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TECHNICAL NOTE

Equilibrium and kinetic studies on biosorption potential of charophyte biomass to remove heavy metals from synthetic metal solution and municipal wastewater

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ABSTRACT

The risk of heavy metal contamination in domestic water causes serious health and environmental problems. Biosorption has been considered as an efficient and alternative way for treatment of heavy metal–contaminated wastewater. The potentials of dried charophytes, *Chara aculeolata* and *Nitella opaca*, to biosorb lead (Pb), cadmium (Cd), and zinc (Zn) from synthetic solutions and municipal wastewater were investigated. The efficiency of metal removal was studied under varied conditions in different sorbent dosages, pH, and contact times. Biosorption isotherm and kinetics were used to clarify heavy metal preference and biosorption mechanism. *C. aculeolata* and *N. opaca* performed well in the biosorption of all three metal ions, with preference towards Pb, followed by Cd and Zn, in the single-metal solutions. Pb adsorption onto algal biomass followed first-order rate kinetics (*N. opaca*) and intraparticle diffusion (*C. aculeolata* and *N. opaca*). These results indicated physical adsorption process between Pb ions and both algal biomasses. Cd and Zn biosorption kinetics fitted the second-order rate model, indicating chemical adsorption between metal ions and both algae. The experimental data of three-metal biosorption fitted well to Langmuir isotherm model, suggesting that the metal ion adsorption occurred in a monolayer pattern on a homogeneous surface. *C. aculeolata* exhibited slightly higher maximum uptake of Pb, Cd, and Zn (105.3 mgPb/g, 23.0 mgCd/g, 15.2 mgZn/g) than did *N. opaca* (104.2 mgPb/g, 20.5 mgCd/g, 13.4 mgZn/g). In multi-metal solutions, antagonistic effect by metal competition was observed. The ability of charophytes to remove Pb and Zn was high in real municipal water (81–100%). Thus, the charophytic biomass may be considered for the treatment of metal contamination in municipal wastewater.

Introduction

The presence of heavy metals in municipal and industrial wastewaters is of great concern, since many treatment plants, particularly the municipal facilities, are often not designed and equipped for handling toxic metal wastes (Shirazi and Marandi 2012). Lead (Pb), cadmium (Cd), and zinc (Zn) are widely used as construction materials and in many industrial and agricultural applications. These metals are often introduced in significant quantities to wastewater by industrial and residential (rural and urban) runoff; consequently, increase of health and environmental risks arise from the presence of toxic metals in the effluent and sludge from wastewater treatment plants (Vargová et al. 2005). Surveys by Vargová et al. (2005),

Johnson et al. (2008), Water Quality Management Bureau, Thailand (2009), Kang et al. (2014), and Onchoke, Janusa, and Sasu (2015) showed that the concentrations of heavy metals in municipal wastewater influent were in the following ranges: <0.05–1.70 mgPb/L, <0.009–0.8 mgCd/L, and 0.13–14.5 mgZn/L.

Most conventional technologies, including chemical precipitation, electrochemical treatment, reverse osmosis, and ion exchange, are ineffective for treatment of wastewater containing low concentrations of heavy metals and may be considered expensive for municipal facilities (Volesky 2001). Biosorption using organic or agricultural solid waste has been proposed

as an alternative, effective, and inexpensive technique for removal of heavy metal ions, which is mainly based on physicochemical sequestration by metal ligands naturally present in dead biomass (Gupta and Rastogi 2009). A number of biosorbents have been investigated for sorption of heavy metals, such as Pb, Cd, and Zn, and materials that are available in large quantities and at low cost are generally preferred (Mohan and Singh 2002; Sheng et al. 2004; Ho 2005; Vilar, Botelho, and Boaventura 2005; Fan et al. 2008; Lawal et al. 2010).

Macroalgae are an attractive choice as biosorbents because they are ubiquitous and abundant in aquatic environments, are easy to harvest, and have high affinity for a variety of metal ions (Gupta and Rastogi 2008; Deng et al. 2009). *Chara* and *Nitella* are major genera of the characean green algae (Characeae) growing abundantly in a wide range of fresh and brackish water bodies (Coops 2002; Schneider et al. 2015). In eutrophic areas, the abundance of some *Chara* and *Nitella* species may reach a nuisance level, reduce other plant and animal diversity, have to be dumped by manpower or biological and chemical control, and produce the regenerative source as massive biomaterial (Królikowska 1997; Petty 2005). A few laboratory studies, including ours, have demonstrated the metal accumulation or biosorption potential of living charophytes (Gomes and Asaeda 2009; Bibi, Asaeda, and Azim 2010; Gao and Yan 2012; Sooksawat et al. 2013). However, data are still lacking on the use of nonliving charophytic biomass for remediation of heavy metals. In the present study, the biosorption potential and mechanisms of dried biomass of *C. aculeolata* and *N. opaca* in removing Pb, Cd, and Zn from synthetic solutions and municipal wastewater samples that contained low concentrations of organic wastes and very low to moderate concentrations of toxic metal ions were examined.

Materials and methods

Preparation of sorbents

C. aculeolata biomass was collected from Bueng Boraphet freshwater reservoir, Nakhon Sawan, Thailand. *N. opaca* was collected from freshwater ponds in Bangkok, Thailand. Whole algal samples were cleaned with tap and distilled water to remove debris and epiphytes, and dried at 60°C in a hot air oven for 24 h. The dried biomass was ground, passed through a 0.625-mm sieve, and stored in a desiccator (Bunluesin et al. 2007; Seolatto, Filhoa, and Mota 2012).

