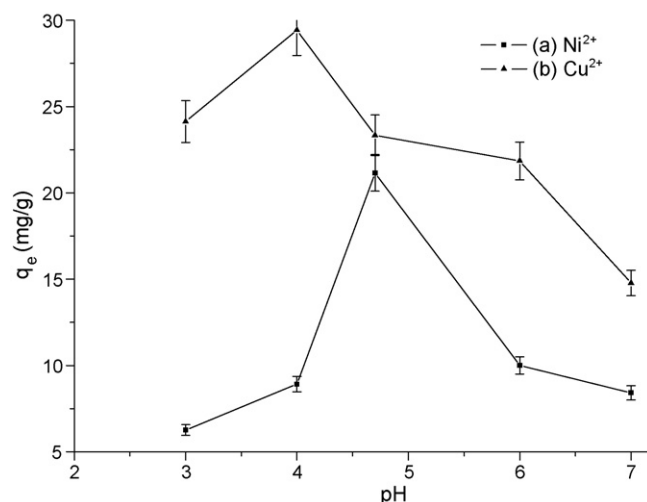
It is reported that [18] the removal of the nickel up to pH 7.0 was only due to the phenomenon of biosorption by biosorbents and not due to the precipitation.

The final pH values were determined and the results were shown in Table 1. The pH value changed a little from initiation to equilibrium. It is indicated that the treated *U. pinnatifida* can transfer the pH for its characteristic.

The maximum uptake capacity for nickel and copper indicated to be in different pH values. This was most probably due to the characteristic of the metal ions were not similar, or the adsorption cites better sorbed to more available metal.

3.3. Effect of biosorbent doze

Biosorbent doze seemed to have a great influence in biosorption process. Doze of biomass added into the solution determine the number of binding sites available for adsorption. The results of the effect of treated *U. pinnatifida* doze (Fig. 3) showed that the biosorption capacity decreased with the increasing in biomass doze, however, it is evident from the figure that the removal values increased with the increase of the doze of the biosorbent from 66% to 82% for the adsorption of nickel and 70% to 88% for the adsorption of copper. The maximum metal ion sorption of an adsorbent may be determined from column experiments, by the use of a large excess of the adsorbate.

Table 1
Comparison between initial and final pH values in nickel and copper biosorption

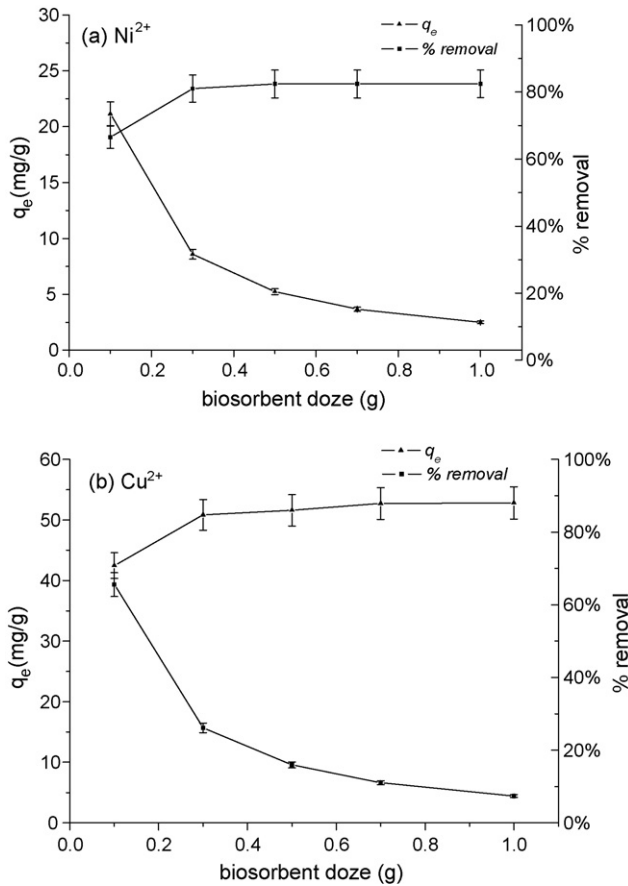| Copper		Nickel	
pH$_i$	pH$_f$	pH$_i$	pH$_f$
3	3.3	3	3.5
4	4.6	4	5.2
5	5.8	4.7	5.3
6	5.88	6	5.6
7	6.49	7	5.9

Fig. 3. Effect of biosorbent doze on biosorption of (a) nickel and (b) copper (biomass in 100 ml of 35 mg/L metal solution for 120 min with pH 4.7 for nickel and pH 4 for copper).

