

Sargassum Fusiforme Extract for Heavy Metal Removal from Waste Solution

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Abstract

Biosorption is a suitable heavy metal remediation technique for the treatment of aqueous effluents of large volume and low pollutant concentration. However, today industrial applications need the selection of efficient low-cost biosorbents. The aim of this work is to investigate brown alga such as *Sargassum fusiforme* (SF) especially habituated in JEJU island in Republic of KOREA as a low-cost biosorbent, for the fixation of metallic ions, namely Cu²⁺, Zn²⁺, Pb²⁺, Ni²⁺, Cd²⁺ and Hg²⁺, in a batch reactor. Biosorption kinetics and isotherms have been performed at pH 5.5. For all of the studied metallic ions, the equilibrium time is about 450 min and a tendency based on the initial sorption rate has been established: Hg²⁺ > Zn²⁺ > Ni²⁺ > Cu²⁺ > Cd²⁺ > Pb²⁺. The adsorption equilibrium data are well described by the Langmuir equation. The sequence of the maximum adsorption capacity is Pb²⁺ ≈ Cu²⁺ >> Ag²⁺ ≈ Ni²⁺ > Cd²⁺ > Zn²⁺ and values are ranged between 1.78 and 0.71 mmol g⁻¹. These results indicate that the SF biomass is a suitable biosorbent for the removal of heavy metals from wastewater and can be tested in a dynamic process. The selected pilot process involves a hybrid membrane process: a continuous stirred tank reactor is coupled with a microfiltration immersed membrane, in order to confine the SF particles. A mass balance model is used to describe the adsorption process and the breakthrough curves are correctly modelled. Based on these results, it is demonstrated that SF is an interesting biomaterial for the treatment of water contaminated heavy metals.

Introduction

Each year a large amount of seaweed is dumped on beaches by tides. In JEJU island, the local government have to harvest it during summer months for the comfort of holidaymakers. These natural organic materials are considered as waste materials, and are treated as domestic wastes. Seaweed is mainly composed of brown macro-alga well known for their high content of alginate substances which could potentially bind metallic ions. Heavy metal pollution is of greatest concern among the kinds of environmental pollution because of the heavy metals' high toxicity and mobility. Lead, mercury, copper, cadmium, zinc and nickel are among the most common pollutants found in industrial effluents. Even at low concentrations, these metals can be toxic to organisms, including humans. The US Environmental Protection Agency (EPA) [1] requires the levels of lead, copper, cadmium, zinc and nickel in drinking water not to exceed 0.015, 1.3, 0.005, 5, 0.04 mg l⁻¹.

A number of techniques such as membrane filtration, reverse osmosis, chemical precipitation, ion exchange, electro-deposition and adsorption have been used to remove the toxic metals from aquatic environments with varying degrees of success. Adsorption is an efficient and economical method that can be used for the removal of heavy metals from wastewaters. However, the cost of the adsorbents to be used is the most important restrictive factor in view of the applicability of the adsorption process [2-6]. In recent years, the methods for removing heavy metals from wastewaters have resulted in the search for the development of alternatives from cheaper and more readily available materials that may be useful in reducing the pollutant content to the levels established by the legislation [7,8]. Biosorption of heavy metals can be an efficient process for ion removal from aqueous solution and an attractive technology for the treatment of industrial wastewaters [9].

The primary objective of the this study is to explore the potential of marine macro algae, *Sargassum fusiforme* (SF), in their natural form for the removal of cadmium, nickel, copper, zinc, mercury and lead from aqueous medium. For this purpose kinetic

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and adsorption studies in batch were performed. The secondary objective is to use this natural low-cost biosorbent in a dynamic process at a laboratory scale pilot: a continuous stirred tank reactor is coupled with a microfiltration immersed membrane.

Materials and Methods

Biosorbent

The extract of SF was used in this work: it was collected on the JEJU Island in Republic of Korea. The biomass was washed twice with tap water and then twice with deionized water. After drying at 60°C, the algae were crushed and sieved. After sieved, extract in the boiled deionized water within 30 min, the weight ratio of SF and water was 1:100, and 50 g of the sieved SF powder used for extraction. The extracted SF solution was filtered with a 0.5 um filter and then cooled at room temperature. The SF extract was used in the experiments as a biosorbent for cadmium, nickel, copper, zinc, mercury and lead. The wet mass was dried at 60°C and was used as the biosorbent.

