Biodegradation (2009) 20:1–13
DOI 10.1007/s10532-008-9194-2

ORIGINAL PAPER

Biosorption of Cd(II) and Pb(II) onto brown seaweed, *Lobophora variegata* (Lamouroux): kinetic and equilibrium studies

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Abstract The present work deals with the biosorption performance of raw and chemically modified biomass of the brown seaweed *Lobophora variegata* for removal of Cd(II) and Pb(II) from aqueous solution. The biosorption capacity was significantly altered by pH of the solution delineating that the higher the pH, the higher the Cd(II) and Pb(II) removal. Kinetic and isotherm experiments were carried out at the optimal pH 5.0. The metal removal rates were conspicuously rapid wherein 90% of the total sorption occurred within 90 min. Biomass treated with $CaCl_2$ demonstrated the highest potential for the sorption of the metal ions with the maximum uptake capacities i.e. 1.71 and 1.79 mmol g^{-1} for Cd(II) and Pb(II), respectively. Kinetic data were satisfactorily manifested by a pseudo-second order chemical sorption process. The process mechanism consisting of both surface adsorption and pore diffusion was found to be complex. The sorption data have been analyzed and fitted to sorption isotherm of the Freundlich, Langmuir, and Redlich–Peterson models. The regression coefficient for both Langmuir and Redlich–Peterson isotherms were higher than those secured for Freundlich isotherm implying that the biosorption system is possibly monolayer coverage of the *L. variegata* surface by the cadmium and lead ions. FT-IR studies revealed that Cd(II) and Pb(II) binding to *L. variegata* occurred primarily through biomass carboxyl groups accompanied by momentous interactions of the biomass amino and amide groups. In this study, we have observed that *L. variegata* had maximum biosorption capacity for Cd(II) and Pb(II) reported so far for any marine algae.

Keywords Brown seaweed · *Lobophora variegata* · Biosorption · Kinetics · Isotherm · FT-IR

Introduction

The global phenomenon of water contamination by toxic heavy metals has acquired serious dimensions and the researchers are engaged in combating this mammoth menace. Cadmium and lead are two of the “big three” toxic metals, the other one being mercury, are of profound concern as toxic contaminant of aqueous environment and becomes concentrated throughout the food chain to the extent of posing serious threat to health. These metals are known to cause renal dysfunction, bone degeneration, lung inefficiency, liver damage and hypertension in

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Electronic supplementary material The online version of this article (doi:10.1007/s10532-008-9194-2) contains supplementary material, which is available to authorized users.

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humans (Carson et al. 1986). Stringent environmental legislation and policies need to be framed and new technologies are quintessential to eliminate metal from contaminated/wastewater. Removal of these pollutants from aqueous effluents has conventionally been accomplished through a range of abiotic processes (Chemielewski et al. 1997; Yabe and de Oliveira 2003). These processes are expensive and at times not fully effective. Recently, a surging interest has been observed in the application of materials of biological origin for removal of heavy metals from diluted large volume solutions. Sorption with bio-materials has become an alternative method for industrial wastewater treatment such as precipitation, adsorption, coagulation etc. (Chu 1999; Matlock et al. 2001; Mehta and Gaur 2005). Biosorption is relatively inexpensive, non-hazardous, and may permit recovery of the metals from the sorbing biomass (Basha and Murthy 2007a, b; Deng et al. 2007). The potential of dead brown seaweeds in the recovery of heavy metal ions from aqueous effluents has been well demonstrated by researchers (Matheickal and Yu 1997; Davis et al. 2003a, b; Yun 2004; Basha et al. 2008).

Seaweeds are harvested or cultivated worldwide and are readily available in massive quantities for the development of highly effective biosorbent materials. Recent investigations by various groups have revealed that selected species of brown seaweeds possess excellent sorption capacities for the removal of Cd and Pb in view of their high uptake capacities and availability in enormous amounts from oceans (Matheickal and Yu 1999; Yu et al. 1999; Lodeiro et al. 2006; Sheng et al. 2007). Suarashtra-Kutchch coast of India is abounding with the seaweed *Lobophora variegata* which could be economically used as a potential biosorbent for heavy metal removal from aqueous solutions. The thallus of *L. variegata* is found to be growing in different shapes—prostrate, erect, flat, deltoid or orbicular. At grown up stage, it is 6 cm wide, 1–3 mm thick and remains attached to substratum by rhizoids. The present study is focused on the feasibility of Cadmium and Lead ion removal from aqueous solution by both raw and pretreated biomass of *L. variegata*. The influence of different paradigms on metal uptake such as aqueous metallic concentration, contact time, pH of solution, and biosorbent concentration was investigated in batch conditions. Various models were tested to investigate the sorption behaviour of kinetic and equilibrium. The mechanism of metal ions sorption at *L. variegata*—solution interface was also studied.

Experimental methods

Materials

The chemicals used in this study were of analytic reagent grade and obtained from Merck India. The stock solution of Cd(II) and Pb(II) (10 mmol for each ion) was prepared by dissolving weighed quantity of the respective nitrate salts in double distilled water. The concentrations of metal solutions ranged from 0.5 to 5.5 mmol l^{-1}. Before mixing with the biosorbent, the pH of each solution was adjusted to the appropriate value for the sorption of Cd(II) and Pb(II) ions by adding 0.1 M NaOH or 0.1 M HNO_3.

