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Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp.

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Abstract

Biosorption of heavy metals can be an effective process for the removal and recovery of heavy metal ions from aqueous solutions. The biomass of marine algae has been reported to have high uptake capacities for a number of heavy metal ions. In this paper, the adsorption properties of a pre-treated biomass of marine algae *Padina* sp. for copper(II) were investigated. Equilibrium isotherms and kinetics were obtained from batch adsorption experiments. The biosorption capacities were solution pH dependent and the maximum capacity obtained was 0.80 mmol/g at a solution pH of about 5. The biosorption kinetics was found to be fast, with 90% of adsorption within 15 min and equilibrium reached at 30 min. The effects of light metal ions on copper(II) uptake were studied and the presence of light metal ions did not affect copper(II) uptake significantly. Fixed-bed breakthrough curves for copper(II) removal were also obtained. This study demonstrated that the pre-treated biomass of *Padina* sp. could be used as an effective biosorbent for the treatment of copper(II) containing wastewater streams. © 2002 Published by Elsevier Science Ltd.

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

1. Introduction

The removal and recovery of heavy metals from wastewater is important in the protection of the environment and human health. A number of technologies such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes have been used to remove copper(II) from wastewater. However, these technologies are most suitable in situations where the concentrations of the heavy metal ions are relatively high. They are either ineffective or expensive when heavy metals are present in the wastewater at low concentrations, or when very low concentrations of heavy metals in the treated water are required (Kuyucak and Volesky, 1988). Biosorption is an alternative technology in which an increased amount of study is being focused. Biosorption utilizes the ability of biological materials to accumulate heavy metals from aqueous solutions by either metabolically mediated or purely physico-chemical pathways of uptake (Fourest and Roux, 1992). The biological materials that have been investigated for heavy metal uptake include fungi (Matheickal et al., 1991), bacteria (Chang et al., 1997), yeast (Volesky et al., 1993), micro-algae (Harris and Ramelow, 1990) and macro-algae (Matheickal and Yu, 1997). Many of these materials are available in large quantities either as industrial waste by-products or from the natural sources.

Marine algae are biological resources, which are available in large quantities in many parts of the world. The use of biomass of marine algae, *Durvillaea potatorum* (Matheickal and Yu, 1997), *Ecklonia radiata* (Matheickal and Yu, 1996) and *Ascophyllum nodosum* (Chong and Volesky, 1995) for heavy metal removal has been reported. *Padina* sp. is a marine algae found along the Surin Island of Southern Thailand. This paper

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studies the biosorption of copper(II) ions from aqueous solutions by using pre-treated biomass of *Padina* sp. The biosorbent was pre-treated by a two-stage process of thermal and chemical modification of the native biomass (Matheickal and Yu, 1997). This study showed that the biomass can accumulate a high amount of copper(II) from aqueous solutions and it is a suitable biosorbent for practical metal recovery applications.

2. Materials and methods

Sun-dried *Padina* sp. samples in ground 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 $CaCl_2$ solution (400 ml) for 24 h under slow stirring. The solution pH was kept constant at pH 5.0 by using 0.1 M HNO_3 or 0.1 M 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 for particle size of 300–600 μm.

All experiments were conducted at room temperature (25 ± 1 °C). For isotherm determination, a series of 125 ml plastic vials were prepared containing copper nitrate solutions (100 ml) of known concentrations, which varied from 0.5 to 4.5 mM. Weighed amounts (200 mg (dry)) of biomass were added to each vial and the mixtures were agitated on the rotary shaker for 24 h. The solution pH was adjusted to the required value by using 0.1 M HNO_3 or 0.1 M NaOH hourly 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 μm membrane filter and the filtrates were analyzed for copper(II) by atomic absorption spectrometry.

Kinetics experiments were conducted in continuously stirred beakers (200 rpm) containing 500 ml of solution and 1 g of biomass. Samples of 1 ml each 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 HNO_3 or 0.1 M 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 (bed volume 6.6 ml). Solutions of copper(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 analyzed for copper(II) concentration by using atomic absorption spectrometry.

3. Results and discussion

3.1. Effect of solution pH on heavy metal adsorption

Earlier studies have indicated that solution pH strongly affects biosorption of heavy metal ions. This effect of pH on copper(II) adsorption by the pre-treated biomass of *Padina* sp. was therefore studied first. The amount of copper(II) adsorption as a function of pH is shown in Fig. 1.

At a pH of less than 2, the amount of copper(II) uptake is small. As pH increases, the amount of uptake increases and the sharpest increase observed between pH 3 and 4. At around pH 5 a plateau is reached. These results show the strong pH dependence of copper(II) biosorption.