Adsorption kinetic and isotherm experiments

To obtain the kinetic curves, 10.3 g of SF were introduced into 1 liter(l) of metallic solution, at pH 5.5 and 20°C, with an initial concentration in the range 4 - 7 × 10⁻⁵ M. At suitable time intervals, the decay of the concentration was followed by atomic absorption measurements (Perkin Elmer AA200). No pH variations have been observed during the sorption. Two kinetic models have been used to describe the experimental data: the pseudo-first-order and pseudo-second-order rate equations [8].

The originator of the pseudo-first-order reaction is

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

The originator of the pseudo-second-order reaction is

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where t is the time (min), q_t and q_e are the metallic concentration of the solid at time t and mass balance time (mmol g⁻¹), k₁ (min⁻¹) and k₂ (g mmol⁻¹ min⁻¹) the rate constant of the pseudo-first-order and pseudo-second-order adsorption. To assess k₁, Equation (1) can be rearranged as follows:

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t \quad (3)$$

Taking into account that the initial sorption rate v₀ (mmol g⁻¹ min⁻¹) can be defined by v₀ = k₂ q_e², Equation (2) can be rearranged as follows:

$$\frac{t}{q_t} = \frac{1}{v_0} + \frac{1}{q_e} t \quad (4)$$

For isotherm experiments, a known dry weight of algae (10.3 g) is equilibrated with 1000 ml of spiked metals ions solution of known concentration (initial concentration range 0.7–24 mg/l) in a glass bottle at 20°C, pH 5.5, in a shaker bath for a determined period of time. The concentration of free metals ions (Cd²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Hg²⁺, Pb²⁺) in the solution after and before adsorption was determined by atomic adsorption. No pH

variations have been measured. The isotherm curves were fit using the Langmuir equation:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (5)$$

where q_{max} is the maximum adsorption capacity (mmol/g), b (l/mmol) is an equilibrium constant relating to the energy of interaction with the surface, and C_e is the solution concentration at equilibrium (mmol/l). On rearrangement to the following simple linear form [10], a plot of 1/q_e against 1/C_e gives a straight line:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b \cdot q_{\max}} \frac{1}{C_e} \quad (6)$$

Dynamic adsorption experiments

The pilot plant unit is represented schematically in Figure 1. It involves a continuous stirred tank reactor (CSTR) coupled with a microfiltration immersed-membrane unit. Originally, it was provided for a biological wastewater treatment unit, which implied an agitation by air bubbling, but this kind of agitation was shown as sufficient for this study since the SF presented a low density. The CSTR is fed with a solution of nickel ions (around 10 mg/l), the reactor volume (V) is adjusted to 24 l and the outlet flow rate (Q) set up at 0.3 l/h with a peristaltic pump. As function of time, this flow rate was found to be stable. The volume of the CSTR remained constant throughout the experiment by a level control that regulated the inlet of the polluted water. Experiments were performed only with the nickel ion and two amounts of SF (10.2 and 20.4 g l⁻¹). The temperature was between 22 and 24°C. After the adsorption step in the CSTR, the separation between the solution and the sorbent particles was realized by filtration in an external immersed-membrane unit. The retentate flux was returned to the CSTR and the heavy metal ion concentration was followed in the permeate in order to obtain the experimental breakthrough. The pH and the temperature were not controlled but continuously monitored. A blank test (without SF) was also performed to check that no competing adsorption occurred through the whole pilot. From the mass balance equation in the CSTR, a model, based on the mass balance in the adsorber, has been developed for the prediction of the breakthrough curves of nickel in the permeate [10]:

$$V \cdot \frac{dC}{dt} = Q \cdot (C_0 - C) - \frac{dq}{dt} \cdot X \cdot V \quad (7)$$

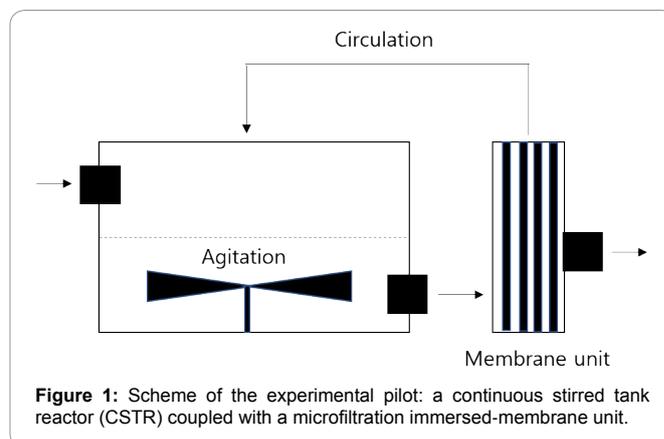


Figure 1: Scheme of the experimental pilot: a continuous stirred tank reactor (CSTR) coupled with a microfiltration immersed-membrane unit.