Preparation of the biosorbent

The brown alga *L. variegata* was collected from Okha port (Latitude 22°28.580′ N, Longitude 69°04.254′ E), Arabian Sea, India. The alga was washed twice with running tap water and five times with deionized water. The washed biomass was oven-dried at 60°C for 24 h, crushed with an analytical mill, sieved (size fraction of 300–600 μm) and stored in polyethylene bottles for use. The raw biomass was chemically modified by a pre-treatment with $CaCl_2$. A sample of 20 g of dried biomass was treated with 0.2 M $CaCl_2$ solution (400 ml) for 24 h under slow stirring (150 rpm). The solution pH was kept constant at pH 5.0. The calcium treated biomass was repeatedly washed with deionized water to remove excess calcium from the biomass. The biomass was then heated in an oven at 60°C for 24 h and sieved for particle size of 300–600 μm (Matheickal et al. 1999).

Biosorption experiments and analytical method

All the experiments were conducted at a constant temperature of 25 ± 2°C to cater to environmentally relevant conditions. Batch equilibrium biosorption experiments were carried out in 250 ml Erlenmeyer flasks containing cadmium chloride and lead nitrate solutions (100 ml) of known concentrations which varied from 0.5 to 5.5 mmol l^{-1}. Weighed amounts of biomass (200 mg) were added to each flask and the mixtures were agitated on the rotary shaker. The pH solution was adjusted to the required value by using HNO_3 or NaOH. After 6 h of agitation, the solution was separated from the biomass by membrane filtration (Millipore 0.45 mm pore size) and the filtrates were analyzed by atomic absorption spectroscopy (AA-680, Atomic absorption/Flame emission spectrophotometer, Shimadzu) for Cd(II) and Pb(II) ions. All the instrumental conditions were optimized for maximum sensitivity as specified by the manufacturer.

Kinetic experiments were conducted on a rotary shaker with constant agitation speed of 200 rpm, containing 100 ml of solution (2 mmol of lead and cadmium) and 200 mg of biomass. The pH of the solution was kept constant at pH 5. Samples were drawn from the mixture at pre-determined time intervals for analysis.

All the biosorption experiments were repeated twice to substantiate the results. The data shown are the mean values of two replicate determinations.

Metal uptake capacity

The amount of metal sorbed at equilibrium, q_e (mmol g^{-1}) which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after biosorption, as per following equation:

$$q_e = \frac{V(C_i - C_e)}{W} \tag{1}$$

where, V is the volume of metal solution (l), C_i and C_e are the initial and equilibrium concentration of metal in solution (mmol l^{-1}), respectively, and W is the mass of dry seaweed (g).

Biomass characterization

The surface area, pore volume and pore size of various forms of *L. variegata* are measured by surface area analyzer (Micromeritics, ASAP 2010) and are given in Table 1. Infrared spectra of unloaded and metal loaded biomasses of *L. variegata* were obtained using a Fourier Transform Infrared Spectrometer (FT-IR GX 2000, Perkin-Elmer). Before the analysis, the wet samples were freeze-dried, and 30 mg of finely ground biomass was palleted with 300 mg of KBr (Sigma) in order to prepare translucent sample disks. The FT-IR spectra were recorded over the wave number range of 400–4,000 cm^{-1} with ten scans at a resolution of 4 cm^{-1}.

Non-linear regression analysis

All the model parameters were evaluated by non-linear regression using DATAFIT® software (Oakdale Engineering, USA). The optimization procedure

Table 1 Characteristics of chemically modified and raw seaweed biomass

Parameter	Seaweed biomass	
	Raw	Treated
Surface area		
Single point surface area (m^2 g^{-1})	0.8126 at P/P_0 0.200247	0.9120 at P/P_0 0.200484
BET surface area (m^2 g^{-1})	1.0125	1.1764
BJH adsorption cumulative surface area of pores between 17,000000 and 150.000000 Å dm (m^2 g^{-1})	0.5024	0.5937
BJH desorption cumulative surface area of pores between 17.000000 and 150.000000 Å dm (m^2 g^{-1})	0.0175	0.0149
Single point adsorption total pore volume of pores (cm^3 g^{-1})	0.001045 of pores less than 1004.7057 Å at P/P_0 0.9072	0.001249 pores less than 866.8675 Å at P/P_0 0.9154
Adsorption average pore diameter (4 V/A by SINGLE POINT) (Å)	55.469	62.349
BJH adsorption average pore diameter (4 V/A by SINGLE POINT) (Å)	29.523	31.246
BJH desorption average pore diameter (4 V/A by SINGLE POINT) (Å)	42.967	85.674

required an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data (Kundu and Gupta 2006). Apart from the regression coefficient (R^2), the residual or sum of square error (SSE) and the standard error (SE) of the estimate were also used to gauge the goodness-of-fit. SSE can be defined as:

$$\mathrm{SSE} = \sum_{i=1}^{m} (Q_i - q_i)^2 \qquad (2)$$

SE can be defined as:

$$\mathrm{SE} = \sqrt{\frac{1}{m-p}\sum_{i=1}^{m} (Q_i - q_i)^2} \qquad (3)$$

where, q_i is the observation from the batch experiment i, Q_i is the estimate from the isotherm for corresponding q_i, m is the number of observations is in the experimental isotherm and p number of parameters in the regression model. The smaller SE and SSE values indicate the better curve fitting.