Pb, Cd, and Zn removal efficiency

Analytical-grade 1000 mg/L standard solutions of Pb $(NO_3)_2$, $Cd(NO_3)_2$, and $Zn(NO_3)_2$ were diluted with Milli-Q water to the indicated concentrations and adjusted to the indicated pH using 0.1 M HCl and 0.1 M NaOH. Biosorption experiments were carried out in 125-ml stoppered conical flasks containing 50 ml of metal solution. The reaction mixture was shaken on a rotary shaker at 150 rpm, 25 ± 2°C for 24 h, or as indicated otherwise, and then filtered through a 0.45-μm Whatman membrane filter. Each filtrate was acidified below pH 2 and determined for remaining metal using a flame atomic adsorption spectrophotometer (FAAS; Variance SpectrAA 55B; Varian Australia Pty Ltd, Australia). All experiments were carried out in triplicate. The negative controls were solutions without algal biomass to ensure the initial metal concentration in the solution (Mohan and Singh 2002; Saeed, Iqbal, and Akhtar 2005; Bunluesin et al. 2007; Pan et al. 2010).

The influence of sorbent dosage (0.1, 0.2, 0.5, 1, 2, 3, and 4 g/L), pH (2, 3, 4, 5, 6, 7, and 8), and contact time (3, 15, 30, 60, 90, 120, 180, and 360 min) on biosorption of Pb, Cd, and Zn were studied. Except where stated, the conditions for biosorption experiments were 2 g/L *C. aculeolata*, 3 g/L *N. opaca*, 10 mg/L metal solutions, pH 4, and contact time 6 h. The efficiency of the sorbent was determined by metal removal efficiency (Lawal et al. 2010) calculated as follows:

$$\text{Removal efficiency (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

where C_i is the initial metal ion concentration (mg/L) and C_e is the final or equilibrium concentration of metal ion in solution (mg/L).

Equilibrium between the amounts of metal adsorbed and desorbed was determined by the point at which no further increase in metal removal from solution was observed. All experiments were performed in triplicate, and the average values were analyzed by an analysis of variance (ANOVA), with differences determined using Tukey honestly significant difference (HSD) multiple-comparison test in the

SPSS for Windows program (version 17; Chicago, IL, USA). The criterion of significance was the .05 level of probability.

Biosorption kinetics

To better understand biosorption mechanisms of the two algal biomasses, the amounts of metal ions sorbed by the biomass (q) at different contact times (3, 15, 30, 60, 90, 120, 180, 360 min) were first calculated. Then these values were tested for fitting to the Langergren's pseudo-first-order and Ho's pseudo-second-order models expressed in the linear forms (Fan et al. 2008) and intraparticle diffusion model (Weber and Morris 1962). Both pseudo-first-order and pseudo-second-order models predict the adsorption rate and mechanism based on the rate-limiting step as physical and chemical adsorption, respectively, between adsorption sites and heavy metal ions. The following equations Equations (2–5) were used to determine the biosorption mechanisms of both algal biomasses. At first, the q values at a given time point (q) or at equilibrium (q_e) were calculated using the following equations (Fan et al. 2008):

$$q = \frac{(C_i - C_e)V}{M} \qquad (2)$$

where q is the amount of metal sorbed (mg/g) at a given time; C_i and C_e are the metal concentrations (mg/L) in the aliquot from reaction mixture taken at initial time point and time t, respectively; V is the solution volume (L); and M is the sorbent dosage (g).

Langergren's pseudo-first-order rate:

$$\log(q_e - q) = \log q_e - \frac{k_{ad1}}{2.303}t \qquad (3)$$

Ho's pseudo-second-order rate:

$$\frac{t}{q} = \frac{1}{k_{ad2}q_e^2} + \frac{1}{q_e}t \qquad (4)$$

where q and q_e (mg/g) are the amounts of metal ions sorbed at time t and at equilibrium time (min), and were calculated using Equations 2 and 3, respectively; k_{ad1} is the specific rate constant of the first-order model and is calculated as the slope of the best-fit line from a plot of log ($q_e - q$) versus t; and k_{ad2} is the specific rate constant of the second-order model and is

determined by the intercept of the best-fit line from a plot of t/q versus t.

Intraparticle diffusion model describes a physical adsorption whose rate-controlling step is diffusion process of metal ions through pores at the sorbents' surface. The q values were plotted against $t^{1/2}$ for all three metals exhibiting an initial curve portion, which corresponds to the boundary layer sorption, followed by a linear portion, which indicates an effect of intraparticle diffusion. The experimental data were applied to the equation given by Weber and Morris (Waranusantigul et al. 2003):

$$q = k_{id}t^{\frac{1}{2}} \qquad (5)$$

where q is the amount of metal adsorbed (mg/g) at time t (min), calculated using Equation 2; and k_{id} is the intraparticle diffusion constant and is determined as the slope of the linear portion of the best-fit line in a plot of q versus $t^{1/2}$.

Biosorption isotherms

To describe the biosorption pattern between biosorbent and adsorbate, Langmuir and Freundlich isotherms were used. Unlike the Langmuir model, which assumes single-layer coating of metal ions on the homogeneous sorbent's surface, the Freundlich model describes sorption behavior on heterogeneous active sites. The amounts of metal ions sorbed were determined at various initial metal concentrations (1, 5, 10, 50, 100, 200, 300, and 400 mg/L) using Equation 2 and applied to the Langmuir and Freundlich isotherms expressed in the linear forms (Davis, Volesky, and Mucci 2003) as follows:

Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \qquad (6)$$

Freundlich model:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (7)$$

where q_e and Q_m are the amounts of metal sorbed at equilibrium and at maximum capacity (mg/g), respectively; K_L is Langmuir equilibrium constant (L/mg), which relates to affinity of metal ions toward the sorbent; K_F is Freundlich equilibrium constant

$(L/g)^{1/n}$, which relates to biosorption capacity; and n is empirical parameter relating to the biosorption intensity, which varies with the heterogeneity of the material.

