

# Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina* sp.

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**“Capsule”:** *Pre-treatment of biomass of the marine alga Padina with calcium resulted in an efficient biosorbent for cadmium(II) from wastewater.*

## Abstract

In this study, the adsorption properties of a pre-treated biomass from marine alga *Padina* sp., a biomass collected from Surin Island, Thailand, for removal of cadmium(II) ions from aqueous solutions was investigated. Batch and column experiments were conducted to determine the adsorption properties of the modified biomass. At a pH of 5, the maximum removal capacity of the biomass is 0.53 mmol/g. The kinetics of cadmium(II) adsorption were fast with 90% of adsorption taking place within 35 min. This study demonstrated that the pre-treated biomass of *Padina* sp. could be used as an efficient biosorbent for the treatment of cadmium(II)-bearing wastewater streams. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Biosorption; Marine algae; *Padina* sp.; Cadmium(II) removal; Wastewater treatment

## 1. Introduction

The release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems (Hutton and Symon, 1986; Nriagu, 1988). Cadmium, which is widely used and extremely toxic at relatively low dosages, is one of the principal heavy metals responsible for causing these problems (Murata et al., 1970; Drash, 1993). The main anthropogenic pathway through which cadmium(II) enters the environment is via wastes from industrial process (Forstner and Wittman, 1981). As heavy metals cannot be destroyed in the natural environment, technologies that can remove and recover the heavy metals from the wastewater are needed. At present, a number of technologies, such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes, are used for the treatment of heavy metal-containing wastewater streams. However, these methods are not effective when the heavy metal concentrations in the wastewater are low (e.g. less than 100 mg/l) (Nriagu,

1988). The technologies are also expensive when a very low concentration of cadmium(II) in the treated water is required (Wilde and Benemann, 1993).

Alternative means of treating wastewater containing low levels of cadmium(II) have been studied. Biosorption of heavy metals is an emerging technology for the treatment of industrial wastewater (Volesky, 1990). Biosorption relates to removal of heavy metals from wastewater streams by either metabolically mediated or purely physico-chemical pathways (Fourest and Roux, 1992). The biological materials that have been investigated for cadmium(II) uptake include fungi (Matheickal et al., 1991), bacteria (Chang et al., 1997), yeast (Volesky et al., 1993) and algae (Yu et al., 1998, 1999; Matheickal et al., 1999). Many of these materials are available in large quantities either as industrial waste by-product or from natural source (Murata et al., 1970). Biomass of marine algae is available in large quantities and can form a good basis for the development of biosorbent materials. However, only a limited number of studies have so far been focused on the use of non-living biomass of marine algae for cadmium(II) removal from wastewater (Fourest and Volesky, 1996). These studies revealed an interesting potential associated with certain algal species such as *Ascophyllum nodosum*, *Sargassum*

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*baccularia*, *Sargassum natans*, *Sargassum fluitans*, *Ecklonia radiata*, *Ecklonia maxima* and *Durvillaea pottatorum*. This paper examines the ability of pre-treated biomass of *Padina* sp. to adsorb cadmium(II) from aqueous solutions. The results indicate that the biosorbents used in this study can provide an efficient and cost-effective technology for the treatment of cadmium (II)-containing wastewaters.

## 2. Materials and methods

Sun-dried *Padina* sp. samples in powdered form were supplied by the Phuket Marine Biological Center, Thailand. Pre-treatment of the biomass was carried out as follows. A sample of 20 g of biomass was treated with 0.2 M  $\text{CaCl}_2$  solution (400 ml) for 24 hours under slow stirring. The solution pH was kept constant at pH 5.0 by using 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  solution if deviations were observed. The calcium-treated biomass was washed several times 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 then sieved to get a uniform particle size of 300–600  $\mu\text{m}$ .

All experiments were conducted at room temperature (25±2°C), in duplicate and average values are reported. Control and preliminary experiments without biosorbent, anion or cation were also performed for each system. No adsorption by the filter membrane, flask, plastic vials or interference with the analytical techniques was observed.