Results and discussion

Biosorption of Cd(II) and Pb(II) by *L. variegata*

The results exhibited that the raw biomass *L. variegata* was able to remove the metal ions from aqueous solutions with high efficiency (1.65 and 1.70 mmol g^{-1} for Cd(II) and Pb(II), respectively). A pretreatment of the biomass with $CaCl_2$ marginally enhanced the removal capacity for both the metals (Table 2). The reported work on the removal of these metal ions by different seaweeds and other adsorbents, as given in Table 2, reveals that the biosorption capacity of *L. variegata* is the highest except *Pseudomonas fluorescens* BM07 (Noghabi et al. 2007) and *Mimosa pudica* for Cd(II) (Chen et al. 2008). A mixture of polysaccharides, mainly alginate, has been found to be responsible for the superior metal-sequesterability of brown seaweeds (Davis et al. 2003b). In addition to its high porosity, the algal cell constituents provide an array of chemical ligands, which provide binding functional groups for the uptake of metal ions. Many metal-binding mechanisms have been postulated to be active in biosorption processes such as ion exchange, complexation, coordination, and microprecipitation (Davis et al. 2003b). Because of the complexity of the composition of the biomaterial, it is quite possible that at least some of these mechanisms are acting simultaneously, to varying degrees, depending on the biosorbent and the solution chemistry.

Table 2 also shows that the pretreatment enhances the biosorption capacity, though moderately. The addition of calcium to alginate, whose main component is alginic acid, produced a cooperative association between chains (preferentially of α-L-guluronic acid and β-D-mannuronic acid), which gave rise to a new molecular structure with large cavities occupied by calcium ions (Matheickal et al. 1999). The rod-like shape of the poly-L-guluronic sections results in an alignment of two chain sections yielding an array of coordination sites (Fig. 1). This description is known as the "egg-box" model (Rees 1981). Also, the calcium retained by alginate played an important role during ion exchange (Figueira et al. 2000). This explains the biosorption improvement observed for Cd(II) and Pb(II). Finally, Fourier-transformed infrared (FT-IR) spectral analyses have shown that cadmium and lead biosorption to *L. variegata* arises from bridging complex formation with the carboxylate groups of the alginate [25], consistent with the above described "egg-box" model of Rees (1981).

Effect of pH

The pH of the aqueous solution is a key controlling parameter in the biosorption process. Thus, the effect of hydrogen ion concentration was examined at various pH (ranging from 1 to 5). Figure 2 summarizes the uptake of Cd(II) and Pb(II) onto biomass of *L. variegata* at various pH. A trend of increasing metal ion binding with increasing pH was observed for raw as well as chemically-modified biomass. Maximum biosorption of the Cd(II) (0.9 mmol g^{-1}) and Pb(II) (0.95 mmol g^{-1}) was observed at pH 5.0.

It is well known that the sorption of metals decreases at low pH values because of competition for binding sites between cations and the products of acid hydrolysis (El-Bishtawi and Ali 2001). El-Bishtawi and Ali (2001) proposed two reactions, involving Pb, for this process, which can be adapted for other divalent metals (Me^{2+}):

Table 2 Sorption characteristics of various adsorbents for Cd(II) and Pb(II) removal

Adsorbent	Raw biomass				Biomass treated with $CaCl_2$				Reference
	Cd(II)		Pb(II)		Cd(II)		Pb(II)		
	pH	Uptake capacity (mmol g^{-1})	pH	Uptake capacity (mmol g^{-1})	pH	Uptake capacity (mmol g^{-1})	pH	Uptake capacity (mmol g^{-1})	
Lobophora variegata	5	1.65	5	1.70	5	1.71	5	1.79	Present work
Ascophyllum nodosum	–	–	–	–	5	0.930	5	1.150	Yu et al. (1999)
Ulva lactuca	5	0.259	5	0.167	–	–	–	–	Sarı and Tuzen (2008)
Cystoseira baccata	4.5	0.9	4.5	0.9	–	–	–	–	Lodeiro et al. (2006)
Durvillaea potatorum	–	–	–	–	4.7	1.10	5	1.550	Matheickal et al. (1999); Matheickal and Yu (1999)
Ecklonia maxima	–	–	–	–	5	1.15	5	1.40	Yu et al. (1999); Matheickal and Yu (1999)
Ecklonia radiate	–	–	–	–	5	1.04	5	1.260	Yu et al. (1999)
Gracilaria edulis	5	0.24	–	–	–	–	–	–	Hashim and Chu (2004)
Laminaria hyperbola	–	–	–	–	5	0.820	5	1.350	Yu et al. (1999)
Laminaria japonica	–	–	–	–	5	1.10	5	1.330	Yu et al. (1999)
Lessonia flavicans	–	–	–	–	5	1.160	5	1.450	Yu et al. (1999)
Lessonia nigresense	–	–	–	–	5	1.100	5	1.460	Yu et al. (1999)
Sargassum baccularia	5	0.74	–	–	–	–	–	–	Hashim and Chu (2004)
Sargassum siliquosum	5	0.73	–	–	–	–	–	–	Hashim and Chu (2004)
Sargassum sp.	5	0.76	5	1.16	–	–	–	–	Sheng et al. (2007)
Caulerpa lentillifera	5	0.042	5	0.138	–	–	–	–	Pavasant et al. (2006)
Laminaria hyperborea, *Bifurcaria bifurcata*, *Sargassum muticum* and *Fucus spiralis*	5	0.15–0.24	5	0.21–0.35	–	–	–	–	Freitas et al. (2008)
Azolla filiculoides	6	1.173	6	1.431	–	–	–	–	Rakhshaee et al. (2006)
Mimosa pudica	7	0.382	7	2.340	–	–	–	–	Chen et al. (2008)
Pseudomonas fluorescens BM07	–	–	–	3.393	–	–	–	–	Noghabi et al. (2007)
Zeolite	5.5	1.16	5.5	1.19	–	–	–	–	Castaldi et al. (2008)

$$Me^{2+} + nH_2O = Me(OH)_n^{2-n} + nH^+ \tag{4}$$

$$nH^+ + nH_2O = nH_3O^+ \tag{5}$$

Protons and oxonium ions (H_3O^+) concentrations are relatively high at low pH and compete with metals for ion exchange. Results from Fig. 2 suggest that this process occurred in the Cd-, Pb-*L. variegata*-pH systems studied here, with the maximum biosorption of both Cd and Pb at pH of 5.

