

Development of seaweed biomass as a biosorbent for metal ions

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Abstract Three seaweed species collected from Hong Kong waters were screened for their adsorption abilities for Cu^{2+} , Ni^{2+} and Zn^{2+} ; and *Ulva lactuca* having the highest metal ion removal capacity (RC) was chosen for further study. Effects of algal biomass and medium pH on the metal ions RC of *Ulva lactuca* were determined and optimized. Under the optimal conditions of the corresponding metal ions, the algal Cu^{2+} , Ni^{2+} and Zn^{2+} RCs were 65.54, 21.00 and 49.54 mg/g, respectively. The presence of other cations and anions affected the metal ions adsorption by the seaweed. The effect was dependent on the combination between the target metal ions and other cations/anions. The kinetic study revealed that the adsorption of Cu^{2+} , Ni^{2+} and Zn^{2+} by *Ulva lactuca* fitted the Langmuir isotherm. Comparing with 0.1 M HCl, citric acid, thiourea, EDTA and HNO_3 , 0.1 M H_2SO_4 efficiently recovered close to 100% adsorbed metal ions from *Ulva lactuca*. In three successive adsorption–desorption cycles, reduction in metal ion RCs was found in the second and third cycles, but almost all adsorbed metal ion could be recovered.

Keywords Biosorbent; metal ions; seaweed

Introduction

All metal ion-related industries produce wastewater that contain metal ions and will cause pollution to aquatic bodies (Blackmore, 1998). If no prompt removal is performed prior to the discharge of metal ions into the environment, different degrees of adverse effects will result to different components in the environment (Volesky and Holan, 1995). Although a wide variety of conventional physical and chemical processes were used to tackle this problem, shortages were still found among these methods (Aksu *et al.*, 1998; Williams *et al.*, 1998). Therefore, new alternatives are needed.

Biosorption is one of the promising alternatives in removal of metal ions from electroplating effluent. Microbial biomass has been successfully used to adsorb metal ions from aqueous solutions (Eccles, 1995). The minute size of microorganisms makes the proper separation of treated solution and microbial biomass to be of prime importance for the success of using microbial biomass as a biosorbent. Immobilization of microbial biomass is a common approach, but the process is costly (Kuyucak and Volesky, 1990). In this study, three seaweeds (all green algae) common in Hong Kong waters were chosen to be screened for their biosorption ability towards Cu^{2+} , Ni^{2+} and Zn^{2+} . The use of biomass of macroscopic algae (i.e. seaweeds) will reduce the cost of separation of seaweed biomass from treated solution. The effects of physico–chemical conditions such as the amount of biomass, pH, presence of other cationic metal ions and anions on the removal ability of the metal ions by the selected seaweed were characterized.

From an application point of view, recovery of metal ions and regeneration of the biosorbent are important. In this study, various acidic solutions were used to desorb metal ions from seaweed biomass and then multiple adsorption–desorption cycles of metal ions were conducted to study the feasibility of using the selected seaweed biomass as a biosorbent for the treatment of solution containing metal ions.

Materials and methods

Seaweed samples

Fresh samples of three seaweed species, namely *Ulva* sp. 1, *Ulva lactuca* and *Ulva* sp. 3 (Figure 1), for metal ion removal and recovery were collected from different sites in Hong Kong waters (Lau, 2000). Collected seaweed samples were washed by tap water to remove sand, silt and epiphytes attached to the surface. The samples were then dried overnight in an oven at 60°C. Dried samples were blended by a Cycotec sample mill (Teactor 1093-001) into powders of size <0.5 mm. Powdered seaweed biomasses were dried again in an oven at 60°C overnight to remove excess moisture and then stored in desiccators before use.

Chemicals used

Stock solution used (10,000 mg/L) of copper ions (Cu^{2+}), nickel ions (Ni^{2+}) and zinc ions (Zn^{2+}) were prepared by dissolving 13.41 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 20.25 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 10.42 g of ZnCl_2 in 500 mL MilliQ water (Millipore, USA), respectively. Desorbing agents used in the present study including 0.1 M hydrochloric acid (HCl), nitric acid (HNO_3), sulphuric acid (H_2SO_4), thiourea (TU), citric acid (CA) and ethylenediaminetetra acetic acid (EDTA) and the pHs of these desorbing agents were adjusted to 1.0 with 1 M HCl or NaOH.

Metal ions adsorption by seaweed biomass

The “batch mode” metal ion adsorption experiments were carried out in 50 mL solution with 100 mg/L of target metal ion with a selected condition for various physico–chemical parameters. The solution was shaken at 200 rpm for 60 minutes on a rotary shaker at 25°C and 1.5 mL of the solution was sampled from the reaction container into an eppendorf tube. After the seaweed biomass was separated by centrifugation by a Sanyo Micro Centaur microfuge at 12,000 rpm for 3 minutes, concentration of metal ions in the supernatant was determined by a Hitachi Z8100 polarized Zeeman atomic absorption spectrophotometer.