Pb, Cd, and Zn biosorption in multi-metal solutions

As wastewater typically contains high concentrations of several metals, the biosorption experiments were conducted to examine characteristics of the algal sorbents in multi-metal solutions. The reaction mixtures were conducted as previously described for the biosorption experiments in single-metal solutions. The synthetic multi-metal solutions were prepared from the standard solutions of $Pb(NO_3)_2$, $Cd(NO_3)_2$, and $Zn(NO_3)_2$ and contained equal concentrations of the metals at 1, 5, 10, 50, 100, and 200 mg/L. The amounts of metal sorbed were calculated using Equation 2 and applied to the Langmuir and Freundlich isotherms using Equations 6 and 7, as previously described.

Pb, Cd, and Zn removal from municipal wastewater

Performance of the algal sorbents was next evaluated in municipal wastewater that contained high Pb, Cd, and Zn concentrations, along with other organic and inorganic substances. Samples of municipal wastewater influent were collected by grab sampling from two different wastewater treatment facilities in Bangkok, Thailand, during the same period of time and stored in plastic bottles. The samples from the Din Daeng plant and the Si Phraya plant were designated as municipal water-1 and municipal water-2, respectively. The water samples were analyzed for water quality (temperature, pH, dissolved oxygen [DO], biochemical oxygen demand [BOD], electrical conductivity, and total dissolved solids [TDS]) prior to filtration to remove solid sediment. The filtrate was then analyzed for Pb, Cd, and Zn concentrations using FAAS (Table 1). Because the original concentrations of Pb, Cd, and Zn were very low to undetectable, standard solutions of $Pb(NO_3)_2$, $Cd(NO_3)_2$, and $Zn(NO_3)_2$ were added to the wastewater samples to bring the estimated final concentrations to 2 mgPb/L, 0.3 mgCd/L, and 6 mgZn/L, which were 10-fold greater than accepted wastewater quality standard (Ministry of Science and Technology, Thailand 1996). The measurable concentrations of the metals in the modified water samples are shown in Table 4, and the removal

Table 1. Water quality parameters and composition of two municipal wastewater samples (before metal supplementation).

Parameter	Municipal water-1	Municipal water-2
Temperature (°C)	32.6 ± 0.2	30.5 ± 0.0
pH	7.2 ± 0.0	7.3 ± 0.0
DO (mg/L)	0.5 ± 0.4	0.3 ± 0.1
BOD (mg/L)	0.5 ± 0.4	0.3 ± 0.1
Electrical conductivity (μS/cm)	568.5 ± 0.7	504.5 ± 2.1
TDS (g/L)	0.3 ± 0.0	0.3 ± 0.0
Metal (mg/L)		
Pb	ND	ND
Cd	ND	ND
Zn	0.058	0.076
Mn	ND	0.05
Na	45.1	28.1
K	8.7	7.28
Mg	10.4	7.39
Ca	35.8	35.4
Anion (mg/L)		
Cl^-	70.2	30.6
NO_3^-	5.6	1.9
NO_2^-	0.89	0.75
SO_4^{2-}	55.2	43.0
PO_4^{3-}	0.6	0.7

ND = not detectable (detection limits: Pb = 0.05 mg/L; Cd = 0.002 mg/L; Mn = 0.025 mg/L).

efficiency of heavy metal ions was calculated by using Equation 1 as previously described.

Results

Effect of sorbent dosage on metal removal efficiency

The sorbent dosage was not critical in Pb removal, as the maximum efficiency was attained by as little as 0.2 g/L biomass for both algae (Figures 1a and 1b). In contrast, the removal efficiency of Cd and Zn increased with the sorbent dosage and reached their respective maxima when 2 g/L *C. aculeolata* and 3 g/L *N. opaca* biomasses were used. Therefore, these optimal sorbent dosages were selected for further studies.