3.4. Kinetic study

Fig. 4 shows the sorption kinetics of copper and nickel ions using the treated *U. pinnatifida*. The sorption of both the metals was rapid in the first 20 min before becoming more gradual
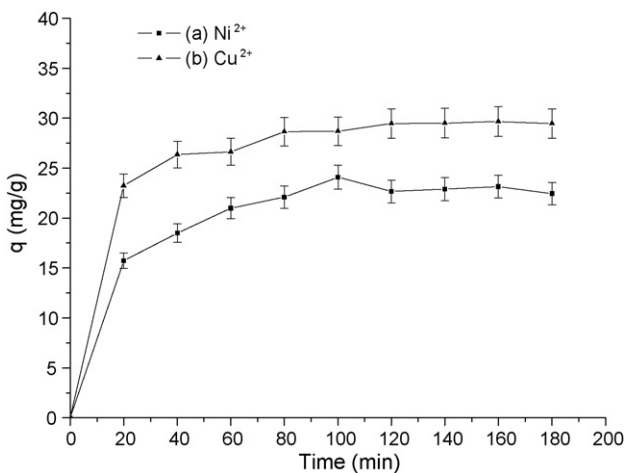

Fig. 4. Effect of sorption time on biosorption of (a) nickel and (b) copper (0.1 g biomass in 100 ml of 35 mg/L metal solution with pH 4.7 for nickel and pH 4 for copper).

until equilibrium was reached at about 100 min. This figure also verifies that sorption took place in two stages: a very rapid surface adsorption and a slow intracellular diffusion. Other studies published in literature also report similar results for sorption reactions such as the sorption of Cd^{2+} by biomass of fungal biosorbents [19], while in some other studies single-step uptake was suggested for different biosorbents [20].

3.5. Sorption isotherm models

Many sorption isotherm models have been successfully applied to experimental data. The simplest isotherm is based on the assumptions that every adsorption site is independent of whether or not adjacent sites are occupied. Among all of the models [21], two-parameter models including Langmuir, Freundlich and Temkin isotherms are widely used. These three isotherm models which can be calculated from the basis equilibrium equations [22] are examined in the present study. The experimental data for isotherm modeling is the results determined in initial concentration effect in Section 3.1.

Linear regression has been frequently used to evaluate the model parameters; however, the non-linear method is to be preferred because this method is more suited to the error structure of the data. The error of the estimates of the parameters can only be calculated consistently from a non-linear fitting procedure [23].

3.5.1. Langmuir isotherm

The Langmuir isotherms assume monolayer coverage of sorption of each molecule onto the surface has equal sorption activation energy. It has traditionally been used to quantify and contrast the performance of different biosorbents. It was originally developed to describe the gas–solid phase adsorption of activated carbon [8]. It has produced good agreement with wide variety of experimental data and can be expressed as follows:

$$q_e = \frac{q_m C_e}{1/b + C_e} \tag{4}$$

where q_m is the maximum amount of adsorption (mg/g), b is the sorption equilibrium constant (L/mg) and C_e is the equilibrium concentration of the copper or nickel ions in the solution (mg/L).

The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process. The essential features of the isotherm were called the equilibrium parameter (E_p) which is defined as follows:

$$E_p = \frac{1}{1 + bC_e} \tag{5}$$

It is reported that, when $0 < E_p < 1$, the sorption system is a favorable isotherm. It can be explained apparently that when $b > 0$, sorption system is favorable [24].

3.5.2. Freundlich isotherm

The Freundlich isotherm equation is also used to describe adsorption from a solution and is given by

$$q_e = K_c C_e^{1/n} \qquad (6)$$

where K_c is a constant for relative adsorptive capacity and n is an affinity constant. The equation can be written as a logarithm function for linear regression analysis [25].

