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KINETIC AND EQUILIBRIUM STUDIES OF LEAD AND CADMIUM BIOSORPTION FROM AQUEOUS SOLUTIONS BY SARGASSUM *SPP.* BIOMASS

***[1]R. Nabizadeh, [1]K. Naddafi, [1]R. Saeedi, [1]A. H. Mahvi, [1]F. Vaezi, [2]K. Yaghmaeian and [1]S. Nazmara**

[1]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

[2]Department of Environmental Health Engineering, School of Health, Semnan University of Medical Sciences, Semnan, Iran

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ABSTRACT

Contamination of the aqueous environment by heavy metals is a worldwide environmental problem. Biosorption of lead (II) and cadmium (II) from aqueous solutions by brown algae *Sargassum spp*. biomass was studied in a batch system. The heavy metals uptake was found to be rapid and reached to 88-96% of equilibrium capacity of biosorption in 15min. The pseudo second-order and saturation rate equations were found in the best fitness with the kinetic data (R^2 > 0.99). The data obtained from experiments of single-component biosorption isotherm were analyzed using the Freundlich, Langmuir, Freundlich-Langmuir and Redlich-Peterson isotherm models. The Redlich-Peterson equation described the biosorption isotherm of Pb^{2+} and Cd^{2+} with high correlation coefficient (R^2 > 0.99) and better than the other equations. The effect of Na^+, K^+, Mg^{2+} and Ca^{2+} on the biosorption of Pb^{2+} was not significant, but the metal ions affected the biosorption of Cd^{2+} considerably. According to the Langmuir model, the maximum uptake capacities (q_m) of *Sargassum* spp. for Pb^{2+} and Cd^{2+} were obtained as 1.70 and 1.02mmol/g, respectively. Although the *Sargassum spp.* used in this study can be classified as an efficient biosorbent.

Key words: Biosorption, sargassum, lead (II); cadmium (II), kinetic, isotherm

INTRODUCTION

Aqueous heavy metals pollution represents an important environmental problem due to their toxic effects and accumulation throughout the food chain. Among heavy metals, lead and cadmium have high priority for removal from aqueous environments (Kapoor *et al*., 1999; Volesky, 2001; Rama *et al*., 2002 and Anonymous, 2002). The conventional technologies for the removal of heavy metals from wastewater mainly include: chemical precipitation, ion exchange, adsorption, membrane processes and evaporation that require high capital investment and running costs (Anonymous, 2000; Gupta *et al*., 2001 and Aksu, 2002). Therefore, there is an urgent need for development of innovative but low cost processes, where metal ions can be removed economically. The search for new treatment technologies has focused on biosorption (Dönmez *et al*., 1999; Figueira *et al*., 2000 and Loukidou *et al*., 2003). Biosorption is a term that describes the removal of heavy metals by the passive binding to nonliving microorganisms (bacteria, fungi and algae) and other biomass (such as peat, rice hull, fruit peel, leave and bark of tree etc.) from an aqueous solution (Davis *et al*., 2003 and Ma and Tobin, 2003). A number of different metal binding mechanisms have been postulated to be active in biosorption such as ion exchange, complexation, coordination, chelation, physical adsorption and microprecipitation (Volesky, 2001). Biosorption has many advantages including low capital and operational costs, the selective removal of metals, biosorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and desorption and no sludge generation. Biosorption technology has been shown to be a feasible alternative for removing heavy metals from wastewater. This technology can utilize naturally

*Corresponding Author: Tel: +98 21 8895 4914, Fax: 88950188, Email: *r_nabizadeh@sina.tums.ac.ir,*

abundant biomass such as seaweeds, and of these *Sargassum* has been identified for its high sorption capacity (Volesky, 2001; Davis *et al*., 2003 and Diniz and Volesky, 2003). Biosorption of lead (II) and cadmium (II) from aqueous solutions using various biomasses has been studied. Cadmium (II) biosorption on *Asppergillus oryzae* reached equilibrium in 1h with 90% of biosorption taking place in the initial 10 min (Kiff and Little, 1986). Kinetic data of cadmium (II) biosorption by chitin presented high correlation with the pseudo second order rate equation (Benguella and Benaissa, 2002). Matheickal and Yu (1999) observed that the maximum uptake capacities of *Durvillaea potatorum* and *Ecklonia radiata* for Pb^{2+} were 1.6 and 1.3 mmol/g, resppectively.