Effect of initial pH on metal removal efficiency

Both *C. aculeolata* and *N. opaca* exhibited maximum removal efficiency of all three metal ions when the solution was initially adjusted to pH 4 (Figures 1c and 1d). For *C. aculeolata*, removal efficiency of Cd was highest in the solutions above pH 3 (Figure 1c). A similar trend was observed for removal of Zn by *C. aculeolata*, but its removal efficiency was reduced in the solution above pH 7. For *N. opaca*, the effects of pH on removal efficiency of Cd and Zn were more pronounced (Figure 1d). Cd was efficiently removed in the solutions above pH 4, whereas the removal efficiency of Zn was optimal between pH 4 and 6.
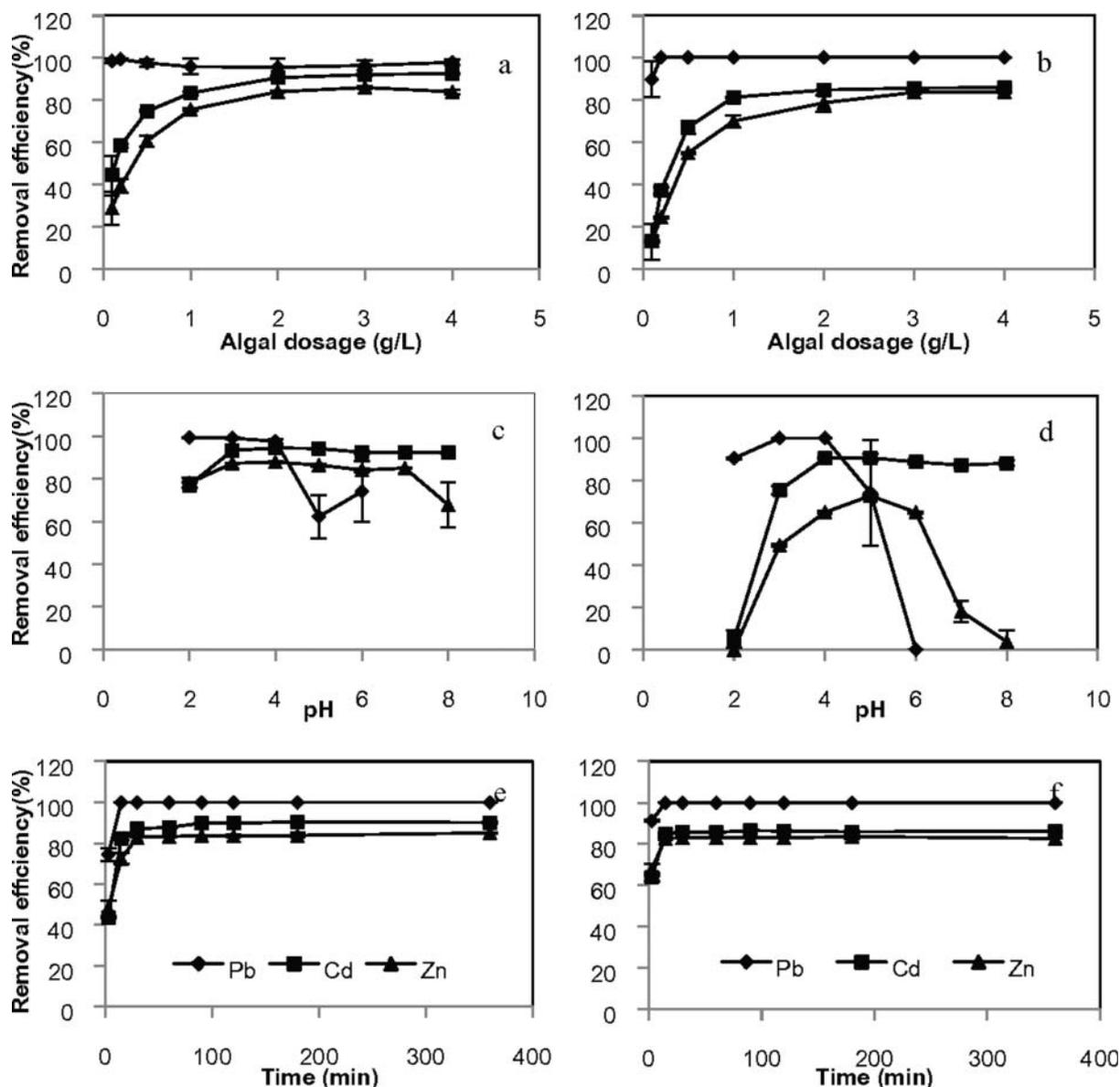
Figure 1. Effects of algal dosage (*a, b*), initial pH (*c, d*), and contact time (*e, f*) on biosorption of Pb (circles), Cd (squares), and Zn (triangles) by *C. aculeolata* (*a, c, e*) and *N. opaca* (*b, d, f*). Initial metal concentrations, 10 mg/L; *Chara* dose, 2 g/L; *Nitella* dose, 3 g/L; contact time, 6 h; temperature, $25 \pm 2°C$; agitation rate, 150 rpm; pH 4. Error bars represent standard deviation of the mean (*n* = 3).

Biosorption of Pb by *C. aculeolata* and *N. opaca* was most efficient between pH 2 and pH 4. At the highest biosorption efficiency, 98%, 95%, and 88% of Pb, Cd, and Zn were removed by *C. aculeolata*, respectively, whereas 100%, 91%, and 65% were removed by *N. opaca*, respectively. Because pH 4 yielded optimal removal efficiency for all three metals by both algal biomasses, this pH value was used for further studies.

Effect of contact time on metal removal efficiency

Pb sorption to *C. aculeolata* biomass reached equilibrium within 15 min, whereas 90 min of contact time was required for Cd sorption, and 30 min for Zn sorption (Figure 1e). The equilibrium for *N. opaca* biosorption was reached relatively sooner, within 15 min for all three metals (Figure 1f).

Biosorption kinetics

Table 2 shows that the sorption kinetics of Cd and Zn onto both algal biomasses fitted well with the pseudo-second-order model (Figures 2a and 2b), exhibiting higher correlation coefficients ($R^2 > 0.99$) than those of the pseudo-first-order model, suggesting chemisorption by ion-exchange process between Cd and Zn

Table 2. Parameters in pseudo-first-order, pseudo-second-order kinetics, and intraparticle diffusion for adsorption of Pb, Cd, and Zn ions by *C. aculeolata* and *N. opaca*.

Heavy metal	q_{exp}	First-order kinetic			Second-order kinetic			Intraparticle diffusion	
		k_{ad1}	q_e	R^2	k_{ad2}	q_e	R^2	k_{id}	R^2
C. aculeolata									
Pb	54.05	0.07	56.75	0.9401	0.001	74.63	0.9422	11.36	0.9776
Cd	3.69	0.05	1.03	0.7468	0.157	3.74	1.0000	0.21	0.6388
Zn	4.48	0.07	1.50	0.8344	0.108	4.60	1.0000	0.23	0.7227
N. opaca									
Pb	27.83	0.16	33.24	0.9130	0.002	37.04	0.8058	5.94	0.9175
Cd	2.37	0.05	0.23	0.5764	1.152	2.37	1.0000	0.07	0.5712
Zn	2.98	0.05	0.20	0.5494	6.793	2.98	1.0000	0.06	0.5308

Note. q_{exp} = metal uptake obtained from the experiments (mg/g); q_e = the theoretical metal uptake (mg/g); k_{ad1} = the first-order rate constant; k_{ad2} = the second-order rate constant; R^2 = correlation coefficient.

