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Journal of Hazardous Materials B92 (2002) 253–262

Journal of Hazardous Materials

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Removal and recovery of lead using nonliving biomass of marine algae

R. Jalali [a,*], H. Ghafourian [a], Y. Asef [a], S.J. Davarpanah [a], S. Sepehr [b]

[a] *Department of Biotechnology, Nuclear Research Center, Atomic Energy Organization of Iran, Tehran, Iran*
[b] *Department of Biology, University of Alzahra, Tehran, Iran*

Received 31 May 2001; received in revised form 17 December 2001; accepted 17 December 2001

Abstract

Batch equilibrium sorption experiments were used for screening for cost-effective marine algal biomass harvested from the Gulf of Persian. Biosorption of lead by eight brown, green and red marine algae was investigated. Biosorption of lead was rapidly occurred onto algal biosorbents and most of the sorbed metal was bound in <30 min of contact. Three species of brown algae, namely *Sargassum hystrix*, *S. natans* and *Padina pavonia*, removed lead most efficiently from aqueous solution, respectively. The applicability of the Langmuir and Freundlich models for the different biosorbents was tested. An increasing uptake of the metal by biosorbents with increasing pH was demonstrated. Desorption of the adsorbed lead on biosorbent was conducted by decreasing the pH values to lower than 1.0. Removal of lead from *Sargassum* biomass was successfully achieved by eluting with 0.1 M HNO_3 for 15 min and a high degree of metal recovery was observed (95%). For optimum operation in the subsequent metal uptake cycle, regeneration of the *Sargassum* biomass was efficiently performed by 0.1 M $CaCl_2$ for 15 min that was total and reversible. In repeated use of biomass experiment, the lead uptake capacity of *Sargassum* biomass was constantly retained (98%) and no significant biomass damage took place after 10 sorption–desorption cycles.

Keywords: Lead biosorption; Desorption and regeneration; Metal removal; Marine algae; Kinetics

1. Introduction

Some industrial processes result in the release of heavy metals in the natural water systems. This has lead to increasing concern about the effects of toxic metal as environmental contaminants. Lead is metal which could be at the top of the environmental concerns [1–4].

* Corresponding author. Tel.: +98-21-61383438; fax: +98-21-8021412.
E-mail address: rjalali@seai.neda.net.ir (R. Jalali).

0304-3894/02/$ – see front matter
PII: S0304-3894(02)00021-3

Lead is used as an industrial raw material for storage battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing [1,3]. Perhaps no other metal, not even arsenic, has had its toxicology as extensively studied as has lead [1].

Conventional methods for removing heavy metals from industrial effluents (e.g. precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation) are often ineffective and costly when applied to dilute and very dilute effluents [2,4–8].

Recently, biological removal processes has been attracting considerable attention for removing heavy metals from aqueous wastes and screening for microorganisms having higher potential for removing heavy metals from wastes has been promising so far [6,9–13]. Microbial removal of heavy metals offers the advantages of low operating cost, minimizing secondary problems with metal-bearing sludges and high efficiency in detoxifying very dilute effluents [2,13].

Metal uptake by microorganisms can occur actively (bioaccumulation) and/or passively (biosorption) [10,11,14–16]. Feasibility studies for large-scale applications demonstrated that the biosorptive processes are more applicable than the bioaccumulative processes because living systems (active uptake) often require the addition of nutrients and hence increase biological oxygen demand (BOD) or chemical oxygen demand (COD) in the effluent, maintenance of a healthy microbial population is difficult due to metal toxicity and other unsuitable environmental factors, potential for desorptive metal recovery is restricted since metal may be intracellulary bound, metabolic products may be form complexes with metals to retain them in solution and mathematical modeling of a nondefined system is difficult [8,17].