3.5.3. Temkin isotherm

Another model, Temkin isotherm, was also used to fit the experimental data. Unlike the Langmuir and Freundlich equation, the Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [26]. The isotherm is as follows:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \qquad (7)$$

where A_T is the equilibrium binding constant corresponding to the maximum binding energy, b_T is the Temkin isotherm constant, T is the temperature (K), and R is the ideal gas constant ($8.315\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$).

Fig. 5 shows the sorption isotherms of nickel and copper ions on the treated *U. pinnatifida*. The sorption capacities for both the metals increased with an increase in the equilibrium metal concentration in solution. The experimental data were modeled according to Langmuir, Freundlich and Temkin isotherm, and the evaluated constants are given in Table 2. It is apparent that the Langmuir and Temkin isotherm were batter fits than the Freundlich isotherm equation for both nickel and copper sorption according to the values of R^2 and ε^2, the highest values of R^2 and the lowest values of ε^2 were 0.984, 0.982 and 0.847, 0.644 for nickel and copper, respectively. Two best values suggested the same results that Langmuir is the best model for nickel and Temkin is best for copper sorption. It is indicated that the sorption of nickel ion is similar to be a monolayer sorption. The sorption of copper is seemed to be a multilayer sorption, and the adsorption takes place on a nonuniform surface.

3.6. Kinetic modeling

In order to investigate the controlling mechanism of biosorption process such as mass transfer and chemical reaction, the pseudo-first-order, pseudo-second-order kinetic and the intraparticle diffusion models were used to test the experimental data of copper and nickel biosorption by treated *U. pinnatifida*. A number of models with varying degrees of complexity have
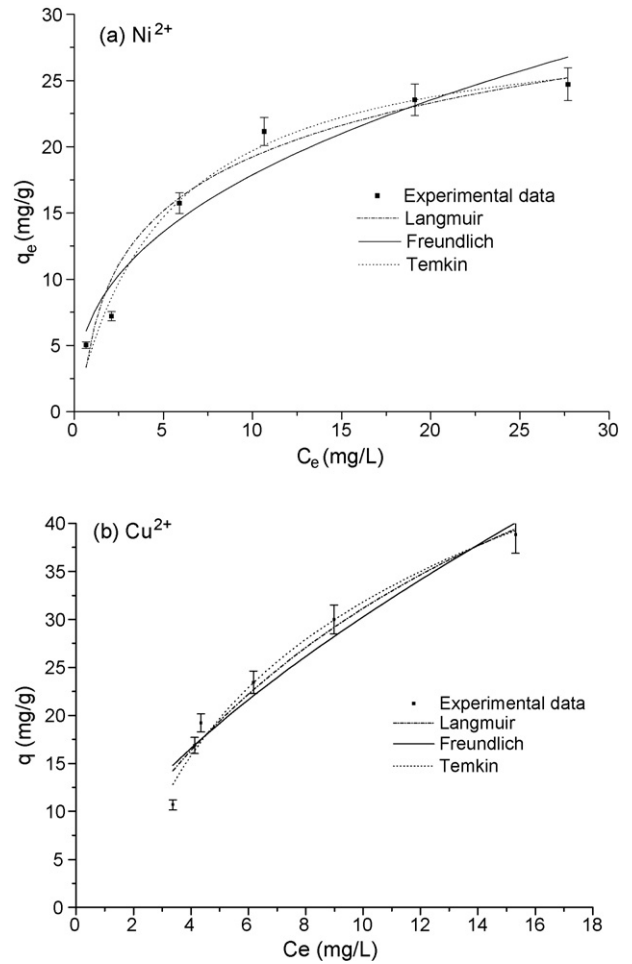

Fig. 5. Adsorption isotherms of (a) nickel and (b) copper on the biomass.

been developed to describe the kinetics of metal biosorption in batch systems. Due to presence of greater number of metal ions in industrial wastewater, the sorption equilibrium was reached much faster due to faster occupancy of sorption sites by metal ions.