The objective of this research was to study the biosorption of lead (II) and cadmium (II) from aqueous environments by brown algae *Sargassum spp*. biomass. Kinetic and isotherm of lead (II) and cadmium (II) biosorption and the effects of pH and light metal ions (Na^+, K^+, Mg^{2+} and Ca^{2+}) on lead (II) and cadmium (II) biosorption were investigated.

MATERIALS AND METHODS

Preparation of biosorbent

The biosorbent used in experiments was brown algae *Sargassum spp*. biomass. The biomass was harvested from Oman Sea on the coast of Chabahar, Iran. The biomass was washed with tap water and deionized water to remove sand and other impurities. The biomass was sundried and then dried in an oven at 70 °C. Dried biomass was ground in a laboratory blender. After this, the biomass was sieved to select particle between 0.2-0.3 mm for use. The biomass was subsequently loaded with H^+ in a solution of 0.1M HCl (biomass concentration of 50 g/L) for 30 min under slow stirring. Later the biomass was washed with de-ionized water to remove excess hydrogen ions. Finally the biosorbent again dried at 70 °C for 24 hr.

Chemicals

Synthetic solutions were prepared using de-ionized water and salts of $Pb(NO_3)_2$, $Cd(NO_3)_2.4H_2O$, NaCl, KCl, $MgCl_2.6H_2O$ and $CaCl_2.2H_2O$ (Merck supplied). Initial pH of solutions was adjusted with a pH meter (CAMLAB Ltd, Model CG842) to the desired values by using 0.1-1M HCl and 0.1-1M NaOH.

Biosorption experiments

In all batch biosorption experiments, solution volume was 1L and the mixture of solution and biosorbent was agitated in 200 rpm. The experiments were conducted at room temperature (20±1 °C). Initial pH of the solutions was adjusted to desired values. The reaction mixture pH was not regulated after the initiation of experiments and final pH was measured.

Kinetic experiments

Kinetic experiments were done in three initial concentrations of Pb^{2+} and Cd^{2+} and fixed initial ratio of adsorbate to biosorbent inside a single component system. Initial metal concentrations were 0.5, 1 and 5 mM and initial ratio of adsorbate to biosorbent was 2 mmol/g, therefore 2.5, 0.5 and 0.25g of the biosorbent were added to experiment vessels with initial metal concentrations of 5, 1 and 0.5 mM, resppectively. Initial pH of solutions was adjusted to 5 and pH of the solutions was monitored continuously. The experiments were continued for 5 hr and samples were drawn from the mixture at predetermined time intervals for analysis.

Equilibrium experiments

Kinetic experiments presented that maximum time required to reach equilibrium was 2 h; therefore, the equilibrium time for equilibrium experiments was chosen 3 hr.

Biosorption isotherm

Biosorption isotherm experiments were conducted in a single component system. The initial Pb^{2+} and Cd^{2+} concentrations were varied from 0.05 to 5 mM. Initial pH of the solutions was adjusted to 5 and then 500 mg of *Sargasssum* spp. biomass was added to experiment vessels.

Effect of pH on biosorption

The effect of pH on equilibrium capacities of Pb^{2+} and Cd^{2+} biosorption was studied in a single component system. Initial heavy metal ions concentration was 1 mM and initial pH of solutions was varied from 2 to 5.5. After pH adjustment, 500 mg of *Sargasssum* spp. biomass was added to experiment vessels.

Effect of light metal ions on biosorption

The effect of Na^+, K^+, Mg^{2+} and Ca^{2+} on equilibrium uptake of Pb^{2+} and Cd^{2+} was studied in a binary system (one heavy metal and one light metal). Initial heavy metal ion concentration was 1mM and initial light metal ion concentration was varied from 0 to 6 mM. Initial pH of the solutions was adjusted to 5 and then 500 mg of *Sargasssum* spp. biomass was added to experiment vessels.

Metal analysis: The biomass was removed by filtration through 0.45µm membrane filters (mixed cellulose ester) and filtrates were analyzed for residual heavy metal (Pb^{2+} or Cd^{2+}) concentration by a flame atomic absorption sppectrophotometer (FAAS, Chem. Tech Analytical, Model ALPHA4).