For isotherm determination, a series of 125-ml plastic vials were prepared containing cadmium nitrate solutions (100 ml) of known concentrations in the range of 0.5–4.5 mM. Weighed amounts (200 mg, dry) of biomass were added to each vial and the mixtures were agitated on a rotary shaker for 24 h. The solution pH was adjusted to the required value by using 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  every hour in the first 4 h. The pH of the solution was measured and adjusted if necessary again after 24 h (no further changes in pH were observed). The biomass was removed by filtration through a 0.45- $\mu\text{m}$  membrane filter (which does not adsorb the heavy metal ions) and the filtrates were analysed for cadmium (II) by atomic absorption spectrometry.

Kinetic experiments were conducted in continuously stirred beakers (200 rpm) containing 500 ml of cadmium nitrate solution and 1 g of biomass. One-millilitre samples were drawn from the mixture at pre-determined time intervals for analysis. The pH of the solution was monitored continuously with a pH electrode and adjusted with 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  solution if deviations were observed.

Fixed-bed experiments were performed in a glass column of 1 cm in diameter, packed with 1 g of biomass. Solutions of cadmium(II) were pumped through the

column at a flow rate of 1.5 ml/min using a peristaltic pump (Gilson Miniplus-2). Effluent samples were collected for every bed volume using a fraction collector (Gilson FC-203) and were analysed for the concentration of cadmium(II) ions by using atomic absorption spectrometry.

## 3. Results and discussion

### 3.1. Effect of solution pH on cadmium(II) adsorption and adsorption equilibrium

Earlier studies have indicated that solution pH is an important parameter which affects biosorption of heavy metal ions (Yu et al., 1998, 1999; Matheickal et al., 1999). The pre-treatment used in this study also improved the chemical and mechanical stability of biosorbents by reducing the amount of total organic carbon content, the swelling volumes and the attrition loss (Matheickal and Yu, 1998). Cadmium(II) adsorption by pre-treated biomass of *Padina* sp. as a function of solution pH was studied (Fig. 1a). At pH less than 1.5, the cadmium(II) uptake capacity was almost negligible. There was an increase in cadmium(II) uptake with increasing pH from 1.5 to 4.5. Within the pH range of 2–4, the cadmium(II) uptake capacity increased rapidly. At pH around 5, the cadmium(II) adsorption capacity levelled off at a maximum value. Various reasons might be attributed to the metal adsorption behaviour of the biosorbent relative to solution pH. The cell wall of *Padina* sp. contains a large number of surface active sites. The pH dependence of metal uptake can largely be related to these active sites and also to the chemistry of the metal in solution. The solution chemistry of transition metal elements is complicated by the hydrolysis phenomenon: when pH increases from an acid value to a neutral value, various hydrolysed species exist and the affinities of these species to cell wall active sites can vary. The effect may be further explained in relation to the competition effect between the  $\text{H}_3\text{O}^+$  ions and cadmium(II) ions. Metal ions that could associate with the cell wall ligands would have to compete with the  $\text{H}_3\text{O}^+$  ions for the active sites. At low pH values, the concentration of  $\text{H}_3\text{O}^+$  far exceeds that of cadmium(II) ions and hence, these ions occupy the binding sites on the cell walls, leaving cadmium(II) ions free in solution. When the pH was increased, the competing effect of  $\text{H}_3\text{O}^+$  ions decreased and the positively charged cadmium(II) ions took up the free binding sites. The metal uptake was hence increased.

Since solution pH has a significant effect on adsorption equilibrium, the cadmium(II) uptake capacity of *Padina* sp. was evaluated using adsorption isotherms obtained at a number of different equilibrium pH values. These isotherms are presented in Fig. 1b.