Effect of physico–chemical conditions on the metal ion adsorption by seaweed biomass

The “batch mode” adsorption was used to determine the effects of various physico–chemical conditions on the metal ion adsorption by seaweed biomass. The tested parameters included seaweed biomass (10, 20, 40, 80, 120, 160 and 200 mg), pH (4.0, 5.0, 6.0, 6.2, 6.4, 6.6, 6.8, 7.0, 7.5 and 8.0), reaction times (0, 1, 2, 5, 10, 15, 30, 45, 60, 90 and 120 minutes), cationic metal ions (Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{6+}) and anions (SO_4^{2-} , Cl^- and $\text{Cr}_2\text{O}_7^{2-}$) concentration (10, 20, 50, 100, 150 and 300 mg/L).

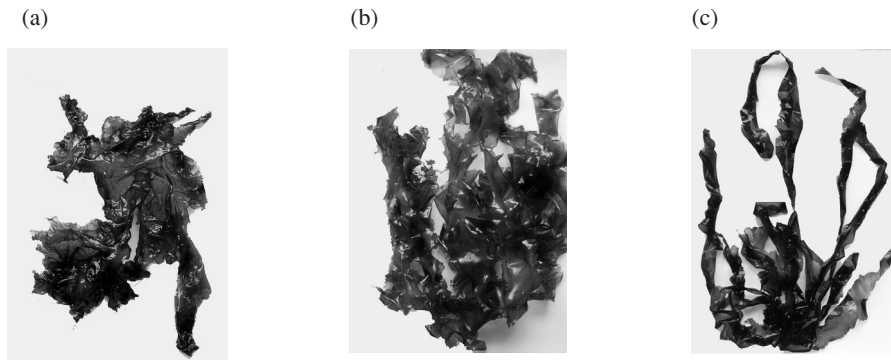


Figure 1 Seaweeds used for metal ions adsorption: (a) *Ulva* sp. 1; (b) *Ulva lactuca*; and (c) *Ulva* sp. 3

Kinetic study of metal ion adsorption by seaweed biomass

The empirical form of the Langmuir adsorption isotherm equation is given as:

$$q_e = \frac{b C_e q_{\max}}{(1 + b C_e)} \quad (1)$$

and the linear form is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{q_{\max} b} \quad (2)$$

where q_e is the removal capacity, C_e is the equilibrium concentration of metal ions in solution, q_{\max} is the maximum adsorption capacity (unit: mg/g or mmol/g), and b is the affinity constant (unit: L/mg or L/mmol).

The Freundlich isotherm holds most of the assumptions suggested in Langmuir isotherms, except that it assumes that sorption takes place on a heterogeneous surface and the binding sites are not equivalent and/or independent (Aksu *et al.*, 1999). In other words, if the data for adsorption from the solution fits the equation, it is possible that the surface is heterogeneous, although the model does not prove the fact solely (Adamson, 1982). The empirical Freundlich adsorption isotherm equation (Volesky, 1990) is given as:

$$q_e = k C_e^{1/n} \quad (3)$$

This equation can be linearized by taking natural log (ln) and given the following form:

$$\ln q_e = \ln k + \frac{1}{n} C_e \quad (4)$$

where k is the adsorbent capacity and $1/n$ is the adsorption intensity.

Recovery of adsorbed metal ions from seaweed biomass

The metal ion desorbing ability of 0.1 M hydrochloric acid (HCl), sulphuric acid (H₂SO₄), nitric acid (HNO₃), citric acid (CA), thiourea (TU) and ethylenediaminetetra-acetic acid (EDTA) with pH 1.0 were compared. A sample of 40 mg seaweed biomass was added to 50 mL 100 mg/L metal ion solution and shaken at the optimized adsorption conditions determined in previous section. The metal ions-loaded seaweed biomass was collected by a Millipore Durapore® membrane and flushed with 750 mL MilliQ water. The collected biomass was transferred to 50 mL desorbing agent and shaken at 200 rpm for 30 minutes. An aliquot of 1.5 mL was sampled and the seaweed biomass was separated by centrifugation. The metal ion concentration of the supernatant was determined by atomic absorption spectrometry. Recovery capacity (ReC, mg metal ions desorbed/g biomass) was determined.