Kinetic modeling: Kinetic of Pb^{2+} and Cd^{2+} biosorption was modeled by the pseudo first-order (Langergren), pseudo second-order, saturation (mixed-order) and second-order rate equations presented below as Eqs. (1)-(4), resppectively:

$$\ln\frac{(q_e-q_t)}{q_e}=-k_1t \qquad (1)$$

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}t \qquad (2)$$

$$\frac{1}{t}\ln\frac{C_0}{C_t}=-\frac{k_0}{K}-\frac{1}{K}\left(\frac{C_0-C_t}{t}\right) \qquad (3)$$

$$\frac{1}{(q_e-q_t)}=\frac{1}{q_e}+kt \qquad (4)$$

where q_e and q_t are the amounts of metal ion sorbed (mmol/g$^-$) at equilibrium and at any time, resppectively; k_1 is the pseudo first-order rate constant of adsorption (min^{-1}); k_2 is the pseudo second-order rate constant of adsorption (gm/mol/min); C_0 and C_t are the concentrations of metal ion (mM) at t=0 and at any time, resppectively; k_0 (mM/min) and K (mM) are saturation rate constants of adsorption and k is the second-order rate constant of adsorption (gm/mol/min) (Benguella and Benaissa, 2002; Metcalf & Eddy, 2003; Azizian, 2004).

Isotherm modeling

The isotherm of Pb^{2+} and Cd^{2+} biosorption was analyzed using the Freundlich, Langmuir, Freundlich-Langmuir and Redlich-Peterson models.

The empirical Freundlich model based on sorption onto a heterogeneous surface is given below by Eq. (5):

$$q_e=K_FC_e^{1/n} \qquad (5)$$

where C_e is equilibrium concentration of metal ion (mM); K_F and n are indicators of biosorption capacity and biosorption intensity, respectively (Loukidou *et al*., 2004; Selatnia *et al*., 2004b).

The Langmuir equation is based on the assumption that maximum adsorption correspponds to a saturated monolayer of solute on the adsorbent surface, that energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir equation is given by Eq. (6):

$$q_e=\frac{bq_mC_e}{1+bC_e} \qquad (6)$$

where q_m is the maximum capacity of biosorption (mmol/g) and b is a constant related to the affinity of the binding sites (mL/mol) (Yalçýnkaya, *et al*., 2002; Sheng, *et al*., 2004).

The three-parameter Freundlich-Langmuir model was developed to improve the fitness found by the Freundlich or Langmuir model. This model is given by Eq. (7):

$$q_e=\frac{bq_mC_e^{1/n}}{1+bC_e^{1/n}} \qquad (7)$$

where b, q_m and n are the Freundlich-Langmuir parameters (Volesky, 2003).

The three-parameter Redlich-Peterson model is given below by Eq. (8):

$$q_e=\frac{K_{RP}C_e}{1+a_{RP}C_e^{\beta}} \qquad (8)$$

where K_{RP} (L/g), a_{RP} (Lmmol^{-1})$^{\hat{a}}$ and $\hat{a}$ (dimensionless) are the Redlich-Peterson constants. $\hat{a}$ lies between 0 and 1. For $\hat{a}$ = 1 the Redlich-Peterson model converts to the Langmuir model (Aksu, 2002 and Volesky, 2003).

RESULTS

Kinetic study

The kinetic profiles of Pb^{2+} and Cd^{2+} biosorption by *Sargassum spp*. were shown in Fig. 1(a)-(b).

Figs. 2 (a)-(d) and 3 (a)-(d) show kinetic modeling of Pb^{2+} and Cd^{2+} biosorption by linear plots of the pseudo first-order, pseudo second-order, saturation and second-order rate equations (Eqs. (1)-(4)). Kinetic parameters of these equations for biosorption of Pb^{2+} and Cd^{2+} by *Sargassum spp*. biomass were shown in Tables 1 and 2.

Isotherm study

Fig. 4(a)-(d) shows isotherm modeling of Pb^{2+} and Cd^{2+} biosorption by linear plots of the Freundlich, Langmuir, Freundlich-Langmuir and Redlich-Peterson models (Eqs. (5)-(8)).