The dependence of metal uptake on pH is related to both the surface functional groups on the cell walls of the biomass and the metal chemistry in solution. As the metals were present in their ionic state at a low pH (e.g., pH < 5; see Fig. 2), the sharp increase in metal biosorption from pH 2–5 could not be

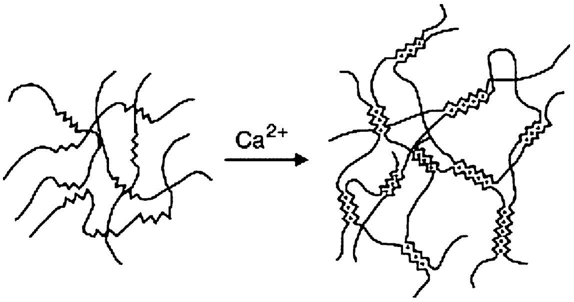

Fig. 1 Schematic representation of the calcium-induced gelation of alginate in accordance with the "egg-box" structure. After Christensen et al. (1990)

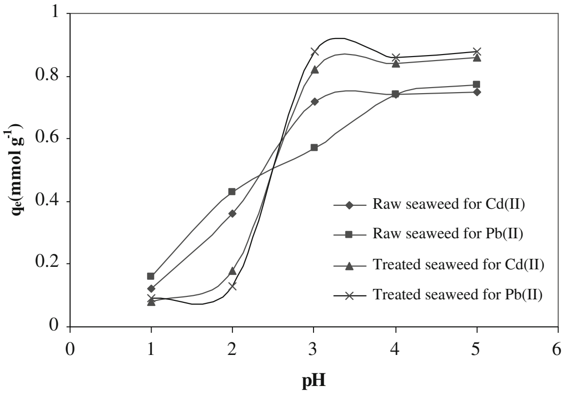

Fig. 2 Effect of pH on Cd(II) and Pb(II) sorption by *L. variegata* (initial metal concentration: 2 mmol l^{-1}, contact time: 360 min, solid to liquid ratio (s/l): 2.0 g l^{-1})

explained by the change in metal specification. This implied that the functional groups on the cell wall and its ionic state at these pHs determined the extent of biosorption. The positively charged hydrogen ions may also have competed with metal ions for binding on the ligands on the cell wall. At lower pH, the higher concentration of the hydrogen ions effectively led to fewer ligands being available for the binding of the metal ions. Increased pH (i.e., fewer H$^+$ ions) results in more ligands were available for metal ion binding, and hence biosorption was enhanced (Matheickal et al. 1999). The typical dependence of metal uptake on pH suggested that the weak acidic carboxyl groups R–COO– (apparent p*Ka* in the range 3.5–5.0) of algal cell wall might act as the probable biosorption sites. A good correlation between the degree of blocking of –COO– groups by esterification in *Sargassum fluitans* and the corresponding decrease in metal uptake were reported (Fourest et al. 1996; Davis et al. 2003a). Similar results were also obtained for the carboxyl groups in the biomass of the freshwater algae *Chlorella pyrenoidosa* and *Cyanidium caldarium* (Gardea-Torresdey et al. 1990).

In order to examine the biosorption potential of raw and treated biomass of *L. variegata* and to ensure that the heavy metals existed in their ionic states during biosorption, the pH in subsequent kinetic and isotherm experiments were maintained at 5.0.

Effect of solid/liquid (s/l) ratio

The effect of s/l ratio on cadmium and lead biosorption was studied at room temperature and at pH 5. Various s/l ratios including 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g l^{-1} were tested, while keeping the volume (100 ml) and the initial concentration of the metal solution (2.0 mmol l^{-1}) constant. Both raw and treated biomass showed a similar behaviour (Figure not shown). The removal rate for both Cd (II) and Pb (II) increased with increasing s/l ratio upto 2.0. However, the increase in s/l ratio above 2.0 g l^{-1} did not show significant increase in the removal rate. The maximum removal rate was more than 90% for both the metals when the s/l ratio is 2.0–3.0 g l^{-1}. Thus the optimum s/l ratio was 2.0 g l^{-1} in terms of the cost effect.

Determination of equilibrium time

The batch experiments carried out to study the relationship between contact time and Cd and Pb uptake by seaweed biomass showed that the equilibrium time was reached in less than 120 and 200 min for Cd(II) and Pb(II), respectively (Fig. 2). It was noticed that the contact time significantly affected the metal uptake; the metal biosorption increased sharply in the first 90 min and tapered off thereafter, as equilibrium was approached. This relatively rapid uptake indicated that the biosorption process occurred mainly on the surface of the sorbent. The uptake of heavy metal ions by biosorbents occurred in two stages: the first rapid and quantitatively predominant and the second slower and quantitatively insignificant (Sag and Kutsal 1996). The rapid stage was probably due to the abundant availability of active sites on the biomass, and with the gradual occupancy of these sites, the biosorption became less efficient in the slower stage (da Costa and Leite 1991). We found that about 90% of the total metal ion biosorption was achieved within 90 min. Therefore, in subsequent equilibrium experiments, 6 h was deemed sufficient to establish equilibrium.

