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Biosorption of cadmium by brown, green, and red seaweeds

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Abstract

Seven species of brown, green, and red seaweeds were examined for their abilities to sequester cadmium ions from aqueous solution. Although all the seaweed types investigated were capable of binding appreciable amounts of cadmium, considerable variability in their biosorption performance was observed. Maximum cadmium uptake capacities at pH 5 ranged from the highest value of 0.74 mmol/g for the brown seaweed *Sargassum baccularia* to the lowest value of 0.16 mmol/g for the red seaweed *Gracilaria salicornia*, representing a 363% difference. In general, brown seaweeds were found to exhibit the best overall cadmium ion removal. Additional experiments were conducted to evaluate the biosorption characteristics of the brown seaweed *S. baccularia*. The equilibrium uptakes of cadmium were similar within the pH 3–5 range but decreased significantly when the solution pH was reduced to pH 2. The presence of background cations such as sodium, potassium, and magnesium and anions such as chloride, nitrate, sulphate, and acetate up to a concentration of 3.24 mmol/l was found to have no significant effect on the equilibrium uptake of cadmium. However, the biosorbent uptake of cadmium was markedly inhibited in the presence of calcium ions at 3.24 mmol/l. Kinetic studies revealed that cadmium uptake was fast with 90% or more of the uptake occurring within 30–40 min of contact time.

Keywords: Adsorption; Algae; Biosorption; Heavy metals; Seaweeds

1. Introduction

The presence of heavy metals in the environment is of major concern because of their toxicity and threat to plant and animal life. Moreover, recovery of heavy metals from industrial waste streams is becoming increasingly important as society realises the necessity for recycling and conservation of essential metals. Anthropogenic sources of heavy metals include process waste streams from metal plating, mining operations, and semi-conductor manufacturing operations. Increasingly strict discharge limits on heavy metals have accelerated the search for highly efficient yet economically attractive treatment methods for their removal. Biosorption is one such emerging technology that has attracted increased attention in recent years. Biosorption exploits the ability of microbial and plant biomass to sequester heavy metal ions from aqueous solution by physicochemical mechanisms. Charged groups such as carboxylate and hydroxyl present in the biopolymers of biomass cell walls are believed to be responsible for the sequestration of metal ions. Different biomass types such as bacteria, fungi, and algae have been screened and studied extensively in the last decade with the aim of identifying highly efficient metal removal biosorbents.

Recent investigations by various groups have shown that selected species of seaweeds possess impressive sorption capacities for a range of heavy metal ions. Seaweeds are a widely available source of biomass as over two million tonnes are either harvested from the oceans or cultured annually for food or phycocolloid production, especially in the Asia-Pacific region [1]. Seaweeds are found throughout the world's oceans and come in three basic colours: brown (Phaeophyta), red (Rhodophyta), and green (Chlorophyta). Brown and red seaweeds are almost exclusively marine, but the vast majority of green-coloured seaweeds are freshwater and terrestrial. The brown colour of the Phaeophyta results from the dominance of the xanthophyll pigment fucoxanthin which masks the other pigments while the red colour of the Rhodophyta is due to the presence of the pigment phycoerythrin which reflects red light and absorbs blue light. The green colour of the Chlorophyta comes from chlorophyll *a* and *b*. Many of the studies to date on metal biosorption by

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Table 1
Biosorption of heavy metals by some reported seaweed species