or, in other terms,

$$\frac{dC}{dt} = \frac{Q \cdot (C_0 - C)}{V \cdot (1 + X \cdot (dq / dC))} \quad (8)$$

with, V the volume of the reactor (litters), C the concentration of nickel in the permeate (mg/l) and C₀ the initial concentration of nickel in the polluted wastewater (mg/l), q the fixation capacity on SF (mg/g), Q the flow rate (l/min), X the concentration of SF (g/l) and T the time (min).

Results

Biosorbent physico-chemical characteristics

The physico-chemical characterizations of the dry material have been determined as previous studies [11,12]. A cationic exchange capacity of 1.15 meq/g of dry weight and a total acidity of 2.26 meq/g of dry weight have been deduced from potentiometric titrations. Moreover, the biomass presents at least three kinds of acidic functional groups with pK_a values close to 2.7, 7.8 and 8.8. The point of zero net proton charge has been also determined at pH 6.3. Calcium and magnesium ions release has been followed and measured, in relation to the metallic ion biosorption, and all of these observations lead us to propose a fixation mechanism by ionic exchange. All of these characteristics lead us to believe that SF is suitable for use as a low-cost biosorbent material for heavy metal removal from polluted aqueous solutions.

Adsorption kinetic

Figure 2 shows the kinetics of metal adsorption onto SF obtained by batch contact time studies, namely, Cd²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Hg²⁺ and Pb²⁺ ions. The plots represent the amounts of metal remaining in solution versus time, for an initial concentration ranged between 4 and 7 × 10⁻⁵ M. For all metals, it is shown that the sorption reactions are fast because equilibrium was reached within 580 min; an important percentage of the metal removed is achieved in the first 300 min of contact time with the adsorbent. In all cases, and despite the change in initial concentration, a sequence based on the initial sorption rate v₀ could be proposed: Hg²⁺ > Zn²⁺ > Ni²⁺ > Cu²⁺ > Cd²⁺ > Pb²⁺. In terms of the rate constant of pseudo-second-order adsorption, two groups could be identified: Hg²⁺, Zn²⁺ and Ni²⁺, which exhibit higher k₂

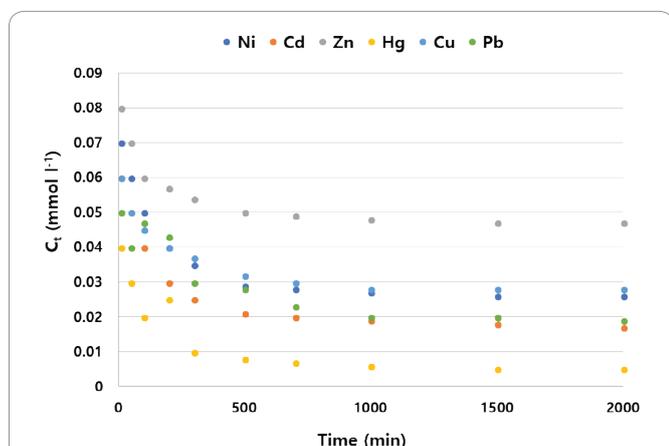


Figure 2: Heavy metal sorption kinetics at pH 5.5, dry FS concentration 10.3 g l⁻¹.

values close to 0.028 g mmol⁻¹ min⁻¹ in comparison with the second group, Cu²⁺, Cd²⁺ and Pb²⁺, with k₂ values of 0.018 g mmol⁻¹ min⁻¹. This tendency can be verified with the pseudo-first-order model. Two groups of ions could be made (except Hg²⁺): Zn²⁺ and Ni²⁺ which have a similar k₁ value determined at 0.081 min⁻¹ with comparable initial concentrations and a second group made with Cu²⁺, Cd²⁺ and Pb²⁺ (considering that Pb²⁺ initial concentration was the lowest) with k₁ values around 0.040 min⁻¹. Finally, the q_e values calculated with the pseudo-second-order model are very similar to the experimental values and ranged roughly from 0.3 to 0.5 mmol g⁻¹. These capacities are high in comparison with the low initial concentration (4 to 7 × 10⁻⁵ mol l⁻¹) which means that the SF promise very good performance in terms of adsorption isotherms. Moreover, it can be noted that the fast sorption kinetics are also interesting when a water treatment process is designed which leads the SF to be a suitable biosorbent for a continuous flow system.