onto the algal biomasses (Bulgariu and Bulgariu 2012). The theoretical metal uptake (q_e) values obtained from the pseudo-second-order model (3.74 and 4.60 mg/g Cd and Zn onto *C. aculeolata* biomass; 2.37 and 2.98 mgCd/g and Zn onto *N. opaca* biomass) were similar to the experimental metal uptake (q_{exp}) data (3.69 and 4.48 mgCd/g and Zn onto *C. aculeolata* biomass; 2.37 and 2.98 mgCd/g and Zn onto *N. opaca* biomass) for sorption of Cd and Zn onto the algal

biomasses, thus confirming that the pseudo-second-order kinetic model was suitable for describing the adsorption kinetics of Cd and Zn by these algal biomasses. The sorption kinetics of Pb fitted better to the pseudo-first-order rate and intraparticle diffusion model for *N. opaca* (Table 2 and Figures 2c and 2d), indicating that the rate-limiting step is physisorption depending on the physical characteristics of *N. opaca* biomass (Fan et al. 2008). When the performances of the two algal sorbents were compared, the results showed that the kinetic constants (k_{ad1} and k_{ad2}) from the fitted model for all three metals sorbed by *N. opaca* were greater than those by *C. aculeolata*, indicating faster rates of metal biosorption by *N. opaca* biomass.

In case of Pb adsorption onto *C. aculeolata* biomass, high correlation coefficients ($R^2 > 0.97$) of the linear portions of the intraparticle diffusion model were observed (Table 2 and Figure 2d), thus the rate-limiting phenomenon on Pb adsorption onto *C. aculeolata* biomass was physisorption through intraparticle diffusion process. When the intraparticle diffusion constants (k_{id}) were compared, the results showed that the k_{id} values were much higher for Pb sorption than for Cd and Zn sorption by both algal
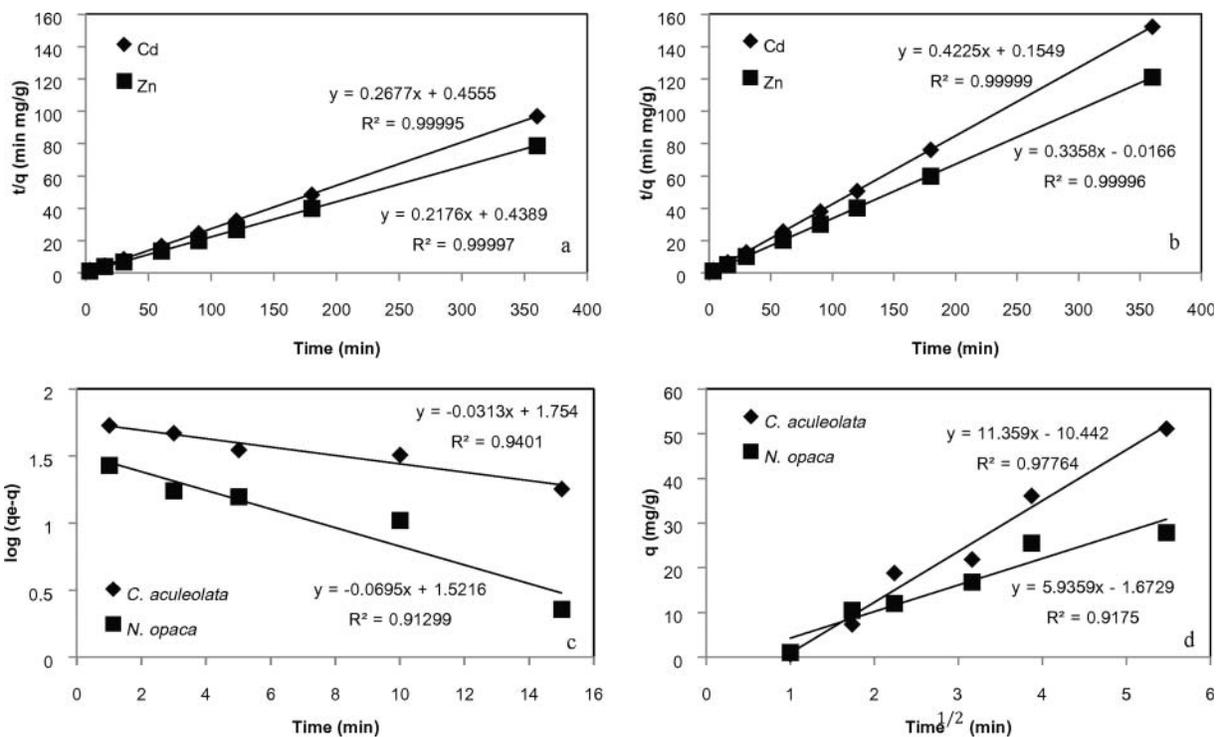

Figure 2. Linear portions of the fitted data to the pseudo-second-order kinetics (*a, b*), the pseudo-first-order kinetic (*c*), and the intraparticle diffusion (*d*). *C. aculeolata* (*a, c, d*) and *N. opaca* (*b, c, d*) were exposed to Pb, Cd, and Zn at pH 4; *Chara* dose, 2 g/L; *Nitella* dose, 3 g/L; temperature, 25 ± 2°C; agitation rate, 150 rpm. The data were derived from averages of triplicate experiments.

sorbents, suggesting that Pb ions exhibit higher mobility through pores of the biomasses and that intraparticle diffusion plays a significant role in the Pb biosorption process.