Seaweed species	Metals	Reference
Pachymeniopsis sp. (red)	Cr(VI)	[2]
Sargassum hystrix (brown)	Pb	[3]
Sargassum natans (brown)		
Padina pavonia (brown)		
Ulva lactuca (green)		
Cladophora glomerata (green)		
Gracilaria corticata (red)		
Gracilaria canaliculata (red)		
Polysiphonia violacea (red)		
Sargassum baccularia (brown)	Cd, Cu	[4–6]
Sargassum sp. (brown)	Cd, Cu, Zn	[7]
Sargassum siliquosum (brown)	Cr(VI)	[8]
Laminaria japonica (brown)	Cd, Cu	[9]
Sargassum kjellmanianum (brown)		
Macrocystis pyrifera (brown)	Cd, Pb	[10,11]
Kjellmaniella crassiforia (brown)		
Undaria pinnatifida (brown)		
Eckonia maxima (brown)	Cd, Cu, Pb, Zn, Ni	[12,13]
Lessonia flavicans (brown)		
Durvillea potatorum (brown)		
Sargassum asperifolium (brown)	Cd, Cu, Ni,	[14]
Cystoseira trinode (brown)	Co(II), Cr(III)	
Turbinaria decurrens (brown)		
Laurencia obtusa (red)		
Ascophyllum nodosum (brown)	Cd, Cu, Ni	[15]
Lessonia flavicans (brown)		
Laminaria hyperborea (brown)		
Durvillea potatorum (brown)		
Sargassum vulgare (brown)	Cd, Cu	[16]
Sargassum fluitans (brown)		
Sargassum filipendula (brown)		
Sargassum muticum (brown)		
Ascophyllum nodosum (brown)	Cd, Cu, Pb	[17–19]
Lessonia flavicans (brown)		
Lessonia nigresense (brown)		
Laminaria japonica (brown)		
Laminaria hyperbola (brown)		
Eckonia maxima (brown)		
Eckonia radiata (brown)		
Durvillaea potatorum (brown)		
Padina sp. (brown)		

seaweeds have largely been restricted to various species of brown seaweeds (see Table 1). On the other hand, green and red seaweed species have not been evaluated to any great extent. Lee et al. [2] screened 48 species of brown, green, and red seaweeds for their uptake capacities of hexavalent chromium while Jalali et al. [3] reported the biosorption of lead by eight species of brown, green, and red seaweeds. This study investigated the biosorption properties of seven different species of brown, red, and green seaweeds harvested from tropical coastal areas using cadmium as a model metal ion. Potential variability in the biosorption behaviour of the seaweed species was evaluated on the basis of their equilibrium cadmium uptake. Based on the results of this initial screening, the best-performing species was selected for further studies.

Table 2
Seaweed species tested in this study

Phaeophyta
- *Sargassum siliquosum*
- *Sargassum baccularia*
- *Padina tetrastomatica*

Chlorophyta
- *Chaetomorpha linum*

Rhodophyta
- *Gracilaria changii*
- *Gracilaria edulis*
- *Gracilaria salicornia*

2. Materials and methods

2.1. Biomass preparation and chemicals

The seven seaweed species collected from the west coast of Peninsular Malaysia are listed in Table 2. Fresh samples of the seaweeds were washed thoroughly with distilled water, dried in an oven to constant weight, and ground to a size range of 500–710 μm. The resulting biosorbent particles were then stored in sealed containers in a desiccator. All chemicals obtained from Fluka (Switzerland) including the cadmium nitrate salt were of analytical grade.

2.2. Biosorption equilibrium

Batch equilibrium experiments were carried out by adding a known amount of each of the seven seaweed species to a series of flasks containing solutions of varying initial cadmium concentrations (0.45–3.56 mmol/l). The flasks were agitated at 200 rpm and 25 °C in a constant temperature rotary shaker. The solution pH was maintained at 5. Sufficient contact time (24 h) was allowed for the metal uptake process to reach equilibrium conditions. After equilibration, solution samples were filtered through 0.45 μm membrane filters, acidified, and analysed for residual cadmium concentration by an inductively coupled plasma spectrometer (Baird 2000, USA). The amount of cadmium taken up by the seaweed particles in each flask was determined using the following mass balance equation

$$q_{\mathrm{e}} = \frac{C_{\mathrm{i}} - C_{\mathrm{e}}}{W} \tag{1}$$

where q_{e} is the quantity of metal taken up by the biosorbent, C_{i} is the initial metal concentration in the solution phase, C_{e} is the metal concentration in the solution phase at equilibrium, and W is the biosorbent dosage (mass of biosorbent per unit volume of solution). Cadmium-free and seaweed-free blanks were used as controls.

Additional equilibrium experiments were conducted using the brown seaweed *Sargassum baccularia*. The effect of pH on the equilibrium uptake of cadmium was investigated in the pH 2–5 range. To investigate the influence of background ions on cadmium uptake, nitrate salts of sodium, potassium, magnesium, and calcium and sodium salts of chloride, nitrate, sulphate, and acetate were used to prepare a series of cadmium solutions with background ionic concentrations in the range 0.162–3.24 mmol/l. The initial concentration of cadmium was fixed at 0.89 mmol/l. These solutions were used in batch equilibrium experiments, as described above.