Most commonly used pseudo-first-order Lagergren model is generally expressed as

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (8)$$

where q_t (mg/g) is the mass of metal adsorbed at time t and K_1 (min^{-1}) is the first-order reaction rate equilibrium constant. The equation can be written as

$$q_t = q_e - q_e \exp(-K_1 t) \qquad (9)$$

Table 2
Calculated equilibrium constants and thermodynamic parameters

Metal	Langmuir				Freundlich				Temkin			
	q_m (mg/g)	b (L/mg)	R^2	ε^2	K_c	n	R^2	ε^2	b_T	A_T (L/mg)	R^2	ε^2
Nickel	29.89	0.193	0.984	0.847	7.172	2.521	0.941	1.682	429.3	2.652	0.961	1.824
Copper	78.88	0.065	0.965	1.397	6.648	1.519	0.947	1.963	144.1	0.617	0.982	0.644

Table 3
Comparison between adsorption parameters of Lagergren pseudo-first-order, pseudo-second-order and inter-particle kinetic models

Metal	Pseudo-first-order				Experimental value	Pseudo-second-order				Inter-particle			
	q_e (mg/g)	K_1	R^2	ε^2	q_e (mg/g)	q_e (mg/g)	K_2 ($\times 10^{-3}$)	R^2	ε^2	K_p	C	R^2	ε^2
Nickel	22.82	0.051	0.987	0.311	24.01	25.04	3.336	0.990	0.213	0.760	14.109	0.73	0.732
Copper	28.87	0.075	0.990	0.270	29.67	30.74	4.842	0.998	0.051	0.672	21.518	0.87	0.190

The pseudo-first-order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites.

The best fit for the experimental data of this study was achieved by the application of pseudo-second-order kinetic equation. The pseudo-second-order equation based on adsorption equilibrium capacity assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites and may be expressed in the form

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where K_2 (g mg^{-1} min^{-1}) is the second-order reaction rate equilibrium constant. A plot of t/q_t against t should give a linear relationship for the applicability of the second-order kinetic model. For non-linear, the equation can be written as

$$q_t = \frac{t K_2 q_e^2}{1 + t K_2 q_e} \tag{11}$$

The intra-particle diffusion model [27] can be defined as

$$q_t = K_p t^{1/2} + C \tag{12}$$

where K_p is the intra-particle diffusion rate constant and C of adsorption constant is the intercept.

Three kinetic models of the biosorption were shown in Fig. 6. The sorption data of nickel and copper ions uptake by treated *U. pinnatifida* fitted with pseudo-first-order and pseudo-second-order kinetic model parameters are tabulated in Table 3. It is clear from the table that coefficient of correlation (R^2) and the Chi-square (ε^2) for the second-order kinetic model is higher and lower in comparison to first-order model, and the estimated value of q_e for the second-order kinetic is approximately close to the experimental values. Both of observations suggested that the pseudo-second-order kinetic model well fit the sorption of nickel and copper by the treated *U. pinnatifida* which relies on the assumption that biosorption may be the rate limiting step. Similar conclusions on the sorption of nickel were found by other researchers such as Zafar et al. entrapped biomass of rice bran [28]; Hanif et al. immobilized biomass of Cassia fistula (Golden Shower) [29] and M. Iqbal, A. Saeed using biomass of hybrid biosorbent [19]. Then other ions researchers such as Pratik M. Choksi and Vishal Y. Joshi [30] entrapped biomass of many natural adsorbents to remove aluminum and nickel found that the pseudo-first order is well fit the data.

The parameters of the intra-particle diffusion model were also presented in Table 3. Low R^2 and high ε^2 indicated apparently that the model did not fit the data well. It gives an indication that
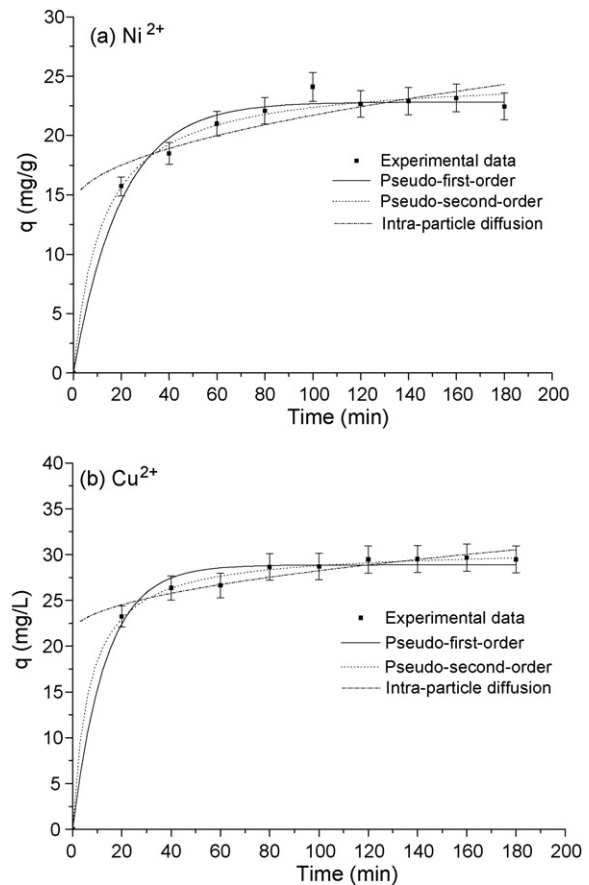