Dynamic modeling

The transient behavior of the batch sorption process was analyzed using the pseudo first-order (Lagergren 1898) and pseudo-second order kinetic models (Ho and McKay 1998). The rate equations are mentioned in Table 3.

The pseudo-first order considered the rate of occupation of sorption sites to be proportional to the number of unoccupied sites. The value of pseudo-first order rate constant, k_1 along with statistical parameters for both Cd(II) and Pb(II) at initial concentration of 2 mmol l^{-1} and pH 5.0 are given in Table 4. It was observed that the biosorption data were satisfactorily represented by the Lagergren model for both the metals only for the first 30 min and thereafter it deviated from theory (Figure not shown). In other words, the biosorption data were well represented only in the region where rapid biosorption occurred i.e. for the first 30 min. Ho and McKay (1998) reported similar observation as the biosorption data were represented well by the Lagergren first-order model only for the rapid initial phase that occurred for a contact time of 0–30 min for basic dyes onto peat particles. This confirmed that it is not appropriate to use the Lagergren kinetic model to predict the biosorption kinetics for the entire biosorption period in the present case.

The kinetic data were further analyzed using a pseudo-second order relation proposed by Ho and McKay (1998) and Fig. 3 shows the predicted kinetics from pseudo-second order model for both Cd(II) and Pb(II) onto *L. variegata*. The pseudo-second order rate constant k_2, the calculated h value, and the corresponding R^2, SE and SSE values are shown in Table 4. The regression coefficient (R^2) values were found to be higher and ranged from 0.9672 to 0.9970, while SE and SSE values were low and ranged from 0.0161 to 0.0801 and 0.0020 to 0.0051, respectively for both the metals. The high R^2 and low SE and SSE values confirmed that the biosorption data were well represented by pseudo-second order model for the entire biosorption period and thus supported the assumption behind the model that the biosorption was due to chemisorption, which was in consonance with the biosorption equilibrium data well represented by Langmuir isotherm equation. Also from Table 4, it was observed that the kinetic data of Cd(II) was well represented by pseudo-second order model as compared to Pb(II). Table 5 presents pseudo-second order model constants of brown marine algae obtained for metal concentrations in the liquid phase similar to those used in the present study. In spite of some differences in the experimental conditions, the initial sorption rates of Cd(II) and Pb(II) are very high while kinetic constants (k_2) are lower than those reported by others.

Table 3 Kinetic and biosorption isotherm models

Kinetic model	Equation	Isotherm model	Equation
Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	Langmuir	$q_e = \frac{q_{\max} K_L C_e}{1+K_L C_e}$ $R_L = \frac{1}{1+K_L C_i}$
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{(1+k_2 q_e t)}$ $h = k_2 {q_e}^2$	Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$
Intraparticle diffusion	$q_t = k_p t^{0.5}$	Redlich–Peterson	$q_e = \frac{K_{\mathrm{RP}} C_e}{1+a_{\mathrm{RP}} C_e^{\beta}}$

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during sorption (Sankar et al. 1999), described by external mass transfer (boundary layer diffusion) and intraparticle diffusion (Weber and Morris 1963). The intraparticle diffusion coefficients for the biosorption of Cd(II) and Pb(II) were calculated from the slope of the plot between the amount of metal sorbed, q_t (mg g^{-1}) versus $t^{0.5}$($\min^{0.5}$) after subjecting it to nonlinear regression analysis (Fig. 4). It was observed that the biosorption process of both Cd(II) and Pb(II) comprised of two phases, suggesting that the intraparticle diffusion was not the rate-limiting step for the whole reaction (Ho and Ofomaja 2005). A first linear portion ended with a smooth curve followed by a second linear portion. The double nature of the curve reflected two-stage external mass transfer followed by intraparticle diffusion of Cd(II) and Pb(II) onto *L. variegata*. Similar results were reported by Aguilar-Carrillo et al. (2006). The intercept of the plot provided an estimation of the thickness of the boundary layer, i.e., the larger the intercept value the greater was the boundary layer effect (Basha and Murthy 2007b). The slope of the second linear portion of the plot has been identified as the intraparticle diffusion rate constant k_p (mg g^{-1} $\min^{-0.5}$). The calculated k_p values for both Cd(II) and Pb(II) are given in Table 4. It was observed that the k_p values for Pb(II),

Table 4 Kinetic and isotherm model parameters for Cd^{2+} and Pb^{2+} biosorption on biomass of *Lobophora variegata*