2.3. Biosorption kinetics

Transient experiments were carried out to measure the kinetics of cadmium uptake by *S. baccularia*. Solution samples were taken at fixed time intervals for cadmium concentration analysis from a continuously stirred vessel containing a known amount of *S. baccularia* and cadmium solution. The pH and temperature of the solution were maintained at pH 5 and 25 °C, respectively. A series of batch kinetic experiments with a fixed biosorbent dosage but varying initial cadmium concentration were conducted.

3. Results and discussion

3.1. Biosorption equilibrium

Fig. 1 shows the experimental cadmium uptake isotherms (symbols) for the seven seaweed species at pH 5 and 25 °C (see below for pH effect). All of the equilibrium isotherms exhibited favourable isotherm behaviour, with a maximum capacity that depended on the biomass type. The three brown seaweeds exhibited the largest adsorption capacity, followed by the green seaweed and then the three red seaweeds. Jalali et al. [3] also reported that brown seaweeds outperformed green and red seaweeds in the biosorption of lead. Note that for the three brown seaweeds there is quite considerable difference between the uptake capacity of *Padina tetrastomatica* and those of the two *Sargassum* species. The presence of alginic acid or alginate, the salt of alginic acid, in the cell walls of brown seaweeds is largely responsible for the higher metal sequestering ability of the three brown seaweed species. Brown seaweeds contain 20–40% of alginic acid on a dry-weight basis. The negatively charged carboxylate groups of alginate can bind metal cations through electrostatic interactions/ion exchange. Dealginated brown seaweeds have been shown to possess much lower capacities for heavy metals compared to virgin seaweeds [15]. However, it should be noted that a red seaweed outperformed several brown and green seaweeds in sequestering negatively charged hexavalent chromium ions [2]. The maximum chromium(VI) adsorption capacity of the red seaweed *Pachymeniopsis* sp. was 225 mg/g at pH 4.5 [2] compared to a maximum adsorption capacity of 16 mg/g for the brown seaweed *S. siliquosum* at pH ≈ 4 [8]. These results suggest that red seaweeds have more cationic sites than brown seaweeds and thus have a relatively low affinity for positively charged metal ions such as cadmium. The cadmium uptake capacities of the brown and red seaweeds reported here are therefore consistent with results presented elsewhere.

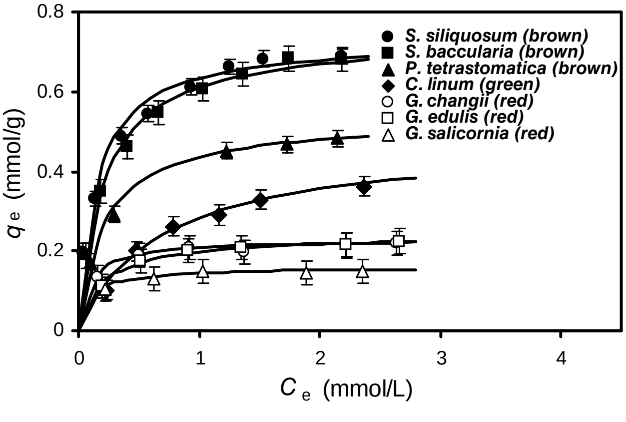

Fig. 1. Biosorption isotherms for cadmium on seven different species of brown, green, and red seaweeds at pH 5. Lines are Langmuir model curves.

The experimental results were correlated with the two-parameter Langmuir isotherm model

$$q_e = q_m \frac{bC_e}{1 + bC_e} \qquad (2)$$

where q_m is the maximum adsorption capacity and b is an affinity constant. Each experimental isotherm was fitted to Eq. (2) by a nonlinear regression analysis to obtain the parameters q_m and b. Table 3 lists the values of the parameters. The isotherm simulations from the Langmuir model are shown as lines in Fig. 1. In all cases, very good agreement was obtained with the experimental measurements. It is well known that the Langmuir isotherm, originally developed to describe gas adsorption, does not reflect any mechanisms of liquid-phase metal adsorption on a solid adsorbent. The equation is used empirically as a functional expression capable of simulating favourable equilibrium uptake curves. Despite its highly idealistic simplicity, the Langmuir isotherm remains a useful and convenient tool for comparing results form different sources on a quantitative basis. Table 4 lists some reported q_m and b values for cadmium uptake by brown seaweeds. In general, the three brown seaweeds tested in this study exhibited q_m and b values comparable to those reported elsewhere for various brown seaweed species. One