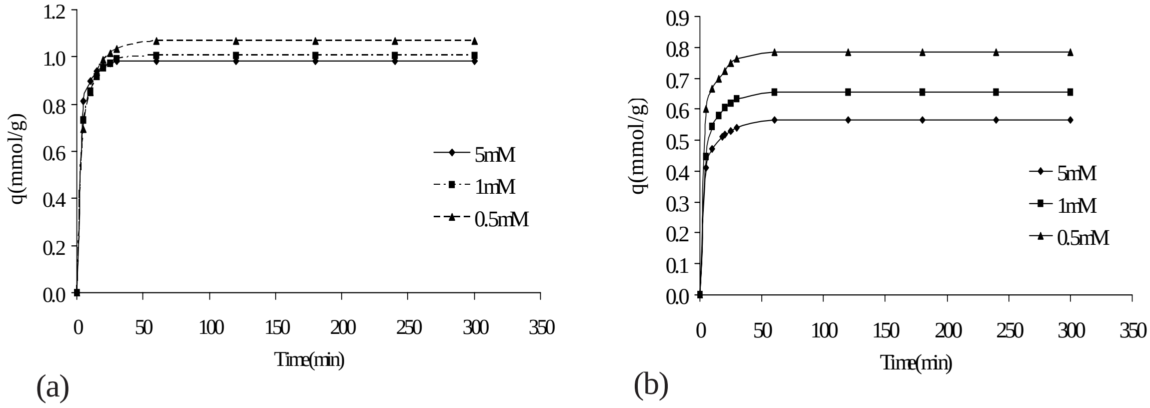

Fig. 1. Kinetic profiles of (a) Pb^{2+} and (b) Cd^{2+} biosorption by *Sargassum spp*. biomass

Table 1. Kinetic parameters of the pseudo first-order and pseudo second-order rate equations for the biosorption of Pb^{2+} and Cd^{2+} by *Sargassum spp*. biomass

Metal ion	C_0 (mM)	Pseudo first-order model			Pseudo second-order model		
		q_e	k_1	R^2	q_e	k_2	R^2
Pb^{2+}	5	0.98	0.21	0.879	0.99	1.86	1.000
	1	1.01	0.14	0.839	1.01	0.83	1.000
	0.5	1.07	0.12	0.880	1.08	0.52	1.000
Cd^{2+}	5	0.57	0.11	0.377	0.57	1.07	1.000
	1	0.65	0.13	0.817	0.66	0.93	1.000
	0.5	0.79	0.12	0.464	0.79	0.87	1.000

C_0 = initial concentration of metal ion.
R = correlation coefficient.

Table 2. Kinetic parameters of the saturation and second-order rate equations for the biosorption of Pb^{2+} and Cd^{2+} by *Sargassum spp*. biomass

Metal ion	C_0 (mM)	Saturation model			Second-order model		
		K	k_0	R^2	q_e	k	R^2
Pb^{2+}	5	-3.88	0.0034	0.999	0.98	4.53	0.507
	1	-0.80	0.0010	0.998	1.01	2.43	0.782
	0.5	-0.40	0.0007	0.997	1.07	0.71	0.825
Cd^{2+}	5	-4.46	0.0011	1.000	0.57	0.98	0.962
	1	-0.88	0.0004	0.999	0.65	1.41	0.760
	0.5	-0.42	0.0002	1.000	0.79	0.91	0.860

C_0 = initial concentration of metal ion.
R = correlation coefficient.

