

Biosorption of cadmium by brown, green, and red seaweeds

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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 re-

sponsible 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
<i>Pachymeniopsis</i> sp. (red)	Cr(VI)	[2]
<i>Sargassum hystrix</i> (brown)	Pb	[3]
<i>Sargassum natans</i> (brown)		
<i>Padina pavonia</i> (brown)		
<i>Ulva lactuca</i> (green)		
<i>Cladophora glomerata</i> (green)		
<i>Gracilaria corticata</i> (red)		
<i>Gracilaria canaliculata</i> (red)		
<i>Polysiphonia violacea</i> (red)		
<i>Sargassum baccularia</i> (brown)	Cd, Cu	[4–6]
<i>Sargassum</i> sp. (brown)	Cd, Cu, Zn	[7]
<i>Sargassum siliquosum</i> (brown)	Cr(VI)	[8]
<i>Laminaria japonica</i> (brown)	Cd, Cu	[9]
<i>Sargassum kjellmanianum</i> (brown)		
<i>Macrocystis pyrifera</i> (brown)	Cd, Pb	[10,11]
<i>Kjellmaniella crassifolia</i> (brown)		
<i>Undaria pinnatifida</i> (brown)		
<i>Eckonia maxima</i> (brown)	Cd, Cu, Pb, Zn, Ni	[12,13]
<i>Lessonia flavicans</i> (brown)		
<i>Durvillea potatorum</i> (brown)		
<i>Sargassum asperifolium</i> (brown)	Cd, Cu, Ni	[14]
<i>Cystoseira trinode</i> (brown)	Co(II), Cr(III)	
<i>Turbinaria decurrens</i> (brown)		
<i>Laurencia obtusa</i> (red)		
<i>Ascophyllum nodosum</i> (brown)	Cd, Cu, Ni	[15]
<i>Lessonia flavicans</i> (brown)		
<i>Laminaria hyperborea</i> (brown)		
<i>Durvillea potatorum</i> (brown)		
<i>Sargassum vulgare</i> (brown)	Cd, Cu	[16]
<i>Sargassum fluitans</i> (brown)		
<i>Sargassum filipendula</i> (brown)		
<i>Sargassum muticum</i> (brown)		
<i>Ascophyllum nodosum</i> (brown)	Cd, Cu, Pb	[17–19]
<i>Lessonia flavicans</i> (brown)		
<i>Lessonia nigrescens</i> (brown)		
<i>Laminaria japonica</i> (brown)		
<i>Laminaria hyperborea</i> (brown)		
<i>Eckonia maxima</i> (brown)		
<i>Eckonia radiata</i> (brown)		
<i>Durvillea potatorum</i> (brown)		
<i>Padina</i> 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
<i>Sargassum siliquosum</i>
<i>Sargassum baccularia</i>
<i>Padina tetrastomatica</i>
Chlorophyta
<i>Chaetomorpha linum</i>
Rhodophyta
<i>Gracilaria changii</i>
<i>Gracilaria edulis</i>
<i>Gracilaria salicornia</i>

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 $^{\circ}\text{C}$ 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

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

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

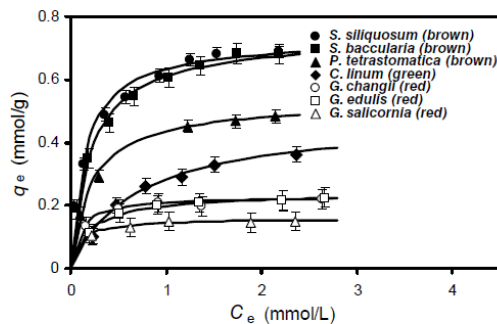


Fig. 1. Biosorption isotherms for cadmium on seven different species of brown, green, and red seaweeds at pH 5. Lines are Langmuir model curves.

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.

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

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

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 from 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)
<i>Sargassum baccularia</i> (brown)	0.74	4.67
<i>Sargassum siliquosum</i> (brown)	0.73	6.60
<i>Padina tetrastomatica</i> (brown)	0.53	4.65
<i>Chaetomorpha linum</i> (green)	0.48	1.43
<i>Gracilaria changii</i> (red)	0.23	9.65
<i>Gracilaria edulis</i> (red)	0.24	4.82
<i>Gracilaria salicornia</i> (red)	0.16	9.04

Full text is available at :

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