Table 3
Langmuir parameters for cadmium biosorption on seven species of seaweeds

Seaweed species	q_m (mmol/g)	b (l/mmol)
Sargassum baccularia (brown)	0.74	4.67
Sargassum siliquosum (brown)	0.73	6.60
Padina tetrastomatica (brown)	0.53	4.65
Chaetomorpha linum (green)	0.48	1.43
Gracilaria changii (red)	0.23	9.65
Gracilaria edulis (red)	0.24	4.82
Gracilaria salicornia (red)	0.16	9.04

Table 4
Comparison of Langmuir parameters for cadmium biosorption on some reported brown seaweed species

Brown seaweed species	pH	q_m (mmol/g)	b (l/mmol)	Reference
Sargassum sp.	6	1.40	6.52	[7]
Ascophyllum nodosum	4	0.9	42	[15]
Lessonia flavicans		0.8	73	
Laminaria hyperborea		0.9	86	
Durvillea potatorum		1.0	49	
Sargassum vulgarie	4.5	0.79	5.33	[16]
Sargassum fluitans		0.71	5.19	
Sargassum filipendula		0.66; 0.70	5.20; 17.4	
Sargassum muticum		0.68	16.1	
Sargassum sp.		0.78; 0.90	7.63; 21.5	
Ascophyllum nodosum	5	0.93; 1.03	4.2; 4.5	[17]
Lessonia flavicans		1.16	5.9	
Lessonia nigresense		1.10	6.0	
Laminaria japonica		1.11	5.0	
Laminaria hyperbola		0.82	5.4	
Eckonia maxima		1.15	6.0	
Eckonia radiata		1.04	4.4	
Durvillaea potatorum		1.18	5.6	
Durvillaea potatorum	5.4	1.12	6.15	[18]
Padina sp.	5	0.53	5.37	[19]

exception is the study by Malik et al. [15] which reported significantly larger b values.

It should be noted that the maximum adsorption capacity q_m is not the only parameter that should be considered in the screening of different biomass species. The performance of a biomass is likely to be determined by both q_m and b. Combining Eqs. (1) and (2) gives the following equation

$$W = \frac{(C_i - C_e)(1 + bC_e)}{q_m b C_e} \tag{3}$$

Eq. (3) may be used to estimate the biosorbent dosage required to achieve a specified level of metal removal in a batch system. For example, the biosorbent dosage required to remove 90% of available cadmium as a function of C_i is given by Eq. (4)

$$W = \frac{9}{q_m b} + \frac{0.9}{q_m} C_i \tag{4}$$

Using the Langmuir parameters listed in Table 3 for *S. baccularia* (brown), *Chaetomorpha linum* (green), and *Gracilaria changii* (red), the relationship between W and C_i for each biomass type can be calculated from Eq. (4). The calculated results are shown in Fig. 2. As expected, the brown seaweed with high values of q_m and b is the most efficient biosorbent, requiring the least amount of biomass to achieve 90% removal. However, although the red seaweed has a q_m value half of that of the green seaweed, it outperforms the green seaweed when C_i is less than 4.5 mmol/l (≈500 mg/l) because of its much higher b value. The red seaweed is therefore a more efficient biosorbent for processing dilute cadmium solutions compared to the green seaweed. This conclusion is not apparent if one compares the red and green seaweeds purely on the basis of q_m.

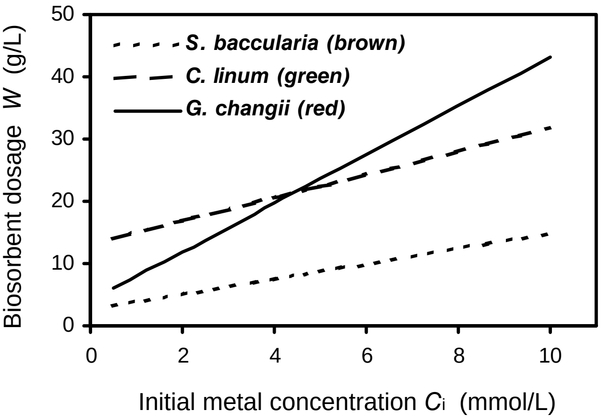

Fig. 2. Biosorbent dosage required to remove 90% of available cadmium as a function of initial metal concentration (Eq. (4)).