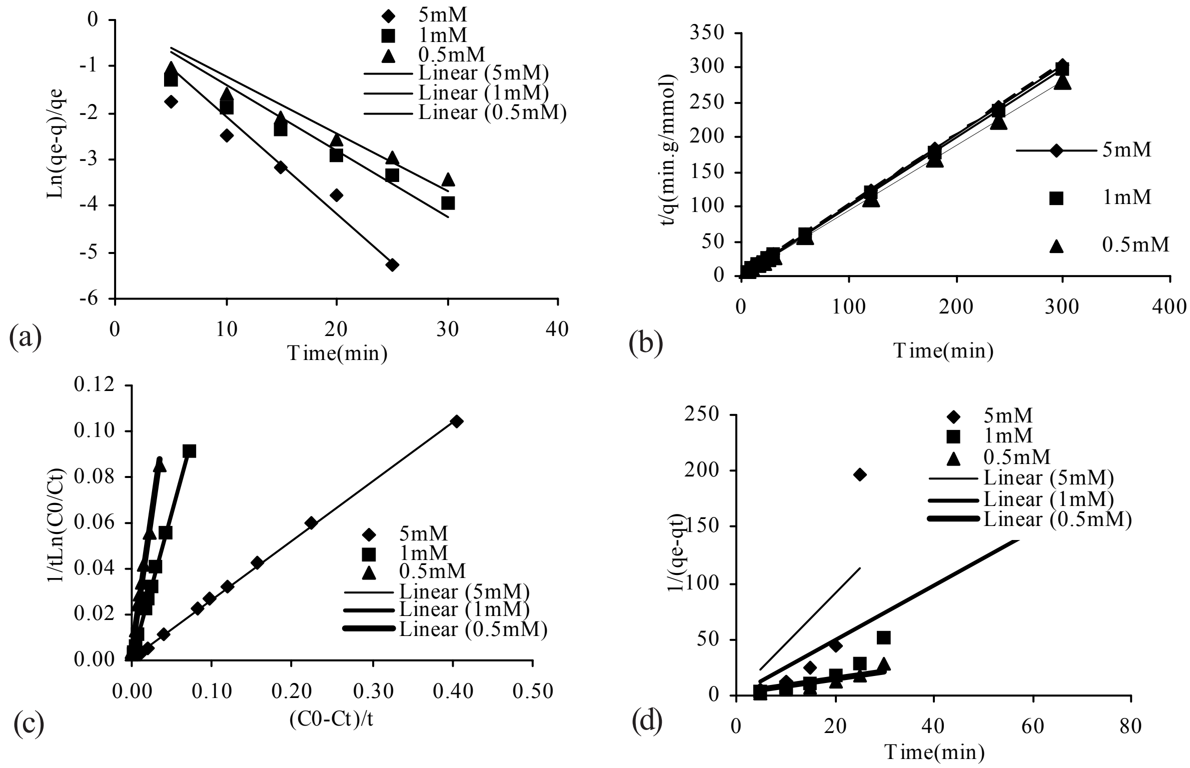

Fig. 2: Kinetic analysis of Pb^{2+} biosorption by linear plots of (a) the pseudo first-order, (b) pseudo second-order, (c) saturation and (d) second-order rate equations

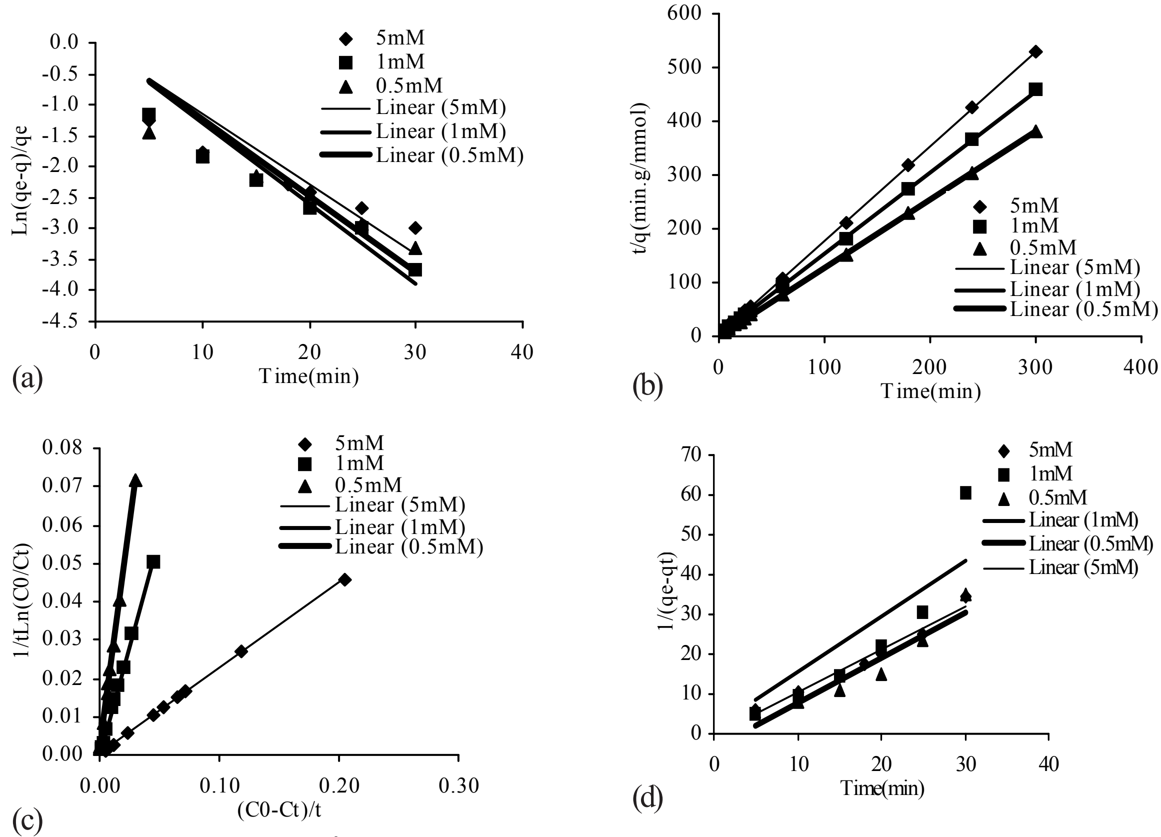

Fig. 3: Kinetic analysis of Cd^{2+} biosorption by linear plots of (a) the pseudo first-order, (b) pseudo second-order, (c) saturation and (d) second-order rate equations

The maximum biosorption capacities (q_m) obtained from this research with those of other biosorbents reported in the literature were given in Table 5.