Biosorption uses biomass raw materials which are either abundant (e.g. marine algae) or wastes from other industrial operations (fermentation wastes) [2,18,19]. Biosorption of heavy metals (Cu, Cd and Zn) on caustic treated yeast immobilized in alginate has been reported and revealed that immobilized yeast could be reactivated and reused in a manner similar to ion-exchange resins [8]. Dried *Chlorella vulgaris*, a unicellular green alga, has been utilized for lead ions sorption and has been suggested as the sorbent for removing lead ions from waste water [3]. Biosorption of metals (Ni, Zn, Cd, Pb, etc.) by bacterial and fungal mycelial by-product (fermentation wastes) and influenced of environmental factors have been investigated [18,19]. However, fermentation wastes abilities are limited, because the species available are restricted [20].

Marine algae, which are abundant, renewable and could be obtained on a large scale very economically from the oceans, practice in a manner similar to ion exchangers for biosorption of heavy metals [2,13]. The main objective of this work was to investigate the ability of selected marine algae biomass to adsorb lead from aqueous solution. The influence of different parameters on the sorption of lead has been investigated.

2. Materials and methods

2.1. Preparation of biosorbents

Fresh samples of brown algae (*Sargassum hystrix*, *S. natans* and *Padina pavonia*), green algae (*Ulva lactuca* and *Cladophora glomerata*) and red algae (*Gracilaria corticata*, *G.*

canaliculata and *Polysiphonia violacea*) were harvested in September from the Persian Gulf on the coast of Qeshm, Iran. The biomass of algae was extensively washed with distilled water and sun-dried on the beach and then dried in an oven at 50 °C overnight. Dried biomass was ground in a laboratory blender and sorted by sieving using the standard test sieves.

2.2. Sorption experiments

2.2.1. Preparation of lead solution

Stock lead solution (1 g/l) was prepared by dissolving 1 g of metallic lead in 50 ml of 1:1 nitric acid and diluting quantitatively to a volume of 1 l using double distilled water. Lead solution of desired concentrations were prepared by diluting of stock solution. The pH of each solution was adjusted to 4.5 with 0.1 M NH_4OH and HNO_3.

2.2.2. Equilibration time

Preliminary experiments were performed to determine equilibrium time for each biosorbent. For this purpose, 100 mg of each dried biomass (size of particles $d = 0.2$–0.5 mm) was added to 50 ml lead solution with a known concentration and initial pH 4.5 in 100 ml Erlenmeyer flasks. The flasks placed on a shaker with constant shaking at 100 rpm, at 30 °C. The pH of solutions during the contact period was adjusted to 4.5 (± 0.2) using small amount of 0.1 M HNO_3 or 0.1 M NH_4OH as required. Samples were periodically withdrawn and the solutions were separated from the biomass by filtration through the filter papers (Whatman No. 40 Ashless).

After appropriate dilution, the concentrations of lead in the filtrates were determined by atomic absorption spectrophotometery (AAS) using a Varian Spectra AA-20 atomic absorption spectrophotometer at the wavelength of 217 nm.

2.2.3. Comparison of algal biosorbents

In order to compare the metal binding properties of the different biosorbents equilibrium sorption experiments were performed at various known lead concentrations for 3 h (time required for the sorption equilibrium) as described above. Metal free and biosorbent free blanks were used as controls.

2.2.4. Effect of pH

The effect of pH values (pH 1–5) of solution on the sorption of lead by three types of biomass (*S. hystrix, S. natans* and *P. pavonia*) was studied.

2.2.5. Recovery of lead and repeated use of biomass

Following the lead sorption batch experiment for 45 min, metal-laden biomass (*S. hystrix*) was separated by filtration and suspended into 15 ml of the eluent solution (0.1 M HNO_3). The filtrate was diluted with distilled water and analyzed by AAS. Desorption of lead from biomass was carried out on a rotary shaker (100 rpm) for 15 min. The biomass was separated by filtration and thoroughly washed with distilled water. The concentration of the lead released into the eluent solution was determined by AAS. The unloaded biomass was regenerated with 15 ml of 0.1 M $CaCl_2$ for 15 min, twice washed with distilled water and

then suspended in the new lead solution for 45 min. The sorption–desorption experiment was continuously performed in 10 cycles.