3.2. Effect of pH

Fig. 3 shows the effect of pH on the equilibrium uptake of cadmium by one of the two best-performing *Sargassum* seaweeds (*S. baccularia*). As can be seen from this figure, the equilibrium uptakes were similar in the pH 3–5 range over the entire range of the solution phase equilibrium concentration of cadmium. However, the equilibrium uptakes of cadmium at pH 2 were much smaller than the uptakes at pH 3–5. At low pH levels protons can compete effectively with cadmium for the binding sites in the biomass. The protonated binding sites are thus no longer available to bind cadmium ions from solution.

3.3. Effect of background cations and anions

Industrial application of a biosorption process must deal with the fact that heavy metal-bearing waste streams often contain other ions that may interfere in the uptake of the heavy metal ions of interest. Equilibrium experiments were conducted to evaluate the effect of common cations such as sodium, potassium, magnesium, and calcium and anions

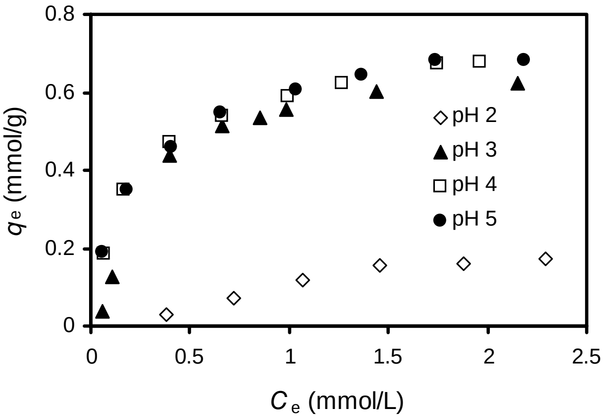

Fig. 3. Effect of pH on cadmium uptake by *S. baccularia*.

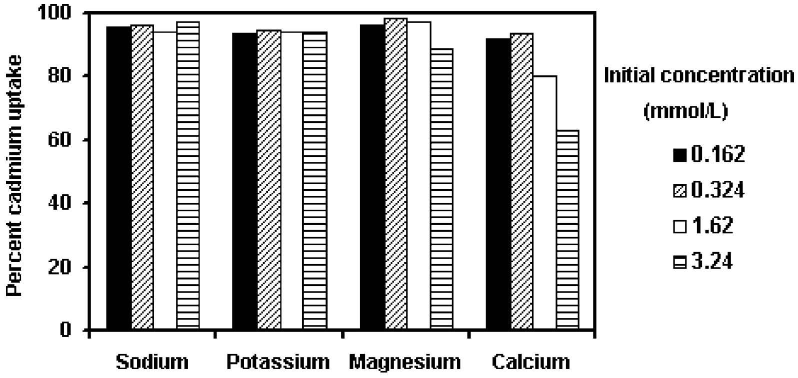

Fig. 4. Effect of background cations on cadmium uptake by *S. baccularia*. Initial cadmium concentration = 0.89 mmol/l.

such as chloride, nitrate, sulphate, and acetate on cadmium uptake by the brown seaweed *S. baccularia*. Fig. 4 displays cadmium uptakes by the *Sargassum* biomass obtained from experiments with the same initial cadmium concentration and biosorbent dosage at several initial light metal concentrations. The bars in Fig. 4 represent cadmium uptakes given as a percentage of the original uptake when no background ions were present in the cadmium solution. Within the concentration range examined, it is evident that the cadmium uptake was not greatly affected by the presence of the nitrate salts of sodium, potassium, and magnesium. By contrast, when both cadmium and calcium ions were present in the solution together, some reduction of the cadmium uptake was observed with increasing calcium concentration. The presence of calcium at an initial concentration of 1.62 mmol/l suppressed the cadmium uptake to only 80% of the original uptake. Increasing the calcium concentration to 3.24 mmol/l caused the cadmium uptake to drop to less than 65%.