Metal absorption isotherm equilibria

Equilibrium adsorption studies were performed to provide the maximum metal adsorption capacities of SF biomass. For all experiments, the lowest final pH value was close to 5.0 ± 0.2 for all of the metal ions studied. Then, no effort was made to control the solution pH during the experiments, and no ionic strength was imposed. The adsorption isotherms of metals by SF are shown in Figure 3.

The values q_{max} and b obtained from Langmuir fit plots are listed in Table 1. The respective determination coefficients r² of the experimental data suggests that the metal ions adsorption follows the Langmuir model and so sorbed species form a monolayer coverage on the adsorbent surface. The sequence

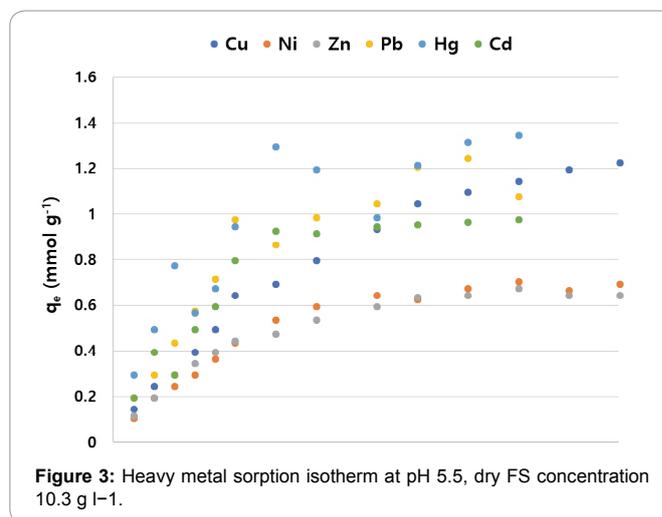


Figure 3: Heavy metal sorption isotherm at pH 5.5, dry FS concentration 10.3 g l⁻¹.

	q _{max} (mmol g ⁻¹)	b (l mmol ⁻¹)	r ²
Pb	1.682	21.22	0.965
Cu	1.730	25.55	0.996
Hg	0.956	172.56	0.937
Ni	0.946	21.44	0.990
Cd	0.852	24.23	0.948
Zn	0.708	39.16	0.981

Table 1: Biosorption capacities for the studies metal ions and Langmuir parameters.

of the maximum adsorption capacity (expressed in mmol g⁻¹) is as follows: Pb²⁺ ≈ Cu²⁺ >> Hg²⁺ ≈ Ni²⁺ > Cd²⁺ > Zn²⁺. The biosorbent really shows a preferential binding capacity for Cu²⁺ and Pb²⁺ cations and the order of magnitude of the q_m values is comparable to ion exchange resin.

From a review of previous publications on the metal ion adsorption onto various algal biomass, natural seaweeds show established cationic ion absorber. Also, the brown algae achieve high sorption capacities. This observation could be correlated with the high content of alginate species in brown algae. The results presented in this study with SF show that this latter species is a very good biosorbent and could be tested in a dynamic adsorption process for water treatment.

Dynamic adsorption experiments

In dynamic treatment processes, the performances are commonly assessed from experimental breakthrough curves that present the profiles of the outlet concentration as a function of time. From the mass balance in the CSTR and considering that the Langmuir adsorption model could be used to describe the term dq/dC, Equation (8) leads to the expression of C_t versus t (Figure 4). First, a blank reference test, without SF (X = 0 g l⁻¹), was performed in order to confirm that no competing adsorption occurred through the whole pilot. The concentration of nickel was close to 10 mg l⁻¹, the pH was 5.0 ± 0.2 and the flow rate was 0.03 l min⁻¹. The clear circles present the experimental data of this test, and it is shown that the modeled curve (8) gives a good description of these experimental points, even if the model slightly overestimates the concentration of mercury in the permeate until 1500 min. Two breakthrough curves (dark symbols in Figure 4) have been then realized with different concentrations of biosorbent and the other operating conditions being similar.

With 0.2 g l⁻¹ of SF, a good fit is obtained between the experimental and modeled data, with a slight overestimation of the concentration during the first 1500 min, and a much better description until the end of the test. This overestimation is also marked with the experiment carried out with the highest amount of SF, but the whole adequacy confirms that the modeled curve is interesting for the prediction of adsorption performances. With these experimental and modeled curves, a dynamic fixation capacity could be deduced from the area difference between the blank test and the breakthrough curves.