All sorption experiments were carried out in triplicate.

2.3. Data evaluation

The amount of metal bound by the biosorbents was calculated as follows:

$$q = \frac{v(C_i - C_f)}{m}$$

where q is the metal uptake (mg metal/g of the biosorbent), v the liquid sample volume (ml), C_i the initial concentration of the metal in the solution (mg/l), C_f the final (equilibrium) concentration of the metal in the solution (mg/l), and m the amount of the added biosorbent on the dry basis (mg).

Sorption models were chosen for comparison with experimental data:

$$\text{The Langmuir model, } q = \frac{q_{max} b C_f}{1 + bC_f}$$

where q_{max} is the maximum metal uptake under the given conditions, b a constant related to the affinity between the biosorbent and sorbate.

$$\text{The Freundlich model, } q = kC_f{}^{(1/n)}$$

where k and n are Freundlich constants.

3. Results and discussion

In the biosorption of lead by algal biosorbents, most of the metal ions were sequestered from solution within the first 30 min and almost no increase in the level of bound metal occurred after 3 h. For example, Fig. 1 shows the kinetics of lead binding to the biosorbent derived from *S. hystrix.* Hence, 3 h was used as the equilibrium time for algal biosorbents.

The comparison of the sorption performance of the biosorbents was achieved under the same environmental conditions (e.g. pH, temperature, ionic strength, etc.). Biosorption equilibrium isotherms were plotted for the metal uptake (q) against the residual metal concentration in solution (Fig. 2.). The (q) versus (C_f) sorption isotherm relationship was mathematically expressed by linearized Langmuir and Freundlich models (Fig. 3. and Table 1). The higher the values of k and n and the lower the value of b, the higher the affinity of algae [3,22]. As shown in Table 1, the regression coefficient (R^2) for each biosorbent shows the most suitable model for describing these sorption processes.

These results indicate that biosorbents derived from three types of brown algae, namely *S. hystrix, S. natans* and *P. pavonia*, have the highest lead removal capacity, respectively. Brown algae in particular are suited for binding metallic ions due to their polysaccharide material content (alginates, xylofucoglycuronans, xylofucoglucans and homofucans). These polysaccharides contain carboxyl and sulfate groups that have identified as the main

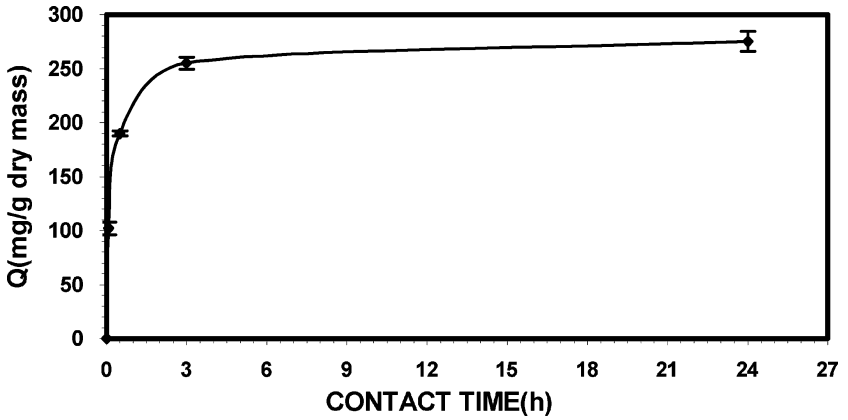

Fig. 1. Kinetics of lead binding to the *S. hystrix* at pH 4.5, initial metal concentration of 500 mg/l, size of particles $d = 0.2$–0.5 mm, biomass density 2 g/l and temperature 30 °C.

metal-sequestring sites [2,13,22,24–26]. These three types of brown algae were investigated in more detail.