Multiple adsorption–desorption cycles of metal ions by seaweed biomass

From the results of comparing desorption ability of various agents, 0.1 M sulfuric acid (H₂SO₄, pH 1.0) was chosen (as it had the highest metal ion recovery ability among the tested desorption agents, data not shown) in the experiment of multiple adsorption–desorption cycles of metal ions by seaweed biomass. In order to make the comparison of RCs of three metal ions, a set of selected (sub-optimal for some metal ion adsorption) conditions was used (Table 2). The procedures followed that in previous sections and three consecutive adsorption–desorption cycles were performed.

Statistical analysis

All experiments in this study were carried out in triplicate. Data were analyzed by one way

analysis of variance (ANOVA, $p < 0.05$) followed by Tukey's multiple comparison tests. The statistic analyses were performed with the aid of computer software, SigmaStat (version 2.0, Jandel Corporation).

Results and discussion

Metal ion removal capacity of three seaweeds

Among three selected seaweeds, *Ulva lactuca* had the highest Cu^{2+} , Ni^{2+} and Zn^{2+} RCs under the following experimental conditions: 50 ml solution at pH 5.0, 20 mg seaweed biomass, 100 mg/L of metal ion and a reaction time of 30 minutes (Table 1). Thus *Ulva lactuca* was chosen for further study.

Effects of physico-chemical conditions on the metal ion removal capacity of *Ulva lactuca*

Various physico-chemical parameters, such as amount of seaweed biomass, pH, reaction time, concentration of cationic metal ions and anions on the metal ions RC by *Ulva lactuca* were studied. Results indicated a slight variation in optimal conditions for adsorption of the three metal ions by the alga. The following conditions were optimal for the adsorption of metal ions by *Ulva lactuca*: 20–40 mg seaweed biomass in 50 mL metal ion solution, pH 4.0–7.6 (Table 2) and a reaction time of 15 minutes (data not shown). In addition, the presence of individual or mixed cationic metal ion or anions could only slightly affect the metal ion RCs of the alga.

Kinetics of metal ion adsorption by *Ulva lactuca*

The results of metal ion RCs by *Ulva lactuca* in the presence of various concentrations of respective metal ions were analyzed by two common monolayer adsorption isotherm models: Langmuir isotherm and Freundlich isotherm. Although Langmuir isotherm better described the metal ion removal by *Ulva lactuca* (Table 3), results also indicated that metal ion removal by *Ulva lactuca* could also be described by Freundlich isotherm (Table 3). However, the major finding was the adsorption is the major mechanism for metal ion removal by *Ulva lactuca*. Among three metal ions, the adsorption kinetics of Cu^{2+} and Zn^{2+} had a better correlation coefficient than that of Ni^{2+} either in the Langmuir or Freundlich isotherm model (Table 3). In addition, based on the q_{max} and $1/n$ of the Langmuir and Freundlich isotherm models, biomass of *Ulva lactuca* can be classified as a good biosorbent.

Table 1 Maximum metal ions RCs of three selected seaweeds at initial pH 5.0

Metal ions	Removal capacity (mg metal ions/g dry seaweed)		
	<i>Ulva sp. 1</i> *	<i>Ulva lactuca</i> *	<i>Ulva sp. 3</i> *
Cu^{2+}	47.26 ± 1.35*	54.76 ± 0.78	51.11 ± 1.93
Ni^{2+}	9.54 ± 1.41	19.29 ± 2.40	15.53 ± 2.01
Zn^{2+}	34.00 ± 3.59	43.55 ± 1.23	30.53 ± 1.48

* Data represents means ± standard deviation of triplicates

Table 2 Optimal and selected conditions for the removal of Cu^{2+} , Ni^{2+} and Zn^{2+} by *Ulva lactuca*

Metal ions	Optimal condition			Selected condition		
	Biomass weight (mg)	pH _i	RC (mg/g)*	Biomass weight (mg)	pH _i	RC (mg/g)*
Cu^{2+}	20	6.6	65.54 ± 2.01	40	5.0	42.29 ± 0.23
Ni^{2+}	40	4.0	21.00 ± 0.64	40	5.0	19.29 ± 2.40
Zn^{2+}	20	7.6	49.54 ± 0.86	40	5.0	30.11 ± 0.34

* Data represents means ± standard deviation of triplicates

Table 3 Langmuir and Freundlich isotherms for adsorption of Cu^{2+} , Ni^{2+} and Zn^{2+} by *Ulva lactuca*

Metal ions	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	r^2	k	$1/n$	r^2
Cu^{2+}	52.08	0.0601	0.9918	8.1531	0.3536	0.9581
Ni^{2+}	27.86	0.0261	0.8527	5.9483	0.2486	0.7139
Zn^{2+}	49.51	0.0354	0.9961	4.6446	0.4412	0.9616