Fig. 6. Adsorption kinetic models of (a) nickel and (b) copper on the biomass.

intra-particle diffusion did not control the rate which consisted with the results taken from the pseudo-second-order that the biosorption may be a rate-limiting step.

4. Conclusions

Inexpensive, effective, readily available materials—*U. pinnatifida* can be used for the removal of heavy metals from solution. Column experiment should be the next research for the biosorption of metal ions by this biomass. From the results of the present study obtained, the following conclusions can be drawn:

1. *U. pinnatifida* can be obtained without excessive cost. Thus, it is cheapness and sufficiency as biomass for sorption of metal ions than other types of biosorbent materials found in literature.

2. The obtained results strongly demonstrated that pH, biomass doze, initial metal concentration and contact time affect the metal ions uptake capacity of biosorbents.

3. *U. pinnatifida* treated by $CaCl_2$ solution can be used for removal of nickel and copper ions from aqueous solutions effectively. The maximum uptake capacity for nickel and copper was 24.71 and 38.82 mg/g at pH 4.7 and 4 initial concentration 50 mg/L for 120 min.

4. The suitability of sorption isotherm models for the sorption of nickel and copper are Langmuir and Temkin, respectively. And the best isotherm models described the isotherm data with high R^2 and low values of ε^2.

5. Metal ion uptake capacity tests have shown that the biosorption process can be better described by pseudo-second-order kinetic model.

References

[1] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of heavy metals and radionuclide from aqueous solutions by pre-treated arca shell biomass, J. Hazard. Mater. 150 (2008) 376–386.

[2] M. Sprynskyy, B. Buszewski, A.P. Terzyk, J. Namieśnik, Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite, J. Colloid Interf. Sci. 304 (2006) 21–28.

[3] X. Feng, Z.C. Wu, X.F. Chen, Removal of metal ions from electroplating effluent by EDI process and recycle of purified water, Sep. Purif. Technol. 57 (2007) 255–261.

[4] P.K. Parhi, K. Sarangi, Separation of copper, zinc, cobalt and nickel ions by supported liquid membrane technique using LIX 84I, TOPS-99 and Cyanex 272, Sep. Purif. Technol. 59 (2008) 169–174.

[5] I. Giannopoulou, D. Panias, Copper and nickel recovery from acidic polymetallic aqueous solutions, Miner. Eng. 20 (2007) 753–760.

[6] K. Azetsu-Scott, P. Yeats, G. Wohlgeschaffen, J. Dalziel, S. Niven, K. Lee, Precipitation of heavy metals in produced water: influence on contaminant transport and toxicity, Mar. Environ. Res. 63 (2007) 146–167.

[7] L. Cassayre, P. Chamelot, L. Arurault, L. Massot, P. Palau, P. Taxil, Electrochemical oxidation of binary copper–nickel alloys in cryolite melts, Corros. Sci. 49 (2007) 3610–3625.

[8] K. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu, M. Velan, Biosorption of nickel(II) ions onto *Sargassum wightii*: application of two-parameter and three-parameter isotherm models, J. Hazard. Mater. B 133 (2006) 304–308.

[9] R. Biesuz, G. Alberti, G. D'Agostino, E. Magi, M. Pesavento, Determination of cadmium(II), copper(II), manganese(II) and nickel(II) species in Antarctic seawater with complexing resins, Mar. Chem. 101 (2006) 180–189.

[10] J.W. Ceri, G.J.E. Robert, Ion exchange in nickel biosorption by seaweed materials, Biotechnol. Progr. 13 (1997) 424–428.