The feasibility of sorption of lead from dilute (10 mg/l) as well as concentrated solutions was tested. As shown in Fig. 4, all the biosorbents can decrease lead concentration to lower than 1.0 mg/l. The US EPA allows solution containing heavy metals to be discharged if the concentration is usually <1.0 mg/l [3].

The external pH can significantly influence biosorption of heavy metals and there may be an optimum pH for maximal rates below or above which a decrease occurs [8,21]. It has been known that uptake of heavy metals by most biosorbents decrease dramatically as the pH of the metal solution decreases from pH 6 to 2.5 [22]. In the present work, biosorption of

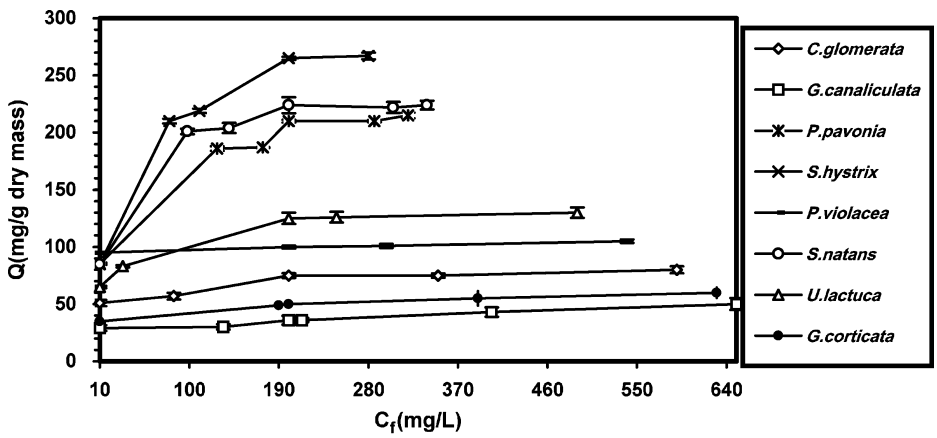

Fig. 2. Comparison of the metal binding properties of the biosorbents at different residual concentrations, pH 4.5, size of particles $d = 0.2$–0.5 mm, contact time 3 h, biomass density 2 g/l and temperature 30 °C.