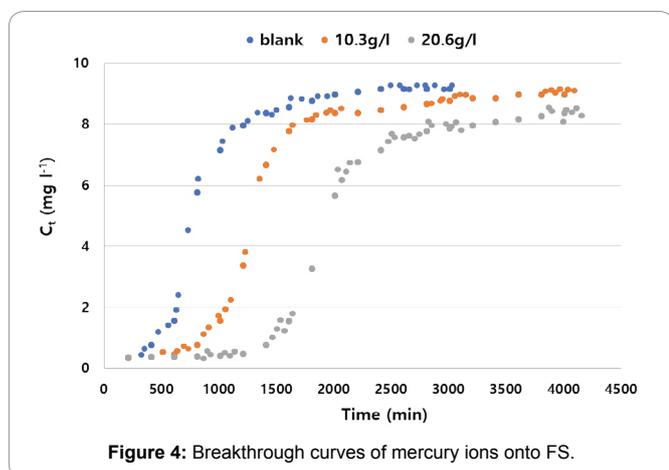


Figure 4: Breakthrough curves of mercury ions onto FS.

	7h	24h	48h
Control	100 ± 8	100 ± 16	100 ± 26
FS	109 ± 14	124 ± 23	133 ± 9

Table 2: Cytotoxicity for fibroblast cells

These capacities (expressed in mg g⁻¹) could be compared with those obtained in a batch reactor from the Langmuir model. In dynamic reactors and for X = 0.2 g l⁻¹ of SF, the experimental and modelled capacities are very close (38.6 and 39.8 mg g⁻¹, respectively). For X = 0.4 g l⁻¹ of SF, the modelled capacity (32.8 mg g⁻¹) is underestimated in comparison with the experimental capacity (44.0 mg g⁻¹), confirming then the tendency observed previously. In all cases, these values are in a very good agreement with the capacities deduced from the batch reactor, both the experimental value (41.0 mg g⁻¹) as well as that modeled by the Langmuir equation (55.5 mg g⁻¹). These results show that the breakthrough curve model could be an interesting and predictive tool for the design of treatment units. The ability of this low-cost sorbent to perform in a dynamic process for wastewater treatment has been demonstrated and further experiments will lead to an optimization of the conditions of use.

Cytotoxicity

The treatment of SF for heavy metal removal shows toxicity, it may be a problem for industrial scale application. To remove heavy metals, in general SF can be overdosed, which is actually difficult to remove from after-uses. In the case of past-well researched chemical compounds for absorbing heavy metals, the high toxicity of the compound itself may prevent its use despite its high efficiency. The SF is a natural seaweed and can be expected not to exhibit toxicity when overdose is applied. fibroblast cell-line(NIH3T3-E1) treated with SF for 48 hours showed no toxicity. SF was administered to each cell at a concentration of 300 mg l⁻¹. After 24 hours and 48 hours, cell viability was measured by MTT assay. After 7 h, the cells showed a survival rate of 103% similar to that of control group (treated vehicle), and survival rates were 124 and 133% at 24 and 48 h, respectively [13-24] (Table 2).

Discussion

The low-cost brown alga Sargassum fusiforme has been investigated for the biosorption of Cu²⁺, Zn²⁺, Pb²⁺, Ni²⁺, Cd²⁺ and Hg²⁺. The sorption kinetic reactions follow the pseudo-first-order and pseudo-second-order model and the sequence based on initial sorption rate is Hg²⁺ > Zn²⁺ > Ni²⁺ > Cu²⁺ > Cd²⁺ > Pb²⁺. The contact time study revealed also a fast fixation of around 580 min. Batch fixation performances follow the sequence Pb²⁺ ≈ Cu²⁺ >> Hg²⁺ ≈ Ni²⁺ > Cd²⁺ > Zn²⁺. With the dynamic process, the performances are assessed from experimental and modeled breakthrough curves. In the case of the biosorption of Hg²⁺ ions, a good description of the experimental points is obtained. The fibroblasts treated with SF at a concentration of 300 mg l⁻¹ for 7, 24 and 48 hours showed apparent non-toxicity. As a result, it is expected that SF can be effectively used as a natural biosorbent agent capable of removing heavy metals such as lead and mercury without specific cytotoxicity from industrial wastewater.

References

- Sheng PX, Ting YP, Chen JP, Hong L. Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J Colloid Interface Sci.* 2004;275(1):131-141.