[11] E.A. Moawed, M.F. El-Shahat, Preparation, characterization and application of polyurethane foam functionalized with a-naphthol for preconcentration and determination of trace amounts of nickel and copper in cast iron and granite, React. Funct. Polym. 66 (2006) 720–727.

[12] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column, Chemosphere 60 (2005) 419–426.

[13] S. Klimmek, H.J. Stan, Comparative analysis of the biosorption of cadmium, lead, nickel and zinc by algae, Environ. Sci. Technol. 35 (2001) 4283–4288.

[14] K. Naddafi, R. Nabizadeh, R. Saeedi, A.H. Mahvi, F. Vaezi, K. Yaghmaeian, A. Ghasri, S. Nazmara, Biosorption of lead(II) and cadmium(II) by protonated *Sargassum glaucescens* biomass in a continuous packed bed column, J. Hazard. Mater. 147 (2007) 785–791.

[15] P.X. Sheng, Y.P. Ting, J. Paul Chen, Biosorption of heavy metal ions (Pb, Cu, and Cd) from aqueous solutions by the marine alga *Sargassum* sp. in single- and multiple-metal systems, Ind. Eng. Chem. Res. 46 (2007) 2438–2444.

[16] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.

[17] J.M. Tobin, D.G. Cooper, R.J. Neufeld, Uptake of metal ions by *Rhizopus arrhizus* biomass, Appl. Environ. Microb. 47 (1984) 821–824.

[18] M. Iqbal, A. Saeed, Production of an immobilized hybrid biosorbent for the sorption of Ni(II) from aqueous solution, Process Biochem. 42 (2007) 148–157.

[19] P.H. Yin, Q.M. Yu, B. Jin, Z. Ling, Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater, Water Res. 33 (1999) 1960–1963.

[20] J.P. Huang, C.P. Huang, A. Morehart, The removal of Cu(II) from dilute aqueous solutions by *Saccharomyces cerevisiae*, Water Res. 24 (1990) 433–439.

[21] F. Pagnanelli, A. Esposito, L. Toro, F. Vegliò, Copper and cadmium biosorption onto sphaerotilus natans: application and discrimination of commonly used adsorption models, Sep. Sci. Technol. 37 (2002) 677–699.

[22] W. Ma, J.M. Tobin, Development of multimetal binding model and application to binary metal biosorption onto peat biomass, Water Res. 37 (2003) 3967–3977.

[23] L.J.A. Gerringa, P.M.J. Herman, T.C.W. Poortvliet, Comparison of the linear Van den Berg/Ruzic transformation and a non-linear fit of the Langmuir isotherm applied to Cu speciation data in the estuarine environment, Mar. Chem. 48 (1995) 131–142.

[24] V.J.P. Poots, J. McKay, J. Healy, Removal of basic dye from effluent using wood as an adsorbent, J. Water Pollut. Contr. Federation (1978) 926–934.

[25] S. Pradhan, S.S. Shukla, K.L. Dorris, Removal of nickel from aqueous solutions using crab shells, J. Hazard. Mater. B 125 (2005) 201–204.

[26] S.B. Deng, Y.P. Ting, Fungal biomass with grafted poly(acrylic acid) for enhancement of Cu(II) and Cd(II) biosorption, Langmuir 21 (2005) 5940–5948.

[27] W. Ma, F.Q. Ya, M. Han, R. Wang, Characteristics of equilibrium, kinetics studies for adsorption of fluoride on magnetic-chitosan particle, J. Hazard. Mater. 143 (2007) 296–302.

[28] M.N. Zafar, R. Nadeem, M.A. Hanif, Biosorption of nickel from protonated rice bran, J. Hazard. Mater. 143 (2007) 478–485.

[29] M.A. Hanif, R. Nadeem, M.N. Zafar, K. Akhtar, H.N. Bhatti, Kinetic studies for Ni(II) biosorption from industrial wastewater by Cassia fistula (Golden Shower) biomass, J. Hazard. Mater. 145 (2007) 501–505.

[30] P.M. Choksi, V.Y. Joshi, Adsorption kinetic study for the removal of nickel(II) and aluminum(III) from an aqueous solution by natural adsorbents, Desalination 208 (2007) 216–231.