Biosorption isotherms

The amount of metals sorbed by both algal biomasses initially correlated with the equilibrium concentrations of the metals in solution until the sorbent capacity eventually became saturated (Figures 3a and 3b). Our experimental data of three-metal biosorption fitted better with the Langmuir model than did the Freundlich model for both algal biomasses ($R^2 > 0.95$; Table 3), suggesting that the sorbents' surface exhibits rather homogenous binding properties. The experimental q_e values (100.3, 42.2, and 15.3 mgPb/g, Cd, and Zn, respectively, in *C. aculeolata* and 80.6, 17.5, and 12.2 mgPb/g, Cd, and Zn, respectively, in *N. opaca*; Figures 3a and 3b) obtained were similar to Q_m (105.3, 23.0, and 15.5 mgPb/g, Cd, and Zn, respectively, in *C. aculeolata* and 104.2, 20.5, and 13.4 mg/g Pb, Cd, and Zn, respectively, in *N. opaca*; Table 3). These indicate that the Langmuir model isotherm can

be used to describe the Pb, Cd, and Zn biosorption by these algal biomasses. The estimated maximum adsorption capacity (Q_m) is shown in Table 3. Notably, the Q_m values for Pb sorption by both algal biomasses were much higher than those of other metals. The Q_m values showed the order of metal preference as Pb > Cd > Zn.

Biosorption in multi-metal solutions

Figures 3c and 3d show the relationship between the amounts of metal ions sorbed by the algal biomass and the equilibrium concentrations of metal ions in multi-metal solutions. As for biosorption in single-metal solutions, the experimental data generally fitted better to the Langmuir model than did Freundlich model ($R^2 > 0.95$; Table 3). Compared with the biosorption in single-metal solutions (Q_m: 105.3, 23.0, and 15.2 mgPb/g, Cd, and Zn by *C. aculeolata* and 104.2, 20.5, and 13.42 mgPb/g, Cd, and Zn by *N. opaca*), the maximum sorption capacity for each metal was lower when the biomass was used to treat the multi-metal solutions (Q_m: 43.1, 6.7, and 7.8 mgPb/g, Cd, and Zn by *C. aculeolata* and 58.1, 2.4, and 3.9 mg/
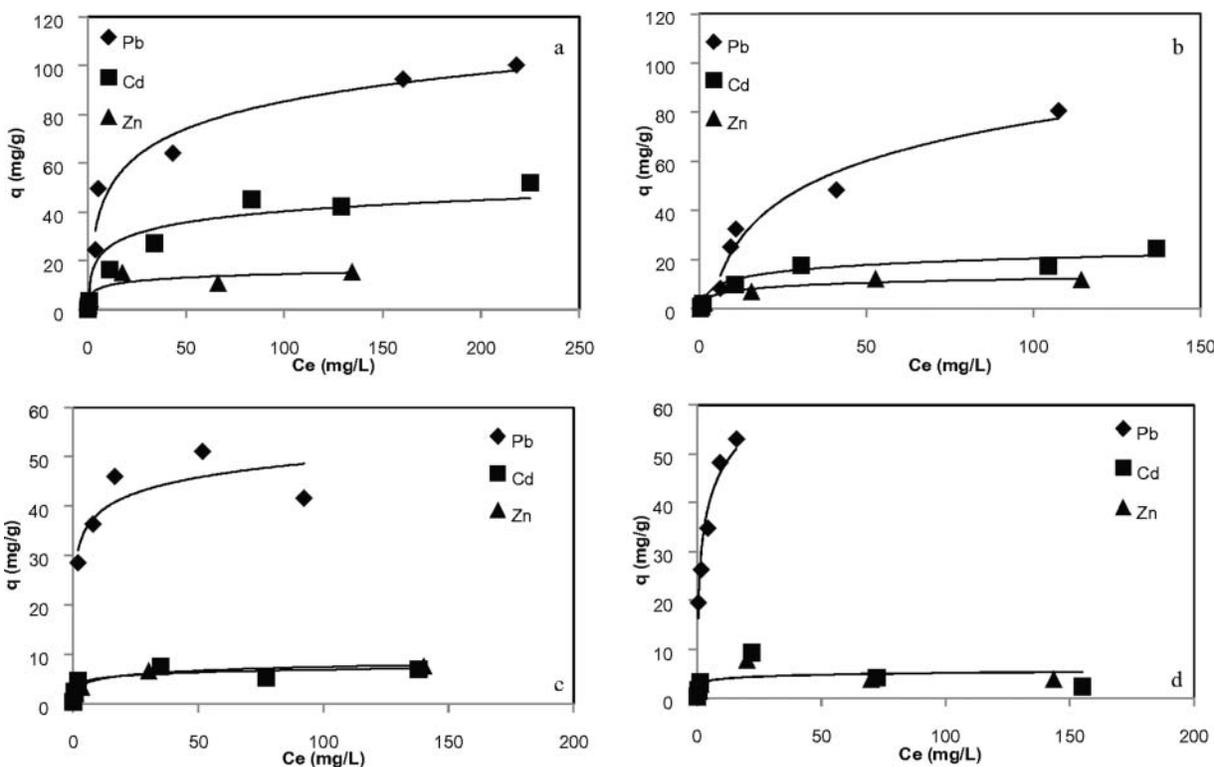

Figure 3. Biosorption isotherms for single-metal solutions (*a, b*) and multi-metal solutions (*c, d*) by using *C. aculeolata* (*a, c*) and *N. opaca* (*b, d*) (pH 4; *Chara* dose, 2 g/L; *Nitella* dose, 3 g/L; contact time, 6 h; temperature, 25 ± 2°C; agitation rate, 150 rpm). The data were derived from averages of triplicate experiments.

Table 3. Biosorption isotherm constants for the adsorption of single-metal solutions and multi-metal solutions by *C. aculeolata* and *N. opaca*.