3.2. Adsorption isotherms

Adsorption isotherms were obtained under constant solution pH values and are shown in Fig. 2. The adsorption isotherm plots have a typical shape of L-2 isotherms, indicating a reduction in the number of active sites on the adsorbents at a high residual heavy metal concentration in the solution phase.

The Langmuir adsorption model was used to correlate the isotherm data obtained at constant solution pH values,

$$q = \frac{bQ_{\max}c}{1 + bc}, \tag{1}$$

where q is the amount of copper(II) adsorbed at equilibrium (mmol/g), c is the copper(II) ion concentration in solution (mM) at equilibrium, $Q_{\max}$ is the maximum adsorption capacity and b is an affinity constant. For determining the equilibrium parameters, Eq. (1) may be written into a linearised form as follows:

$$\frac{c}{q} = \frac{1}{Q_{\max}b} + \frac{c}{Q_{\max}}. \tag{2}$$

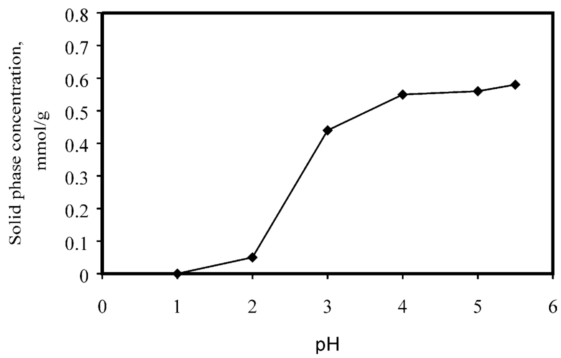

Fig. 1. Amount of copper(II) adsorption by pre-treated biomass of *Padina* sp. at various pH (dose: 2 g/l, initial copper(II) concentration: 2 mM).

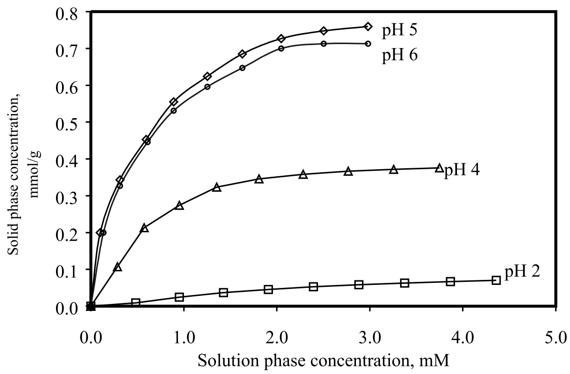

Fig. 2. Adsorption isotherms of copper(II) onto pre-treated biomass of *Padina* sp. at various pH with the Langmuir model (solid line).

Table 1
Langmuir isotherm constants for copper(II) adsorption

pH	Q_{max} (mmol/g)	b	r^2
2	0.17	6.23	0.99
4	0.46	7.14	0.99
5	0.80	7.98	0.99
6	0.79	7.95	0.99

The parameters in Eq. (2) were then obtained by using a least square linear regression analysis on each set of isotherm data and are presented in Table 1.

From Table 1, the adsorption capacity Q_{max} increases with the increase in solution pH, supporting the effect of solution pH on copper(II) adsorption. A comparison of the maximum adsorption capacity (Q_{max}) of *Padina* sp. with those of some other adsorbents reported in literature is given in Table 2. The adsorption capacity of *Padina* sp. (0.80 mmol/g) was relatively high when compared with other adsorbents.

3.3. Adsorption kinetics

Fig. 3 presents a typical set of results from kinetic experiments of copper(II) adsorption onto the biomass of *Padina* sp. at different initial concentrations. It was observed that 90% of the total soluble copper(II) were removed from solutions within 15 min of agitation. Afterwards, there were slower rates of uptake to about 30 min and no further significant adsorption were observed beyond this period. This was the same for all the initial metal concentrations for *Padina* sp. biomass studied.

3.4. Effects of light metal ions

The effect of the presence of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} ions (one at a time) in the solution on the copper(II) uptake capacity of the biosorbents was investigated. A concentration of 10 mM of the light metal ions was used to study the effect. The results are compared in Fig. 4. It is seen from the figure that the effect of Na^{+} on copper(II) uptake was negligible at a concentration of 10 mM, and K^{+}, Mg^{2+} and Ca^{2+} reduced the removal efficiency by 4%, 11% and 13%, respectively. This could be a significant advantage of algal adsorbents over the commercially available ion exchange resins as the binding of Ca^{2+} and Mg^{2+} to these resins often reduces their efficiencies.