The inhibition effect of calcium on cadmium uptake is indicative of calcium competition with cadmium ions for the available binding sites in the cell walls of *S. baccularia*. Williams and Edyvean [20] demonstrated an ion exchange relationship between nickel ion uptake and calcium release for a brown seaweed. de Franca et al. [21] reported that the uptake of zinc by a brown seaweed was adversely affected by the presence of calcium. Desorption studies reported by Lee and Volesky [22] showed that sequestered cadmium and copper ions were successfully eluted from brown seaweed biomass using calcium-salt solutions. The results of this study confirm these previous observations. It can therefore be concluded that calcium could present serious interference with the biosorption of various heavy metal ions by brown seaweeds.

The influence of common anions such as chloride, nitrate, sulphate, and acetate on cadmium uptake by *S. baccularia* was investigated. Overall, Fig. 5 shows that the cadmium uptakes were not greatly affected by the presence of the four anions up to the maximum concentration of 3.24 mmol/l examined in this study. Nevertheless, the presence of acetate at an initial concentration of 3.24 mmol/l suppressed the cadmium uptake to 90% of the original uptake. It is well known that metal ions in water undergo hydrolysis and complexation reactions with some anions which may influence the binding of the metals to solid surfaces. Under the experimental conditions employed here (initial cadmium concentration = 0.89 mmol/l; initial acetate concentration = 3.24 mmol/l; pH 5) the major cadmium species in the presence of acetate are the divalent Cd^{2+} (88.4%) and monovalent $Cd(acetate)^{+}$ (11.1%) according to a computer program (CHEAQS) for calculating chemical equilibria in aqueous solutions. The 10% reduction

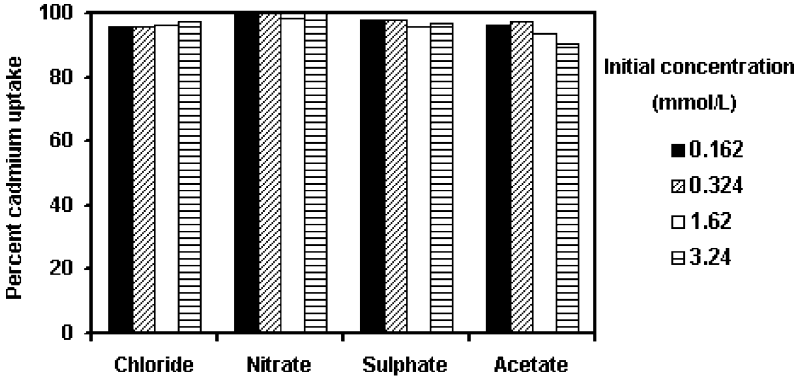

Fig. 5. Effect of background anions on cadmium uptake by *S. baccularia*. Initial cadmium concentration = 0.89 mmol/l.

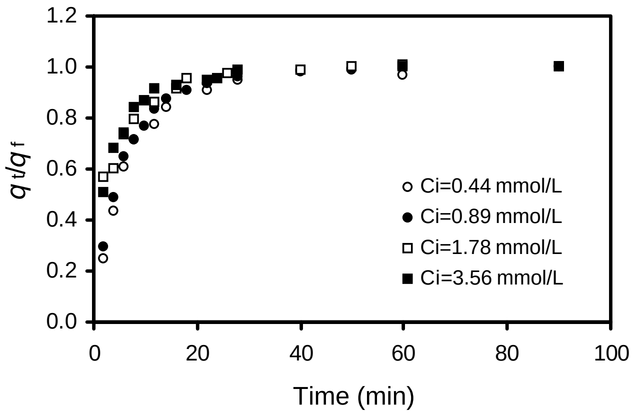

Fig. 6. Kinetics of cadmium biosorption by *S. baccularia* at four different initial metal concentrations (C_i), q_t and q_f are the instantaneous and final cadmium concentrations in the biosorbent phase, respectively.

in cadmium uptake seems to suggest that the complex Cd(acetate)$^+$ does not bind to *S. baccularia*. The other anion that is expected to form complexes with cadmium is sulphate. The major cadmium species in the presence of sulphate at an initial concentration of 3.24 mmol/l are the divalent Cd^{2+} (76.7%) and nonionised $CdSO_4{}^0$ (22.3%). Because the presence of sulphate did not lower the uptake of cadmium, it may be concluded that the nonionised complex $CdSO_4{}^0$ is able to bind to *S. baccularia*.