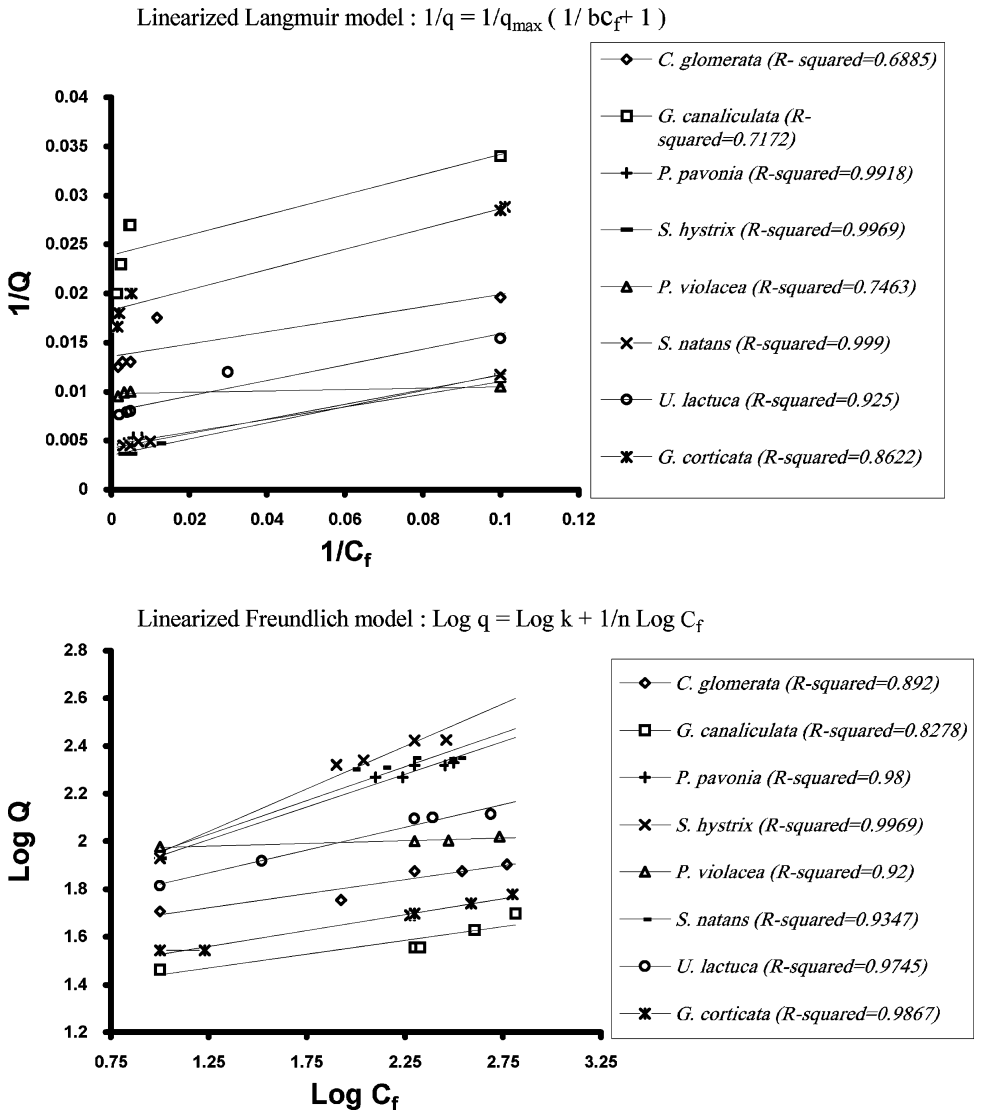

Fig. 3. The linearized Langmuir and Freundlich models for lead uptake by marine algae as represented by the regression lines.

lead from aqueous solution was more efficient at higher pH values. The highest removal of lead by *Padina* and *Sargassum* biomass was occurred at pH 4–5 and significantly decreased by reducing the pH values to 1.0 (Fig. 5). Investigation of pH values above 5.5 was not possible since lead precipitation appeared. These results suggest that increasing hydrogen ions inhibit the adsorption of lead to cation binding sites. We chose pH 4–5 for further experiments.

Table 1
Experimental and calculated lead uptakes (derived from the Langmuir and Freundlich models) by different biosorbents

Biosorbent type	Experimental values		Langmuir parameters					Freundlich parameters				
	q_{10} (mg/g)	q_{200} (mg/g)	q_{10} (mg/g)	q_{200} (mg/g)	q_{max} (mg/g)	b ($\times 100$)	R^{2a}	q_{10} (mg/g)	q_{200} (mg/g)	k	n	R^{2a}
U. lactuca	65	125	63.2	120.5	126.5	9.9	0.925**	66	117.5	42.5	5.2	0.974**
C. glomerata	51	75	50.2	71.8	73.5	21.6	0.69 ns	49	69.9	37.5	8.5	0.892*
G. corticata	35	50	33	52.3	54	15.8	0.862**	33.7	50.2	24.8	7.5	0.987**
G. canaliculata	29	36	29.2	40.9	41.8	23.2	0.717 ns	27.6	38.6	21.3	8.7	0.827*
S. hystrix	85	265	85.7	255	285	4.3	0.997**	89.7	260	39.5	2.8	0.968**
S. natans	85	224	85.5	218.5	238	5.6	0.999**	91	213	47.4	3.5	0.935**
P. violacea	95	100	94.8	101	102	132	0.75 ns	94.5	101	89.8	45.2	0.92*
P. pavonia	85.5	210	91	203	217.4	7.2	0.992**	86.9	199.8	46.3	3.65	0.98**

q_{10} and q_{200} represent metal uptakes at the equilibrium residual concentrations of 10 and 200 mg/l, respectively, ns: not significant.