Table 2
Uptake capacities (Q_{max}, mmol/g) for copper(II) of various adsorbents

Adsorbent	Q_{max}
Lignite (Allen and Brown, 1995)	0.10
S. fluitans (Kratochvil et al., 1995)	0.96
A. nodosum (Chong and Volesky, 1995)	0.99
C. vulgaris (Aksu et al., 1992)	0.67
Vaucheria Species (Crist et al., 1981)	0.60
Z. ramigera (Aksu et al., 1992)	0.46
Pseudomonas aeruginosa (Chang et al., 1997)	0.30
R. arrhizus (Tobin et al., 1984)	0.25
Aspergillus oryzae (Huang et al., 1991)	0.07
E. radiata (Matheickal, 1998)	1.11
D. potatorum (Matheickal, 1998)	1.30
L. japonica (Matheickal, 1998)	1.20
Padina sp. (This study)	0.80

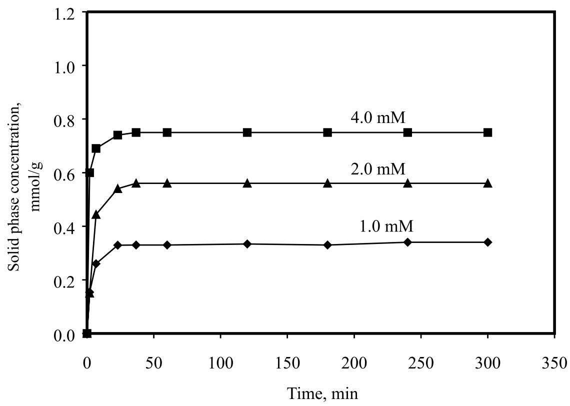

Fig. 3. Adsorption kinetics of copper(II) onto pre-treated biomass of *Padina* sp. at various initial concentrations (dose: 2 g/l, speed: 200 rpm, pH kept at 5).

3.5. Fixed-bed breakthrough curves

Fixed-bed breakthrough curves at various feed concentrations of copper(II) were obtained to illustrate the suitability of column operations (Fig. 5). The breakthrough curves followed the typical S-shaped curve for column operation with favorable adsorption isotherms. The adsorption column containing 1 g (dry weight) of

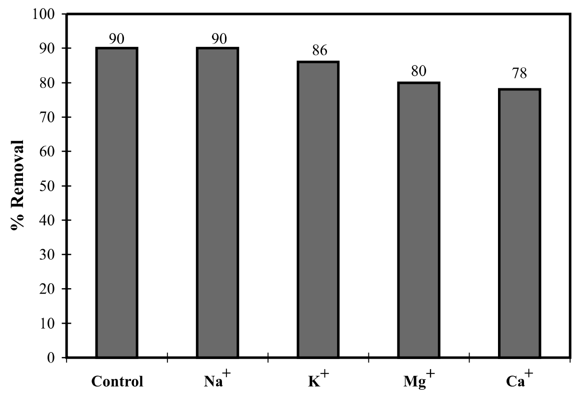

Fig. 4. Removal efficiencies of *Padina* sp. in the presence of various light metal ions (copper(II) concentration: 2 mM, dose: 2g/l, pH kept at 5).

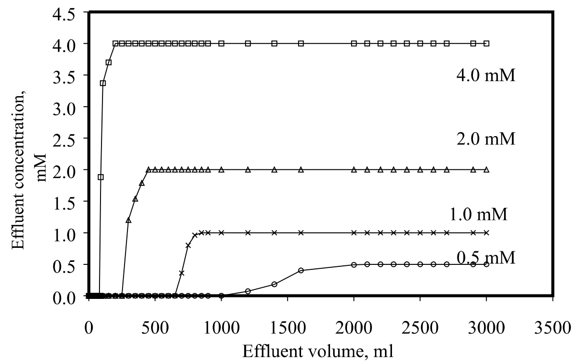

Fig. 5. Fixed-bed breakthrough curves for copper(II) removal by *Padina* sp. with various feed concentrations (dose: 2 g, bed volume: 6.6 ml, flow rate: 1.5 ml/min).

the biomass could purify 1.6 l of 0.5 mM copper solution before breakthrough, and it purified 0.8, 0.4 and 0.2 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 concentration were calculated by integrating the breakthrough curves between the breakthrough and saturation point. The adsorption capacities of column for various initial concentrations ranged between 0.78 and 0.83 mmol/g, which agree well with the maximum value of 0.80 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 copper(II) ions bearing wastewater streams. The adsorption capacities were solution pH dependent and a maximum adsorption capacity was obtained to be 0.80 mmol/g at a solution pH of about 5. The kinetics of adsorption by this biomass was rapid with 90% of total adsorption occurring within 15 min. The presence of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} did not significantly interfere with the binding of copper(II) ions. The biomass can be used in fixed-bed operations.

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