3.4. Biosorption kinetics

Information on the kinetics of metal uptake is required for selecting optimum operating conditions for full-scale batch metal removal processes. Fig. 6 depicts the concentration-time profiles for cadmium uptake by *S. baccularia* at various initial metal concentrations. The rates of cadmium uptake were similar in the initial metal concentration range of 0.44–3.56 mmol/l and the biosorption process reached the equilibrium state after approximately 30–40 min of contact time.

Mathematical models that can describe the transient behaviour of a batch biosorption process operated under different experimental conditions are very useful for scale-up studies or process optimisation. A number of models with varying degrees of complexity have been developed to describe the kinetics of metal biosorption in batch systems. For example, a model incorporating biosorption equilibrium and kinetics as well as intraparticle diffusion has been used to describe cadmium uptake by *Sargassum fluitans* [23]. However, such models are cast in the form of nonlinear partial differential equations and a numerical method must be applied to solve the complicated equations. Application of these models in modelling biosorption kinetics is therefore tedious and time-consuming. As a result, an attempt has been made to simulate batch transient uptake data using two relatively simple rate models.

Table 5
Parameters of kinetic models (Eqs. (5) and (6)) from regression of transient uptake data obtained at different initial cadmium concentrations

	C_i (mmol/l)			
	0.44	0.89	1.78	3.56
k_1 (min^{-1})	0.140	0.157	0.236	0.257
k_2 (min)	3.796	3.140	1.850	1.738

The first model, a first order kinetic model known as the Lagergren equation, takes the form [24]

$$\frac{q_t}{q_f} = 1 - \exp(-k_1 t) \tag{5}$$

where q_t and q_f are the metal concentration in the biosorbent phase at time t and at equilibrium, respectively and k_1 is a rate constant. The second kinetic model considered in this work is given as [24]

$$\frac{q_t}{q_f} = \frac{t}{t + k_2} \tag{6}$$

where k_2 is a rate constant. The experimental transient data presented in Fig. 6 were fitted by both models using a nonlinear least-squares method to determine the rate constant of the two models. The minimisation algorithm is based on a combination of Gauss–Newton and Levenberg–Marquardt methods. The fitted values of k_1 and k_2 are tabulated in Table 5.

Both models were capable of closely simulating the four experimental transient profiles presented in Fig. 6. Note that the rate coefficients k_1 and k_2 presented in Table 5 are a function of the initial metal concentration with k_1 increases with increasing initial metal concentration and k_2 decreases with increasing metal concentration, reflecting the different mathematical forms of Eqs. (5) and (6). Given that metal biosorption may involve a range of mechanisms such as chelation, ion exchange, and physical adsorption, it was considered adequate for the purpose of this study to use semi-empirical rate models, such as those illustrated herein, for description of biosorption transient data. However, an important observation from this exercise is that the rate coefficients of simplified rate models must be properly correlated with major system variables such as initial metal concentration before the models can be used for process design and optimisation studies.

4. Conclusions

Comparison of the biosorption behaviour of seven different species of brown, green, and red seaweeds indicated that the brown seaweeds, especially the *Sargassum* species, showed excellent cadmium sequestering capabilities. The following ascending order of their Langmuir maximum adsorption capacity (q_m) at pH 5 was observed: red $<$ green $<$ brown. However, it was demonstrated that the performance of a biosorbent is dependent upon the two Langmuir equilibrium parameters q_m and b. A biosorbent with a low q_m and a high b could outperform a biosorbent with a high q_m and a low b, especially in cases where the metal ion to be removed is present at trace levels. The equilibrium uptakes of cadmium by one of the two best-performing brown seaweeds (*S. baccularia*) were similar within the pH 3–5 range but decreased significantly when the pH was reduced to pH 2. The extent of cadmium uptake by *S. baccularia* appeared to be unaffected by the presence of common background cations such as sodium, potassium, and magnesium and anions such as chloride, nitrate, sulphate, and acetate up to the examined concentration level of 3.24 mmol/l. However, the biosorbent uptake decreased with increasing calcium ion concentration. At an initial calcium concentration of 1.62 mmol/l, the cadmium uptake was 80% of the original uptake and dropped to less than 65% when the initial calcium concentration was increased to 3.24 mmol/l. The rates of cadmium uptake could be successfully simulated using two different single-parameter rate models provided the relationships between the rate coefficients and initial metal concentration have been properly accounted for in the modelling strategy.

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