2. David Kratochvil, Bohumil Volesky. Biosorption of Cu from ferruginous wastewater by algal biomass. *Water Res.* 1998;32(9):2760-2768.
3. David Kratochvil, Bohumil Volesky. Advances in the biosorption of heavy metals. *Trends in Biotech.* 1998;16(7):291-300.
4. Andrés Y, Texier AC, Le Cloirec P. Rare earth element removal by microbial biosorption: a review. *Environ Technol.* 2003;24(11):1367-1375.
5. Gerente C, Reddad Z, Andres Y, Le Cloirec P. Competitive adsorption of metals and organics onto a low cost natural polysaccharide. *Environ Technol.* 2004;25(2):219-225.
6. Gérente C, Lee VCK, Le Cloirec P, McKay G. Application of chitosane removal of metals from wastewaters by adsorption – mechanisms and model review. *Crit. Rev. Environ Sci Technol.* 2007;37(1):41-127.
7. Texier AC, Andrés, Y, Le Cloirec P. Selective biosorption of lanthanide (La, Eu, Yb) ions by *Pseudomonas aeruginosa*. *Environ Sci Technol.* 1999;33(3):489-495.
8. Reddad Z, Gerente C, Andres Y, Le Cloirec P. Adsorption of several metal ions onto a low cost biosorbent: kinetic and equilibrium studies. *Environ Sci Technol.* 2002;36(9):2067-2073.
9. Jinbai Yang, Bohumil Volesky. Removal and concentration of uranium by seaweed biosorbent. *Process Metallurgy.* 1999;9:483-492.
10. Reddad Z, Gérente C, Andrés Y, Thibault JF, Le Cloirec P. Cadmium and lead adsorption by a natural polysaccharide in MF membrane reactor: experimental analysis and modelling. *Water Res.* 2003;37(16):3983-3991.
11. Boulinguez B, Le Cloirec P, Wolbert D. Revisiting the determination of Langmuir parameters - application to tetrahydrothiophene adsorption onto activated carbon. *Langmuir.* 2008;24(13):6420-6424.
12. Ahmady-Asbchin S, Andrés Y, Gérente C, Cloirec PL. Biosorption of Cu (II) from aqueous solution by *Sargassum fusiforme*. *Bioresource Technol.* 2008;99(14):6150-6155.
13. Romera E, González F, Ballester A, Blázquez ML, Muñoz JA. Biosorption of heavy metal by *Fucus spiralis*. *Bioresource Technol.* 2008;99(11):4684-4693.
14. Kaewsarn P, Yu Q. Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina* sp. *Environ Pollut.* 2001;112(2):209-213.
15. Davis TA, Volesky B, Vieira RHSF. *Sargassum* seaweed as biosorbent for heavy metal. *Water Res.* 2000;34(17):4270-4278.
16. Fourest E, Volesky, B. Alginate properties and heavy metal biosorption by marine algae. *Appl Biochem Biotechnol.* 1997;67(3):33-44.
17. Romera E, Gonzalez F, Ballester A, Blazquez ML, Muñoz JA. Comparative study of biosorption of heavy metals using different types of algae. *Bioresource Technol.* 2007;98(17):3344-3353.
18. Cochrane EL, Lu S, Gibb SW, Villaescusa I. A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media. *J Hazard Mater.* 2006;137(1):198-206.
19. Davis TA, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* 2003;37(18):4311-4330.
20. Jalali R, Ghafourian H, Asef Y, Davarpanah SJ, Sepehr S. Removal and recovery of lead using nonliving biomass of marine algae. *J Hazard Mater.* 2002;92(3):253-262.
21. Sanchez A, Ballester A, Blazquez ML, González F, Muñoz J, Hammami A. Biosorption of copper and zinc by *Cymodocea nodosa*. *FEMS Microbiol Rev.* 1999;23(5):527-536.
22. Prasher SO, Beauguard M, Hawari J, et al. Biosorption of heavy metal by red algae (*Palmaria palmata*). *Environ Technol.* 2004;25(10):1097-1106.
23. Vilar VJP, Botelho CMS, Boaventura RAR. Influence of pH, ionic strength and temperature on lead biosorption by *Gelidium* and agar extraction algal waste. *Process Biochem.* 2005;40(10):3267-3275.
24. Ozer A, Ozer D, Ekiz HI. The equilibrium and kinetic modelling of the biosorption of copper (II) ions on *Cladophora crispata*. *Adsorption.* 2005;10(4):317-326.