Table 4 Metal ion RC and recovery capacity (ReC) of *Ulva lactuca* during three adsorption–desorption cycles. Experimental conditions: biomass: 40 mg in 50 mL, initial metal ion concentration = 100 mg/L, initial pH = 5.0, desorbing agents: 0.1 M H_2SO_4 (pH 1.0), time for sorption or desorption = 30 minutes, shaking rate = 200 rpm and temperature = 25°C

Metal ions	Adsorption–desorption cycle	RC (mg metal ion/mg dry seaweed)	ReC (mg desorbed metal ion/mg dry seaweed)
Cu^{2+}	1st	$38.59 \pm 1.10^{\text{a}}$	$37.41 \pm 0.86^{\text{A}}$
	2nd	$22.16 \pm 0.70^{\text{b}}$	$22.43 \pm 0.57^{\text{B}}$
	3rd	$21.42 \pm 0.87^{\text{b}}$	$21.63 \pm 0.42^{\text{B}}$
Ni^{2+}	1st	$31.53 \pm 0.81^{\text{a}}$	$29.11 \pm 0.09^{\text{A}}$
	2nd	$21.93 \pm 0.88^{\text{b}}$	$20.80 \pm 0.53^{\text{B}}$
	3rd	$19.88 \pm 1.67^{\text{b}}$	$19.97 \pm 0.23^{\text{B}}$
Zn^{2+}	1st	$32.91 \pm 0.62^{\text{a}}$	$29.35 \pm 0.17^{\text{A}}$
	2nd	$21.91 \pm 0.55^{\text{b}}$	$18.73 \pm 0.06^{\text{B}}$
	3rd	$20.52 \pm 0.44^{\text{c}}$	$\pm 0.16^{\text{C}}$

* Data represents means \pm standard deviation of triplicates. Data with the same letter are statistically identical ($p < 0.05$) and comparisons were performed between data of same metal ion in different adsorption (lower case letters) or desorption (upper case letters) cycles

Multiple adsorption–desorption cycles experiment

In order to compare the feasibility of using seaweed biomass for multiple uses, a set of multiple adsorption–desorption cycles of metal ions by seaweed biomass was carried out (Table 4). For all three metal ions, the metal ion RCs of *Ulva lactuca* were high (about 30–38 mg metal ion/g dry seaweed biomass) of in the first cycle, and close to 100% of adsorbed metal ion could be recovered by washing with 0.1 M H_2SO_4 (pH = 1.0) (Table 4). However the metal ion RCs of the alga were significantly reduced in the second cycle, even though almost 100% adsorbed metal ions could be recovered by acid wash (Table 4). The reduction of the metal ion RC of the alga after the acid wash may be due to the destruction or morphological alteration of the binding sites on the biosorbent surface (Chu *et al.*, 1997). A similar reduction in metal ion RC was reported in multiple adsorption–desorption cycles of Cd^{2+} by *Sargassum baccularia* (Chu *et al.*, 1997). Then the algal metal ion RCs in the third cycle remained at the same level of that of the second cycle (Table 4). These results suggested that the use of seaweed biomass in multiple cycle adsorption–desorption of metal ion is feasible except the operation should be designed with a lower metal ion RC of biosorbent similar to those in the second and third cycles. The complete recovery of adsorbed metal ions in multiple adsorption–desorption cycles from the biosorbent supports the reuse of algal biomass.

Conclusions

- The order of Cu^{2+} , Ni^{2+} and Zn^{2+} adsorption affinity by the three green seaweed species studied was in the order of *Ulva lactuca* > *Ulva* sp. 3 > *Ulva* sp. 1. As a result, *Ulva lactuca* was selected for further studies.
- The optimal physico–chemical conditions of metal ions removal by *Ulva lactuca* varied for each target metal ion. However the adsorption of metal ions could be completed

within 15 minutes. The effect of mix-cations and mix-anions on Cu^{2+} , Ni^{2+} and Zn^{2+} RCs varied and was dependent on the combination of cationic metal ions and anions. In general, their effects on the algal metal ion RCs were not significant.

- The relative binding affinity of the selected metal ions by *Ulva lactuca* under the respective optimal condition was in the order of $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$.
- The biosorption of Cu^{2+} and Zn^{2+} by *Ulva lactuca* was better described by both Langmuir and Freundlich adsorption isotherms, while the biosorption of Ni^{2+} by *Ulva lactuca* was less fit both adsorption isotherms.
- The study of multiple adsorption–desorption of metal ions by algal biosorbent using 0.1 M H_2SO_4 indicated that the metal ion RCs were reduced after the first cycle and then remained constant for the following cycles. However, close to 100% loaded metal ions were recovered by acid wash in these cycles. The results suggested that biomass of *Ulva lactuca* can be used in multiple adsorption–desorption processes to remove and recover metal ions from aqueous solution.

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