Models	Raw biomass		Treated biomass	
	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
Kinetic models				
Pseudo-first-order				
k_1 (min^{-1})	0.0234	0.0160	0.0144	0.0118
R^2	0.8832	0.8927	0.9409	0.9791
SE	0.2319	0.2359	0.1248	0.0595
SSE	0.2150	0.4451	0.0936	0.0213
Pseudo-second-order				
q_e (mmol g^{-1})	0.8385	1.1075	1.0639	1.4836
k_2 (g $mmol^{-1}$ min^{-1})	0.0665	0.0103	0.0235	0.0042
h (mmol g^{-1} min^{-1})	0.0467	0.0126	0.0266	0.0094
R^2	0.9952	0.9672	0.9970	0.9874
SE	0.0801	0.0161	0.0501	0.0741
SSE	0.0051	0.0020	0.0041	0.0042
Intraparticle diffusion				
k_p (mmol g^{-1} $min^{-0.5}$)	0.0044	0.0425	0.0203	0.0366
R^2	0.5768	0.8968	0.8194	0.8320
SE	0.0099	0.0309	0.0165	0.0294
SSE	0.0004	0.0038	0.0010	0.0026
Isotherm models				
Freundlich				
K_F (l g^{-1})	0.2938	0.4547	0.4251	0.4683
n	1.2738	1.0309	1.1002	1.1022
R^2	0.9061	0.9288	0.9489	0.9722
SE	0.1906	0.1059	0.0711	0.0485
SSE	0.1455	0.0561	0.0303	0.0141
Langmuir				
q_m (mmol g^{-1})	2.8652	2.8050	2.3140	2.6040
K_L (l $mmol^{-1}$)	0.1572	0.1061	0.0978	0.0669
R_L	0.7608	0.8249	0.8364	0.9863
R^2	0.9819	0.9747	0.9903	0.9907
SE	0.0362	0.0586	0.0306	0.0352
SSE	0.0118	0.0310	0.0085	0.0111
Redlich–Peterson				
K_{RP} (l g^{-1})	6.4418	1.8894	1.6463	1.7504
a_{RP} (l $mmol^{-1}$)	0.4673	0.1276	0.1206	0.1174
β	0.7214	0.6282	0.6389	0.5781
R^2	0.9711	0.9708	0.9787	0.9722
SE	0.0259	0.0356	0.0617	0.0382
SSE	0.0040	0.0076	0.0228	0.0879

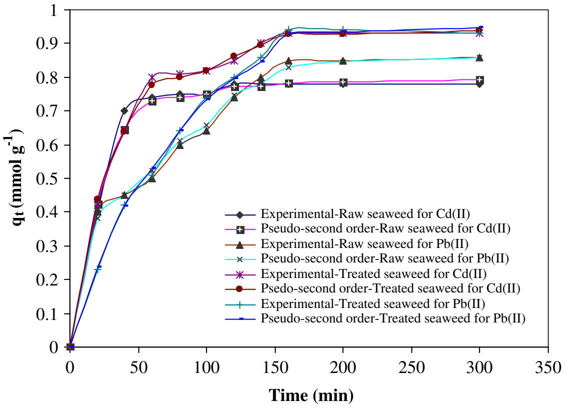

Fig. 3 Experimental and predicted kinetics from pseudo-second order model for sorption of Cd(II) and Pb(II) by *L. variegata*

both raw as well as treated seaweed, were more than Cd(II). The observed higher values of k_p corresponded to lower values of pseudo-second order rate constant, k_2 (Table 4), indicating that the intraparticle diffusion retarded the biosorption process for Pb(II). This also indicated that the biosorption process was rather complex and involved more than one diffusive mechanism.

Due to double nature of intraparticle diffusion (both film and pore diffusion), and in order to determine the actual rate-controlling step involved in the metal biosorption process, the kinetic data were further analyzed using the kinetic expression given by Boyd et al. (1947):

$$F = 1 - \frac{6}{\Pi^2}\exp(-B_b t) \tag{6}$$

where, B_b is a constant and F is the fractional attainment of equilibrium at time t given by

$$F = \frac{q_t}{q_e} \tag{7}$$

To compute $B_b t$, Eq. 6 is substituted into Eq. 7 and the kinetic expression becomes

$$B_b t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{8}$$

Thus, the value of $B_b t$ can be computed for each value of F, and then plotted against time (Fig. 5) to configure the so-called Boyd plots. The linearity of these plots was employed to distinguish between external-transport- (film diffusion) and intraparticle-transport-controlled rates of sorption (Wang et al. 2006). A straight line passing through the origin indicated sorption processes were governed by particle-diffusion mechanisms; or else they were

Table 5 Pseudo-second order model constants of various biosorbents for Cd(II) and Pb(II) removal

Seaweed	Pseudo-second order model constants				Reference
	Cd(II)		Pb(II)		
	$k_2 \times 10^{-2}$ (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	$k_2 \times 10^{-2}$ (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	
Laminaria hyperborea	2.4	23.9	2.04	51.7	Freitas et al. (2008)
Bifurcaria bifurcata	0.43	6.37	1.76	25.7	
Sargassum muticum	0.9	16	0.69	13.1	
Fucus spiralis	1.14	10.4	0.97	26.8	
Lobophora variegata	0.0235–0.0665*	2.66–4.67**	0.0042–0.0103*	0.94–1.26**	Present work

* (g mmol^{-1} min^{-1}), ** (mmol g^{-1} min^{-1})

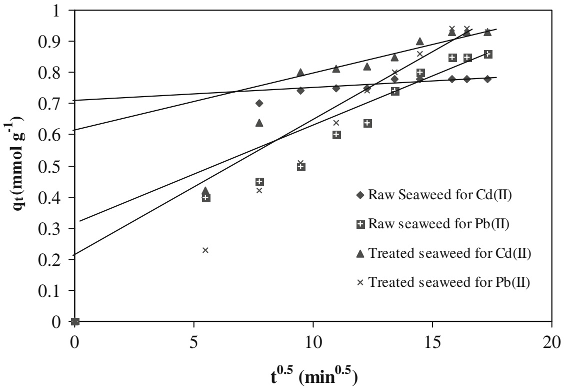

Fig. 4 Intraparticle diffusion plot for sorption of Cd(II) and Pb(II) by *L. variegata*