Effect of pH on biosorption

Fig. 5 shows the effect of pH on equilibrium uptake capacities of *Sargassum spp.* biomass for Pb^{2+} and Cd^{2+}.

Effect of light metal ions on biosorption

The effect of Na^{+}, K^{+}, Mg^{2+} and Ca^{2+} on equilibrium capacities of Pb^{2+} and Cd^{2+} biosorption by *Sargassum spp.* biomass was shown in Fig. 6.

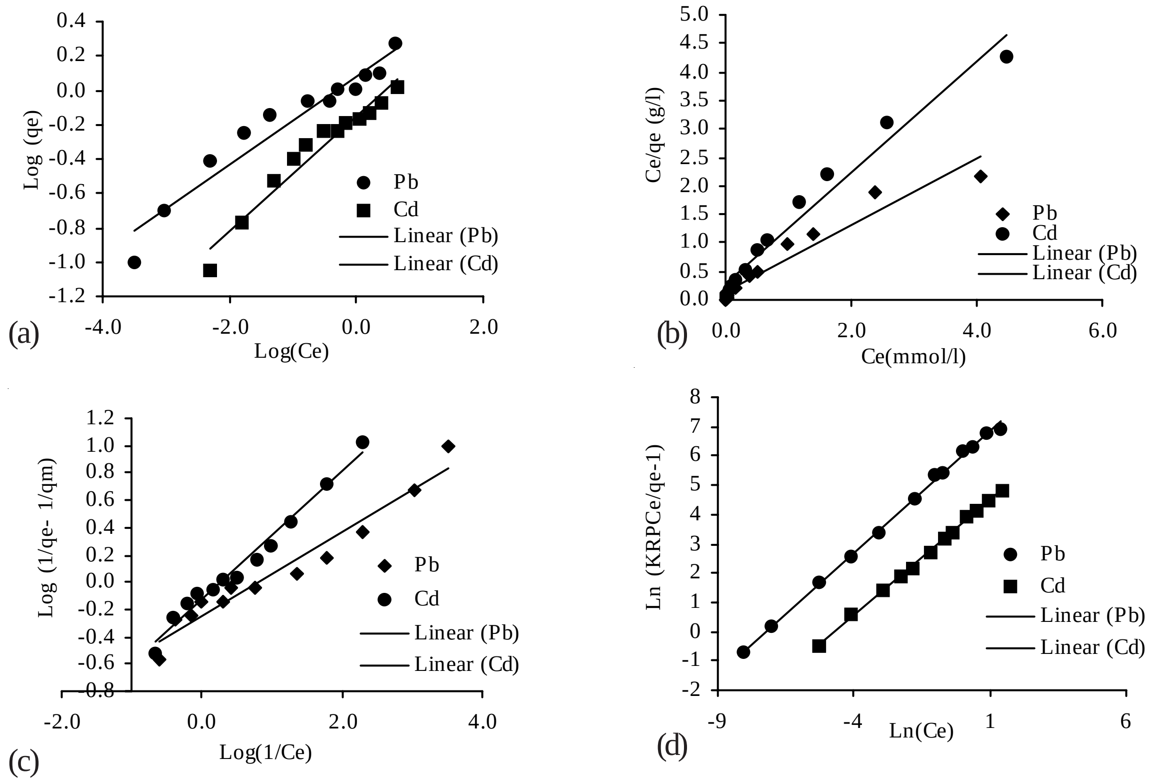

Fig. 4: Isotherm analysis of Pb^{2+} and Cd^{2+} biosorption by linear plots of (a) the Freundlich, (b) Langmuir, (c) Freundlich-Langmuir and (d) Redlich-Peterson models

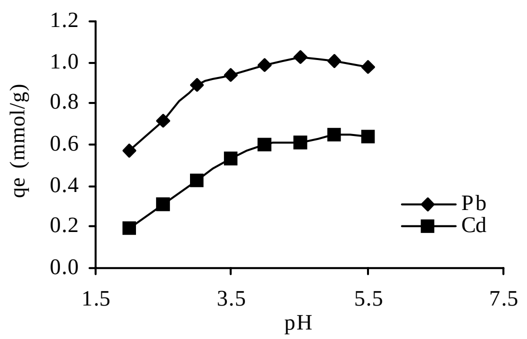

Fig. 5: Effect of pH on equilibrium capacities of Pb^{2+} and Cd^{2+} biosorption by *Sargassum spp.* biomass.