	Langmuir model											
	Single-metal solutions						Multi-metal solutions					
	C. aculeolata			*N. opaca*			*C. aculeolata*			*N. opaca*		
Heavy metal	Q_m	K_L	R^2	Q_m	K_L	R^2	Q_m	K_L	R^2	Q_m	K_L	R^2
Pb	105.26	0.0610	0.9877	104.17	0.0283	0.9561	43.10	1.5163	0.9867	58.14	0.5566	0.9855
Cd	23.04	0.1163	0.9814	20.45	0.0908	0.9824	6.65	0.5168	0.9709	2.38	0.1452	0.9516
Zn	15.15	0.1743	0.9645	13.42	0.0804	0.9734	7.81	0.2868	0.9997	3.89	1.0822	0.9934

	Freundlich model											
	Single-metal solution						Multi-metal solution					
	C. aculeolata			*N. opaca*			*C. aculeolata*			*N. opaca*		
Heavy metal	n	K_F	R^2	n	K_F	R^2	n	K_F	R^2	n	K_F	R^2
Pb	3.58	22.45	0.8612	1.95	7.47	0.9443	8.25	28.46	0.6797	3.55	24.30	0.9823
Cd	1.97	3.95	0.9552	1.72	1.63	0.9281	3.37	2.10	0.7968	2.47	1.59	0.7170
Zn	2.00	2.00	0.8745	2.19	1.73	0.9367	2.45	1.47	0.8909	2.20	1.18	0.6733

Note. Q_m = maximum adsorption capacity (mg/g); K_L = Langmuir constant; K_F = Freundlich constant; n = Biosorption intensity.

g Pb, Cd, and Zn by *N. opaca*), suggesting antagonistic effects between metals in the solutions. However, the higher Langmuir constant (K_L) values (0.56–1.52, 0.15–0.52, and 0.29–1.08 L/mg Pb, Cd, and Zn, respectively) suggest that metal ions bound more strongly to the sorbents when other metal ions were present in the solution. Interestingly, the Q_m values showed the different order of metal preference as Pb > Zn > Cd by both algal biomasses.

Biosorption in municipal wastewater

Pb and Zn ions in both the synthetic multi-metal solution and the municipal wastewaters were effectively removed by both algal sorbents, yielding posttreatment Pb and Zn concentrations that were lower than the limits currently permitted in Thailand (Table 4). More than 70% of Cd could also be removed by the algal sorbents under the test condition. However, the

posttreatment Cd concentration still exceeded the permissible level.

Discussion

Removal efficiency of Pb, Cd, and Zn by two charophytic algae correlated with the amount of algal biomass. This correlation is probably attributed to the increased availability of metal binding sites, as previously suggested by Vijayaraghavan, Palanivelu, and Velan (2006) and Waranusantigul et al. (2003). Similar amounts of *C. aculeolata* (2 g/L) and *N. opaca* (3 g/L) were required for optimal removal efficiency of the metal ions, in agreement with the comparable maximum sorption capacities exhibited by the two algal sorbents (Table 3). The low sorbent dosage requirement, compared with *Ceramium virgatum* (10 g/L) and seed husk waste (20 g/L), underscores the potential of charophytic biomass in treatment of heavy

Table 4. Removal of heavy metal ions from synthetic solution and municipal wastewater by *C. aculeolata* and *N. opaca*.

| | Synthetic solution | | | Municipal water-1 | | | Municipal water-2 | | | |
| | | Final concentration (mg/L) | | | Final concentration (mg/L) | | | Final concentration (mg/L) | | |
Pollutant	Initial concentration (mg/L)	*C. aculeolata*	*N. opaca*	Initial concentration (mg/L)	*C. aculeolata*	*N. opaca*	Initial concentration (mg/L)	*C. aculeolata*	*N. opaca*	Permissible limit in Thailand (mg/L)
Pb	1.143	ND (100)	ND (100)	1.615	ND (100)	ND (100)	1.513	ND (100)	ND (100)	0.20
Cd	0.387	0.038 (90.2)	0.050 (87.1)	0.401	0.072 (82.1)	0.104 (74.0)	0.396	0.072 (82.0)	0.110 (72.1)	0.03
Zn	5.804	0.734 (87.3)	1.086 (81.3)	6.315	1.221 (80.7)	1.167 (81.5)	6.371	1.134 (82.2)	1.147 (82.0)	5.00

Note. Numbers in parenthesis are percentages of metal removed. ND = not detectable (detection limit of Pb = 0.05 mg/L).

metals in large volumes of wastewater (Sari and Tuzen 2008; Lawal et al. 2010). The metal biosorption efficiency of *N. opaca* was highly affected by solution pH (Figure 1d). pH affects both the availability of heavy metal ions in solution (Ho 2005; Vilar, Botelho, and Boaventura 2005) and the ionic state of binding sites on the sorbent surface, which is mainly composed of polysaccharides, proteins, and lipids (Ahalya, Ramachandra, and Kanamadi 2003; Davis, Volesky, and Mucci 2003; Pérez et al. 2008). Although the maximum sorption efficiency of all three metal ions by *N. opaca* biomass was observed at pH 4, such high acidity is uncommon among municipal wastewaters, where pH values are usually near neutral to slightly acidic. Thus, the *C. aculeolata* biomass, the sorption efficiency of which was less influenced by pH (Figure 1c), may be more generally useful for treatment of wastewater.