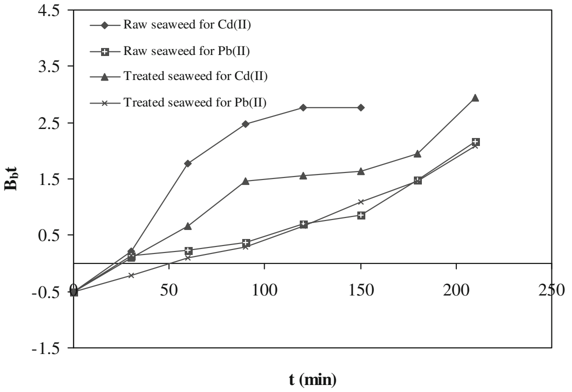

Fig. 5 Boyd plot for sorption of Cd(II) and Pb(II) by *L. variegata*

governed by film diffusion (Mohan and Singh 2002). In our case, the plots were neither linear nor passed through the origin (Fig. 5). This indicated that film diffusion was the rate-limiting biosorption process for Cd(II) and Pb(II) on both raw and treated *L. variegata*. However, further studies are required to establish this observation. Similar type of results were reported by El-Kamash et al. (2005) and Wang et al. (2006).

Effect of initial metal ion concentration on biosorption

The metal uptake mechanism was particularly dependent on the initial metal concentration: at low concentrations metals were adsorbed by specific sites, while with increasing metal concentrations the specific sites were saturated and the exchange sites were filled (Lehmann and Hater 1984). The amount of Cd(II) and Pb(II) biosorbed per unit mass of the raw biomass (i.e. equilibrium biosorption capacity, q_e) increased from 0.20 to 1.65 and 0.15 to 1.70 mmol g^{-1}, respectively, with increase in the equilibrium concentration from 0.5 to 5.5 mmol l^{-1}. However, the treated biomass showed an increase in biosorption capacity from 0.27 to 1.71 and 0.17 to 1.79 mmol g^{-1} for Cd(II) and Pb(II), respectively. The increase in biosorption capacity with initial concentration might be due to higher availability of metal ions in the solution. Moreover, higher initial concentration provided increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collision between metal ions and biosorbent.

Biosorption isotherm models

Analysis of equilibrium data was important for developing an equation that could be used to compare different biosorbents under different operational conditions and to design and optimize an operating procedure. To examine the relationship between biosorption and aqueous concentration at equilibrium, various sorption isotherm models were widely employed for fitting the data (Vijayaraghavan et al. 2006). In the present investigation the equilibrium data were analyzed using two-parameter models like Langmuir (Langmuir 1916), Freundlich (Freundlich 1906) and a three-parameter model, Redlich–Peterson (Redlich and Peterson 1959) isotherm models. Although these models did not enlighten on the mechanistic aspect of biosorption, they remain a useful and convenient tool for comparing results from different sources on a quantitative basis, providing information on sorption potential and reproducing the usual equilibrium uptake process behaviour with easily interpretable constants.

The Langmuir model served to estimate the maximum metal uptake values where they could not be reached in the experiments. The value of K_L is a coefficient attributed to the affinity between the sorbent and sorbate (Langmuir 1916). The value of n, of the Freundlich model, falling in the range of 1–10 indicates favorable sorption and Redlich–Peterson isotherm has three isotherm constants, namely, K_{RP}, a_{RP} and β ($0 < \beta < 1$), which characterize the isotherm. The model constants of Langmuir, Freundlich and Redlich–Peterson (RP) models along with regression coefficients (R^2), standard error (SE) of the estimate and residual or sum of squares error (SSE) are given in Table 4. Figure 6 show the fitted equilibrium data of Cd(II) and Pb(II) to Langmuir and RP isotherm expressions. It was observed that the equilibrium data of Cd(II) and Pb(II) fitted both the Langmuir and RP expressions with acceptable regression coefficient values ranging from 0.9747 to 0.9907 and 0.9707 to 0.9787, respectively. However, SE and SSE values were lower in case of RP model as compared to Langmuir. The low correlation coefficient as well as high SE and SSE values for the Freundlich isotherm as compared to Langmuir and RP confirmed the non-applicability of this model for both Cd (II) and Pb(II) on raw and treated biomass. The higher regression coefficients for the Langmuir and RP isotherms predicted the monolayer coverage of metals on *L. variegata* biomass. The good fit of the Langmuir and RP isotherms were not the same even when the coefficient of determinations was high for both isotherms. The essential characteristics of Langmuir isotherm can be explained in terms of the dimensionless separation factor, R_L (Hall et al. 1966). The R_L values indicated (Table 4) that Cd(II) and Pb(II) biosorption on to *L. variegata* is favorable.

Table 6 presents the comparison of Langmuir parameters of *L. variegata* biomass for the Cd(II) and Pb(II) with those of various seaweed biomasses in literature. The maximum biosorption capacity (q_m) of *L. variegata* biomass for these metal ions is higher while K_L values are much lower than that of other biomasses. However, the exact comparison becomes difficult because of the different experimental conditions (pH, temperature, sampling periods, and initial metal concentration).

Fourier transform infrared (FT-IR) analysis

FT-IR spectroscopy has been frequently used to detect vibrational frequency changes in seaweeds (Sheng et al. 2004). It offers excellent information on the nature of the bonds present and allows identification of different functional groups on the cell surface. FT-IR analysis of the *L. variegata* was carried out using KBr method by incorporating the sample into a KBr pellet.