[a] F-test was used to determine the level of significance.

** $P = 0.01$.

* $P = 0.05$.

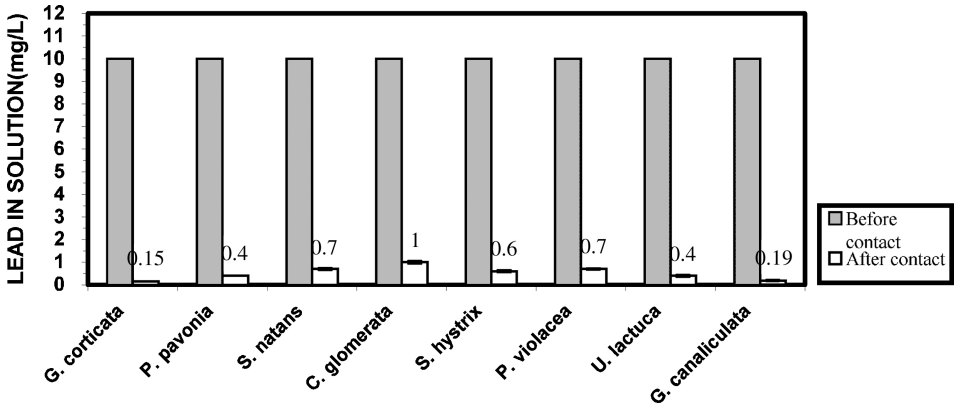

Fig. 4. Biosorption of lead from dilute solution by different marine algae at pH 4, initial metal concentration 10 mg/l, biomass density 2 g/l, size of particles $d = 0.2$–0.5 mm, contact time 3 h and temperature 30 °C.

Regeneration without damaging the capacity of the biosorbent is a very important factor for the success of the biosorbent technology development. When fixed bed sorption columns are considered for the application of biosorption in continuous flow processes, the overall efficiency of the sorption process performance is evaluated by eluate metal concentration upon feed metal concentration [13]. Recovery of the adsorbed lead on *Sargassum* biomass was carried out by 0.1 M HNO_3 for 15 min. Lead released to this dilute mineral acid with 95% elution efficiency.

Heavy metal biosorption by inactive biomass had been improved by Ca^{2+} and/or Mg^{2+} saturation of biomass [23]. Regeneration of the biosorbent, after desorption of the bound Pb^{2+} and subsequent water washing with 0.1 M $CaCl_2$ was very efficient and as shown in

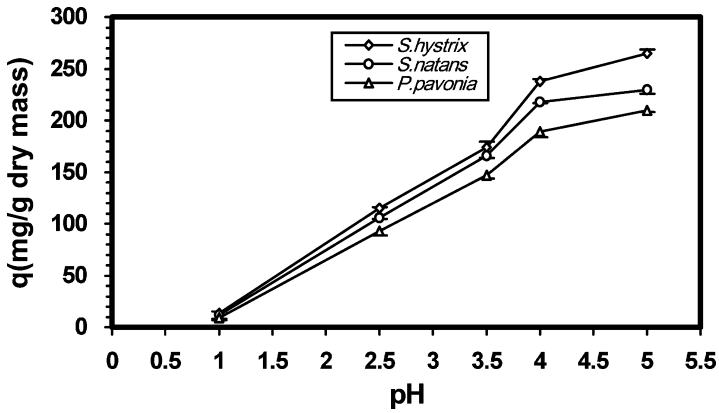

Fig. 5. The effect of pH on biosorption of lead by biomass of *S. hystrix, S. natans* and *P. padina* at initial metal concentration of 463.5 mg/l, biomass density 2 g/l, size of particles $d = 0.2$–0.5 mm, contact time 3 h and temperature 30 °C.