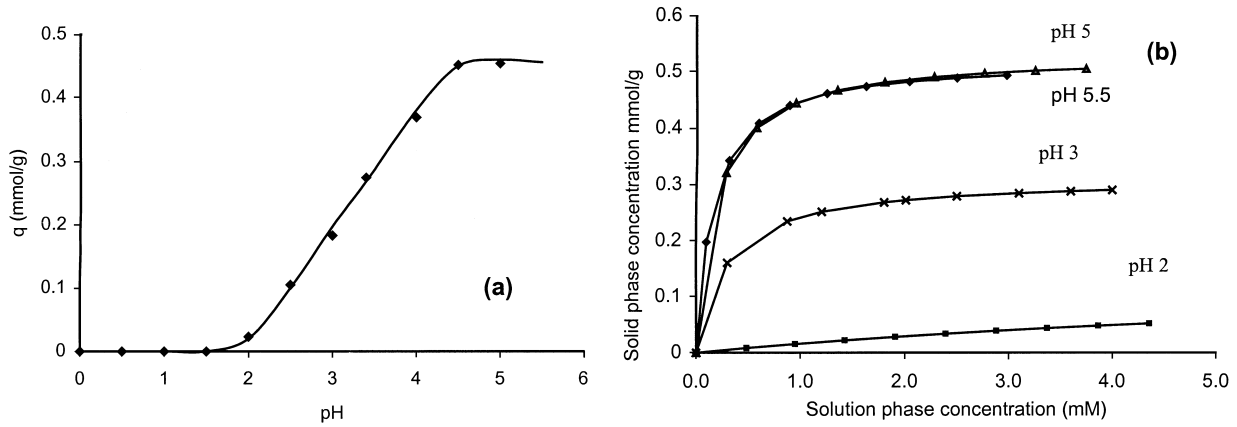


Fig. 1. (a) Cadmium(II) uptake by *Padina* sp. as a function of pH (adsorbent dose, 2 g/l; initial concentration, 2 mM); (b) cadmium(II) adsorption isotherms for *Padina* sp. for different pH values.

The maximum cadmium(II) adsorption capacity ( $Q_{max}$ ) and affinity constant ( $b$ ) of pre-treated biomass of *Padina* sp. at different equilibrium pH values were calculated and are given in Table 1. A comparison of adsorption capacity ( $Q_{max}$ ) of this biosorbent with those of different adsorbents reported in the literature is given in Table 2. Many of these adsorbents, such as activated carbon, natural zeolites and ion exchange resins are commonly used in many practical metal recovery applications.

Although direct comparison of the biosorbent used with other reported adsorbents is difficult due to the varying experimental conditions employed in those studies, in general, the adsorption capacity of the

pre-treated biomass of *Padina* sp. (0.53 mmol/g) is considerably high. However, its capacity is less than a biosorbent of marine algae of *D. potatorum* and less than that of Duloite GT-73 resins (Matheickal et al., 1991, 1999).

### 3.2. Kinetics and fixed-bed adsorption

Kinetic experiments were carried out to evaluate the potential of the biosorbent for commercial application. Fig. 2a presents the results of the kinetic experiments on the adsorption of cadmium(II) onto the pre-treated biomass of *Padina* sp. at different initial cadmium(II) concentrations. It was observed that 90% of the total soluble cadmium(II) was removed from the solution within 35 min of agitation. Afterwards, there was a small decrease in the soluble cadmium(II) concentration during the test period of 5 h. However, this slow rate of adsorption of heavy metals by marine algal biosorbents has not been observed in the kinetic studies conducted previously for similar metal concentration (Tobin et al., 1984). The observation made in this study is consistent with the concept of non-homogeneity of the algal

Table 1  
Langmuir parameters for adsorption isotherms

pH	$Q_{max}$ (mmol/g)	$b$ (1/mM)	$R^2$
5.5	0.52	6.15	0.98
5	0.53	5.37	0.99
3	0.31	3.59	0.86
2	0.16	0.11	0.34

Table 2  
Cadmium(II) adsorption capacities of reported biosorbents

Adsorbent	$Q_{max}$ (mmol/g)	References
<i>Rhizopus arrhizus</i>	0.27	Tobin et al., 1984
<i>Penicillium chrysogenum</i>	0.39	Fourest et al., 1994
<i>Pseudomonas aeruginosa</i>	0.38	Chang et al., 1997
<i>Saccharomyces cerevisiae</i>	0.34	Matheickal et al., 1991
Peat moss	0.20	Gosset et al., 1986
Clinoptilolite	0.21	Curkovic et al., 1997
Fe(III)/Cr(III) hydroxide	0.42	Namasivayam and Ranganathan, 1995
Duloite GT-73	0.59	Matheickal et al., 1991
Granulated activated carbon	0.07	Ramos et al., 1997
Pre-treated <i>Durvillaea potatorum</i>	1.12	Matheickal et al., 1999
Pre-treated <i>Padina</i> sp.	0.53	This study