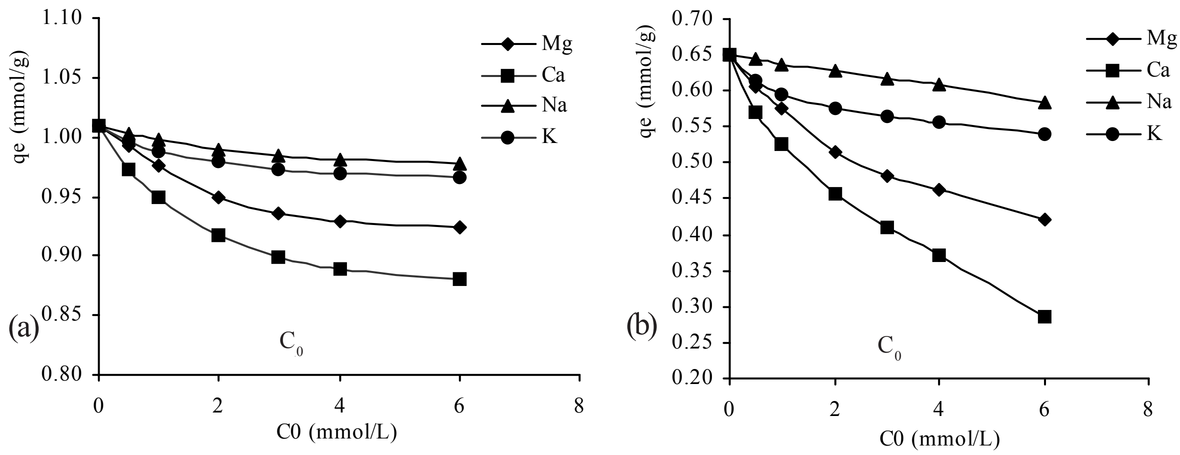

Fig. 6. Effect of Na^+, K^+, Mg^{2+} and Ca^{2+} on equilibrium capacities of (a) Pb^{2+} and (b) Cd^{2+} biosorption by *Sargassum spp*. biomass (C_0 = initial concentration of light metal ions).

DISCUSSION

Kinetic study: According to Fig. 1, Pb^{2+} and Cd^{2+} uptake was relatively fast for all the concentrations studied. At the initial Pb^{2+} concentration of 5mM, the system reached to equilibrium within 30min. In general, the heavy metals uptake reached to 88-96% equilibrium capacity of biosorption in 15 min. This rapid kinetic has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy. Similar rapid metal uptake has been reported for the biosorption of Pb^{2+} using *Ecklonia radiata* wherein the system reached over 50-60% of the equilibrium uptake capacity in 10 min (Matheickal and Yu, 1996). The kinetic of chromium (III) biosorption by *Sargassum spp*. biomass was fast, reaching 60% of the total uptake capacity in 10min (Cossich *et al*., 2002). The biosorption of lead (II) by *Durvillaea potatorum* was rather rapid and 90% of the total uptake occurred in 30min (Matheickal and Yu, 1999). The pseudo second-order and saturation rate equations described the biosorption kinetic of Pb^{2+} and Cd^{2+} with high correlation coefficient ($R^2 > 0.99$) and better than the other equations. Kinetic analysis of Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} biosorption by *Mucor rouxii* represented that the pseudo second-order rate equation described the biosorption kinetic better than the Langergren model (Yan and Viraraghavan, 2003).

The rate constants of the pseudo second-order rate equation for Pb^{2+} biosorption were obtained 1.86, 0.83 and 0.52gm/mol/min at initial Pb^{2+} concentrations of 5, 1 and 0.5mM, resppectively. In addition, the rate constants of saturation rate equation for Pb^{2+} biosorption were determined to be 0.0034, 0.0010 and 0.0007mM/min at initial Pb^{2+} concentrations of 5, 1 and 0.5mM, resppectively. The rate constants obtained from the pseudo second-order rate equation for Cd^{2+} biosorption were 1.07, 0.93 and 0.87gm/mol/min at initial Cd^{2+} concentrations of 5, 1 and 0.5 mM, resppectively. Also the rate constants of saturation rate equation for Cd^{2+} biosorption were determined to be 0.0011, 0.0004 and 0.0002mM/min at initial Cd^{2+} concentrations of 5, 1 and 0.5mM, resppectively. An increase in initial concentration of Pb^{2+} and Cd^{2+} led to an increase in the rate constant value, therefore there was a direct relationship between initial concentration of Pb^{2+} and Cd^{2+} and the rate of Pb^{2+} and Cd^{2+} biosorption by *Sargassum spp*. biomass. In other words, the biosorption of Pb^{2+} and Cd^{2+} by *Sargassum spp*. was faster in higher initial metal ion concentration.