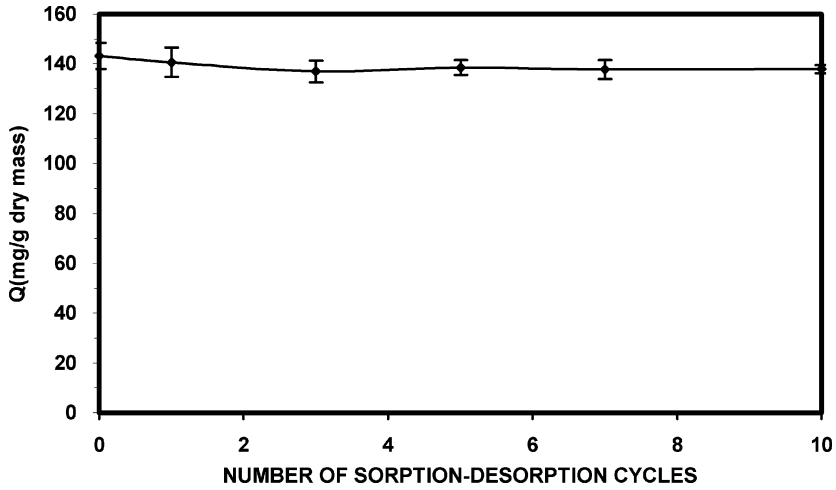

Fig. 6. Biosorption of lead using *S. hystrix* biomass several times, initial metal concentration in each step 374 mg/l, pH 4.5, biomass density 2 g/l, size of particles $d = 0.2$–0.5 mm, contact time in sorption step 45 min, desorption agent 0.1 M HNO_3, regeneration agent 0.1 M $CaCl_2$, desorption time 15 min, regeneration time 15 min and temperature 30 °C.

Fig. 6, the lead uptake capacity of biomass after the 10th sorption–desorption cycle was similar to that after the first cycle (98%).

Holan et al. have shown that biosorption of cadmium by reinforced *Ascophyllum* biomass was consecutively performed in five sorption–desorption cycles [24]. Mattuschka and Straube have also reported that removal of silver by a waste biomass of *Streptomyces noursei* does not cease after four cycles [18].

More recent studies with fungal biomass and seaweed in particular have demonstrated a dominant role of ion exchange metal binding for sequestering of heavy metals [8,22,23, 25,26]. In the present study, constancy of removal capacity of Ca^{2+} regenerated *Srgassum* biomass after several uptake/elution cycles and decrease in the pH of solution (in batch experiment performed without pH adjustment) revealed that an ion exchange between the metal and H^+ or Ca^{2+} occurred.

4. Conclusions

The present study shows the potential of the dead marine algae biomass as the biosorbents for lead removal. The amount of lead taken up by marine algae increased rapidly during the first 30 min and then increased slightly with time. Three types of brown algae (*S. hystrix, S. natans* and *P. pavonia*) were more effective in removing lead from concentrated solutions than other investigated species. Langmuir and Freundlich isotherms were used as sorption models for describing the effects of lead concentration after equilibrium and *F*-test indicated the most suitable model for each biosorbent at $P = 0.01$ and 0.05. When the initial concentration of lead was low (10 mg/l), all the biosorbents derived from marine

algae decreased lead concentration to lower than US EPA permissible concentrations. The external pH was significantly influenced biosorption of lead on algal biomass and removal of lead from aqueous solution was more efficient at higher pH values (pH 4–5). Lead was successfully recovered by relatively simple nondestructive treatments (0.1 M HNO_3) and repeated use of biomass with negligible subsequent changes of biosorbent capacity was possible.

The present study shows that biosorbent derived from marine algae could be used for biosorption of lead ions in a manner similar to ion-exchange resins and three types of marine brown algae (*Sargassum hystrix, S. natans* and *P. pavonia*) can be considered, as an alternative treatment facility or as a replacement of an existing lead-removal technology, for sequestering lead from industrial effluents in continuous flow processes.

Acknowledgements

The authors acknowledge the contribution of H. Foroutan and N. Rahimi in atomic absorption analyses and thank F. Talebnia for helpful discussions.

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