The kinetic experiments showed that the sorption of Cd and Zn to both algal biomasses was in accord with the pseudo-second-order model, suggesting that the metal ions were removed from solution mainly through chemical process as ion-exchange adsorption (Lee, Kuan, and Chern 2007). The pseudo-first-order and the pseudo-second-order rate kinetics are based on the sorption capacity of the solid phase. In most experiments, the sorption kinetics fitted to the pseudo-second-order model, indicating chemisorption occurring by valence forces through sharing or exchange of electrons between sorbent and sorbate, and in some cases, complexation, coordination, and/ or chelation, have been reported (Febrianto et al. 2009). The sorption kinetics of Pb to *N. opaca* agreed with the intraparticle diffusion model and also the first-order model due to their high correlation coefficients ($R^2 = 0.9175$ and 0.9130, respectively). Consistent with high k_{id} value (Table 2), this therefore indicates that physical interactions, possibly initial boundary liquid film diffusion (Boyd, Adamson, and Myers 1947; Febrianto et al. 2009) than intraparticle diffusion through pores of the *N. opaca* biomass, occurred during the Pb adsorption process. Similarly, the correlation coefficients of Pb biosorption for the pseudo-first-order and the pseudo-second-order kinetics were relatively high ($R^2 = 0.9401$ and 0.9422, respectively) by *C. aculeolata* biomass, indicating both physical and chemical interactions between Pb ions and the algal biomasses contributed to the Pb biosorption (Limcharoensuk et al. 2015). Nevertheless, in the

present study, the intraparticle diffusion seems to be more important ($R^2 = 0.9776$) for describing the rate-limiting step of Pb biosorption to *C. aculeolata* biomass.

The absorption parameters explain the higher maximum sorption capacity for Pb in comparison with Zn and Cd in the single-metal solutions (Table 3), and its larger ionic radius, a chemical property with high electronegative interaction, may be the reason for fixing firmly with active groups in algal cell components (Sheng et al. 2004). The presence of other metal ions in solution, as in the multi-metal solution experiments, increased the affinity of metal ions toward the algal sorbent, but decreased the maximum sorption capacity of each metal and altered the metal preference by both algal biomasses. These changes were probably caused by the competition of metal ions in the solution for the sorbent's binding sites. In realistic condition, municipal wastewater contains cations such as Na, K, Ca, and Mg, which can reduce mobility of heavy metals and compete for algal binding sites (Vilar, Botelho, and Boaventura 2005), and anions such as nitrate and chloride, which can form complex with sorbent and then reduce metal biosorption (Deng et al. 2009). However, *C. aculeolata* and *N. opaca* biomasses performed well, lowering the Pb and Zn concentrations in municipal wastewater to a level below the permissible limits (Table 4). In the metal mixtures, Zn was more preferable by the biomass than Cd. The Cd concentrations in posttreatment water samples were still higher than permissible levels. The use of biosorption may typically be more efficient in primary treatment of wastewater, lowering a low to moderate concentration of heavy metals prior to the secondary treatment.

C. aculeolata and *N. opaca* biomasses displayed sorption capacities comparable to or higher than those reported for other algal materials, such as *Spirogyra hyalina* (31.3 mgPb/g and 18.2 mgCd/g), *Cladophora rivularis* (48.1 mgPb/g), and *Cladophora fracta* (0.3 mgCd/g and 2.5 mgZn/g) (Jafari and Senobari 2012; Ji et al. 2012; Kumar and Oommen 2012). The dried biomass of *C. aculeolata* and *N. opaca* had sorption capacities comparable to those of other sorbents from agricultural wastes or abundantly available biomasses elsewhere reported to have high potential for heavy metal treatment (Table 5). However, in practical use, different sources of wastewater will differ in composition and water quality; therefore, additional

Table 5. Maximum sorption capacity (Q_m, mg/g) of comparable sorbents.

Sorbent	Biomass (g/L)	Single-metal solution			Multi-metal solution			Other components	Reference
		Pb	Cd	Zn	Pb	Cd	Zn		
Maize cob and husk	20	465.7	493.7	495.5	—	—	—	—	Igwe, Ogunewe, and Abia 2005
Sargassum sp.	3	214.0	—	24.2	44.2	—	7.3	Cu, Mn	Vijayaraghavan et al. 2009
C. aculeolata	2	105.26	23.04	15.15	43.10	6.65	7.81	—	This study
N. opaca	3	104.17	20.45	13.42	58.14	2.38	3.89	—	This study
Black gram husk	10	49.97	39.99	33.81	—	—	—	—	Saeed et al. 2005
P. simplicissimum	1	30.37	21.50	25.54	13.38	6.94	18.72	—	Fan et al. 2008
Humid *Tremella fuciformis* (jelly fungi)	48	24.40	22.76	20.13	24.68	10.04	13.58	—	Pan et al. 2010
Mangifera indica L (mango)	5	24.40	—	18.93	19.29	—	15.09	—	Ashraf, Maah, and Yusoff 2010
Auricularia polytricha (jelly fungi)	4	21.19	21.83	14.16	10.27	2.37	3.18	—	Pan et al. 2010
Sphagnum moss	1.67	18.6	—	9.46	13.7	—	1.28	Cu, Ni	Zhang and Banks 2005
Activated carbon derived from bagasse	6	—	38.03	31.11	—	29.77	19.02	Cu	Mohan and Singh 2002

experiments using various wastewater samples should be performed and further evaluation of the performance of sorbents in a practical process design, such as continuous-flow column, is also needed.

Conclusion

Dried biomass of *C. aculeolata* and *N. opaca* displayed high potential for biosorption of Pb > Cd > Zn in single-metal solutions and for treatment of multi-metal solutions (Pb > Zn > Cd) and municipal wastewater containing above-permissible-limit concentrations of the metals. Maximal removal efficiency by *C. aculeolata* in 10 mg/L metal solutions required 2 g/L sorbent dosage, or 3 g/L *N. opaca* at pH 4. *C. aculeolata* had a wider range of pH (3–7) for optimal biosorption of Cd and Zn than *N. opaca* did. The maximum sorption capacity of *C. aculeolata* was comparable or superior to *N. opaca* and many other reported biomass materials. Therefore, *C. aculeolata* biomass may be better for utilization in treatment of water contaminated with low metal concentrations, including municipal wastewaters.

Acknowledgments

Funding

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