Isotherm study: Isotherm data are basic requirements for the design of biosorption reactors, moreover analysis of biosorption isotherm is important to develop an equation which accurately represents the results and which can be used for design purposes (Volesky, 2001; Aksu, 2002).

The Redlich-Peterson equation described the isotherm of Pb^{2+} and Cd^{2+} biosorption by *Sargassum spp*. biomass with high correlation coefficient ($R^2 > 0.99$) and better than the other models. Also the other models were found in relatively good fitness with the experimental data ($R^2 > 0.93$). According to Langmuir equation, the maximum capacities of Pb^{2+} and Cd^{2+} biosorption (q_m) were obtained 1.70 and 1.02mmol/g, resppectively. The Langmuir parameter q_m (maximum uptake capacity) is a suitable measure for comparing different sorbents for the same sorbate. Although due to the various experimental conditions employed in different studies, comparison of their results is difficult, but maximum uptake capacity of *Sargassum spp*. biomass for Pb^{2+} and Cd^{2+} far exceed those of most of the biosorbents (Table 5); consequently, the *Sargassum spp*. used in this study can be classified as a good biosorbent.

Effect of pH on biosorption

Other studies on heavy metal biosorption have presented that pH was an important parameter affecting the biosorption process (Yan and Viraraghavan, 2003; Selatnia *et al*., 2004a).

The effect of pH on Pb^{2+} and Cd^{2+} biosorption was studied in the initial pH range of 2 to 5.5. At higher pH values, the experiments were not conducted to avoid formation of insoluble Pb^{2+} and Cd^{2+} hydroxides. The optimum initial pH values for Pb^{2+} and Cd^{2+} biosorption were determined as 4.5 and 5, resppectively. The sharpest increase in Pb^{2+} uptake was obtained between pH 2 and 3. The sharpest increase in Cd^{2+} uptake was determined between pH values of 2 and 4. The dependence of Pb^{2+} and Cd^{2+} biosorption on pH could be largely related to ionic state of binding sites on the algal cell wall (Matheickal and Yu, 1996; Sheng *et al*., 2004). Measurement of final pH represented the simultaneous release of H^+ with the uptake of heavy metal ions, because final pH of solutions was less than initial pH of solutions, therefore ion exchange confirmed to be one of the biosorption mechanisms. Other studies with seaweed and fungal biomass have indicated ion exchange as the dominant mechanism of biosorption (Fourest and Roux, 1992; Schiewer and Volesky, 1996; Ahuja *et al*., 1999; Volesky, 2001).

Effect of light metal ions on biosorption

Industrial effluents contaminated with heavy metals contain various kinds of impurities such as light metal ions (Na^+, K^+, Mg^{2+} and Ca^{2+}) that affect the heavy metal removal processes. Matheickal and Yu (1999) investigated the effect of Na^+, K^+, Mg^{2+} and Ca^{2+} on biosorption of Pb^{2+} by *Durvillaea potatorum* and *Ecklonia radiata*. The results showed that the biosorbents had much higher relative affinities for Pb^{2+} than for the light metal ions. The presence of Na^+, K^+, Mg^{2+} and Ca^{2+} in solution did not affect the biosorption capacity of Cu^{2+} by *Padina spp*. significantly (Kaewsarn, 2002).

The effect of Na^+ and K^+ on Pb^{2+} uptake by *Sargassum spp*.
biomass was insignificant even at 6 mM concentration of these ions, but Mg^{2+} and Ca^{2+} had influence on Pb^{2+} biosorption. The equilibrium capacity of Pb^{2+} biosorption was reduced at initial Mg^{2+} and Ca^{2+} concentration of 6 mM by 8% and 13%, resppectively. The presence of Na^+, K^+, Mg^{2+} and Ca^{2+} in solution affected the biosorption of Cd^{2+} conciderably, so that equilibrium uptake capacity of Cd^{2+} was reduced at initial concentration 0.5-6mM of Na^+, K^+, Mg^{2+} and Ca^{2+} by 1-10%, 6-17%, 7-35% and 12-56%, resppectively.

Altogether the *Sargassum spp.* used in this study can be classified as an efficient biosorbent because of rapid kinetic, remarkable biosorption capacity and selective removal of metals. Thus the biosorbent has a high potential for application in full-scale for removal of heavy metals from aqueous environments.

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