The FT-IR spectra of raw and treated seaweed, when loaded with metals shows shifting wave number. Shift in wavelength showed that a metal

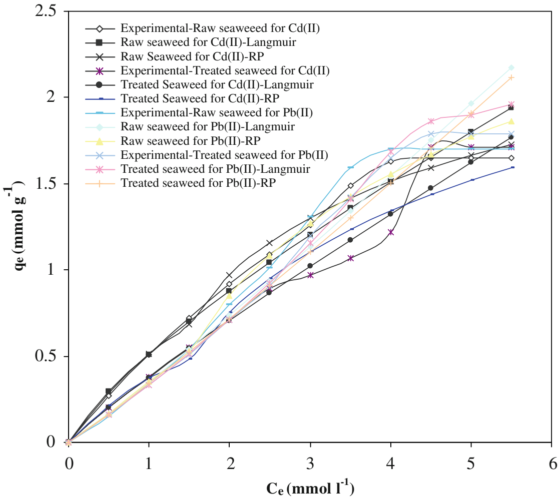

Fig. 6 Isotherms obtained for the biosorption of Cd(II) and Pb(II) by *L. variegata*

Table 6 Langmuir constants of various biosorbents for Cd(II) and Pb(II) removal

Seaweed	Langmuir constants				Reference
	Cd(II)		Pb(II)		
	q_m (mmol g^{-1})	K_L (1 mmol^{-1})	q_m (mmol g^{-1})	K_L (1 mmol^{-1})	
Ascophyllum nodosum (1)	1.27	40.1	1.03	4.5	Yu et al. (1999)
Ascophyllum nodosum (2)	1.15	34.1	0.93	4.2	
Lessonia avicans	1.45	58.6	1.16	5.9	
Lessonia nigresense	1.46	41.8	1.10	6.0	
Laminaria japonica	1.33	66.8	1.11	5.0	
Laminaria hyperbola	1.35	16.5	0.82	5.4	
Ecklonia maxima	1.40	87.8	1.15	6.0	
Ecklonia radiata	1.26	28.9	1.04	4.4	
Durvillaea potatorum	1.55	496	1.18	5.6	
Lobophora variegata	2.31–2.86	0.098–0.157	2.60–2.80	0.067–0.106	Present work

binding process takes place on the surface of alga (Matheickal and Yu 1997). The extent of band shifting also gives an indication of the degree of interaction of functional groups with metal cations.

The carboxylic group contained the minor groups as O–H stretching, C–O stretching and O–H bending (Sheng et al. 2004). The O–H bending group was seen to shift clearly at a wave number of 1,415 cm^{-1} for all metal loaded seaweed except raw seaweed loaded with Pb(II). This result suggested that the O–H bending group of carboxylic acid was involved in the metal binding process.

For amine group there were changes in wave number for N–H stretching in raw seaweed and raw seaweed loaded with Cd(II) and Pb(II) with respect to biosorption. The change in wave number for N–H stretching was observed from 3,440 cm^{-1} to 3,438 cm^{-1} and 3,406 cm^{-1} for treated seaweed with Cd(II) and Pb(II), respectively. For N–H bending group, the wave number was 1,633 cm^{-1} and 1,632 cm^{-1} for raw seaweed and treated seaweed, respectively. The change in the intensity of the bands suggested change in the amino groups present in the biomass. Shifting was observed in all metal loaded biomass except treated seaweed with Cd(II), indicating a clear role of amine group in the metal uptake.

The FT-IR spectroscopic analysis indicated shift in wave number from 3,430 to 3,406 cm^{-1} and 3,440 to 3,406 cm^{-1} representing N–H stretching of amide group for raw and treated seaweed loaded with metals, respectively. This indicated that N–H stretching of amide group was also involved in the sorption of Cd(II) and Pb(II).

Conclusions

Biosorption performance of both raw and treated biomass of locally derived macroalgae, *L. variegata* was investigated for the removal of cadmium and lead from aqueous solutions. The comparison of metal biosorption performance was based on expressing metal uptake against the key equilibrium biosorption parameters such as solution pH, biomass dosage, initial concentration of metal ions and time required for sorption equilibrium. Results demonstrated that higher pH (5.0) favored metal ion removal. Kinetic studies showed that about 90% of the total metal ions biosorption occurred within 90 min and the data were described by a pseudo-second order model obtaining the kinetic rate constant and the equilibrium biosorption capacity of the alga. Analysis of mechanistic steps involved in the biosorption process indicated that the biosorption process is particle-diffusion-controlled. Experimental results were well modeled according to the Langmuir as well as Redlich–Peterson sorption isotherms. The maximum uptake capacities for cadmium and lead were 1.65 and 1.71 mmol g^{-1} for raw biomass and 1.71 and 1.79 mmol g^{-1} for treated biomass. The presence and participation of carboxylic as well as amino and amide groups in metal uptake was confirmed by FT-IR analysis. The results of this study demonstrated that the brown seaweed *L. variegata* constituted a promising material for the development of a low cost biosorption technology for the removal of Cd(II) and Pb(II) from wastewaters.

Acknowledgments The authors acknowledge the kind support of Dr. P. K. Ghosh, Dirctor, CSMCRI during the course of the study. The financial support received from GSBTM, Department of Science and Technology, Govt. of Gujarat and Ministry of Earth Sciences, Govt. of India for carrying out this project is thankfully acknowledged.

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