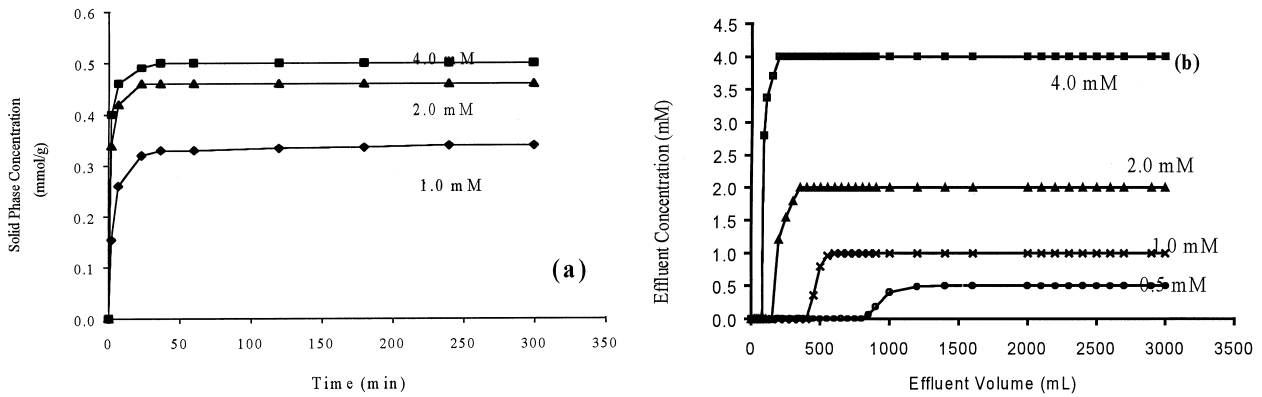


Fig. 2. Cadmium(II) adsorption kinetics and breakthrough curves for fixed-bed operation by *Padina* sp. (adsorbent dose, 2 g/l; (a) speed of agitation, 200 rpm; (b) flow rate, 1.5 ml/min).

surface, which contains a variety of active sites. The sites that serve as adsorption sites may differ both with respect to the strength of the metal sorptive bond and the rate of adsorption onto the active sites. This will result in different rates of metal uptake by the biosorbent and in general can be classified into fast and slow uptake. The initial rapid metal uptake observed in this study has a significant practical importance as it will facilitate shorter adsorption columns ensuring efficiency and economy.

Fig. 2b shows the fixed-bed breakthrough curves for cadmium(II) adsorption onto pre-treated *Padina* sp. biomass. The breakthrough curves followed the typical S-shape curve for column operation. The adsorption column containing 1 g (dry wt.) of the biomass could purify 1.0 l of 0.5 mM cadmium(II) solution before breakthrough, and it purified 0.5, 0.2 and 0.1 l of the solutions when the feed concentrations were 1.0, 2.0 and 4.0 mM, respectively. The total uptake capacities of the fixed-bed for the different initial concentrations were calculated by integrating the breakthrough curves between the breakthrough and saturation point. The adsorption capacities of column for various initial concentrations ranged between 0.50 and 0.54 mmol/g, which agree well with the maximum value of 0.53 obtained from batch experiments.

#### 4. Conclusions

The study indicated that the pre-treated biomass of the *Padina* sp. could be used as an efficient biosorbent material for the treatment of cadmium(II) ion-bearing wastewater streams. The adsorption capacities were solution pH dependent and a maximum adsorption capacity was determined to be 0.53 mmol/g at a solution pH of 5. The adsorption capacity for cadmium(II) of *Padina* sp. was found to be relatively high when compared with those of many other adsorbent materials reported in heavy metal recovery and removal

applications. The kinetics of adsorption by this biomass was rapid with 90% of the total adsorption occurring within 35 min. The biomass can be used in fixed-bed operations.

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