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Biosorption of cesium by native and chemically modified biomass of marine algae: introduce the new biosorbents for biotechnology applications

R. Jalali-Rad[a,*], H. Ghafourian[a], Y. Asef[a], S.T. Dalir[a], M.H. Sahafipour[a], B.M. Gharanjik[b]

[a] *Department of Biotechnology, Nuclear Research Center, Atomic Energy Organization of Iran, Tehran, Iran*
[b] *Offshore Fisheries Research Center, Chabahar, Iran*

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Abstract

Biosorption batch experiments were conducted to determine the cesium binding ability of native biomass and chemically modified biosorbents derived from marine algae, namely ferrocyanide algal sorbents type 1 and type 2 (FASs1 and FASs2). The applicability of the Langmuir and Freundlich isotherms for representation of the experimental data was investigated. The cesium sorption performances of the various types of sorbents were compared using the maximum capacities (q_{max} values) obtained from fitting the Langmuir isotherm to the values calculated from the sorption experiments, which FASs type 1 and type 2 showed better sorption performances for cesium. FASs1 and FASs2 derived from formaldehyde and glutaraldehyde crosslinked *Padina australis* exhibited lower sorption capacities than those prepared from the non-crosslinked one. Most of the cesium ions were bound to FASs1, derived from *Sargassum glaucescens* and *P. australis*, in <2 min and equilibrium reached within the first 30 min of contact. Biosorption of cesium by FASs1 derived from *P. australis* and *Cystoseria indica* was constantly occurred at a wide range of pH, between 1 and 10, and the highest removal took place at pH 4. The presence of sodium and potassium at 0.5 and 1 mM did not inhibit cesium biosorption by algae biomass. The maximum cesium uptake was acquired using the large particles of FAS2 originated from *S. glaucescens* (2–4 mm). Desorption of cesium from the metal-laden FASs1 (from *P. australis*, *S. glaucescens* and *Dictyota indica*) was completely achieved applying 0.5 and 1 M NaOH and KOH, although the cesium sorption capacity of the biosorbents (from *C. indica* and *S. glaucescens*) decreased by 46–51% after 9 sorption–desorption cycles.

Keywords: Cesium biosorption; Desorption; Marine algae; Ferrocyanide algal sorbents; Crosslinked biomass

1. Introduction

Stable cesium (^{133}Cs), that is the rarest of the alkali metals, has little economic value and no essential biological role. However, nuclear technology has resulted in the large amount release of radioactive Cs isotopes into the environment. ^{137}Cs has been a matter of serious concern because of its long half-life of 30 years and high water solubility. Thus, hazardous quantities of ^{137}Cs will remain in the environment for centuries and living organisms easily absorb ^{137}Cs mistaking it for harmless potassium [1–7].

Alternative technologies for removal of other heavy metals and radionuclides, such as metal precipitation and chelating agents, have been ineffective for Cs removal [2]. To date, the removal of Cs radioisotopes from radioactive waste effluents has relied largely on ion-exchange methods. Natural and synthetic zeolites (e.g. mordenite, clinoptilolite, erionite, chazabite and aluminosilicates) have been used for large-scale separation of ^{137}Cs from low- and intermediate-level radioactive waste effluents [2]. However, one disadvantage of the application of zeolites relates to the competitive interactions of other monovalent cations, in particular Na^+ and K^+

* Corresponding author. Tel.: +98 21 61383438; fax: +98 21 8021412.
E-mail addresses: rjalali@aeoi.org.ir, rjalalirad@yahoo.com (R. Jalali-Rad).

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Nomenclature

b	Langmuir constant (ml/mg)
C_f	final metal concentration (mg/l)
C_i	initial metal concentration (mg/l)
FAS1	Ferrocyanide Algal Sorbent type 1
FAS2	Ferrocyanide Algal Sorbent type 2
k	constant in Freundlich model
n	constant in Freundlich model
q	metal uptake (mg metal/g biomass)
q_{max}	Langmuir parameter, maximum metal uptake (mg metal/g biomass)

in waste effluents, that can considerably block Cs^+ adsorption [2,8]. More selective ion exchangers, such as insoluble hexacyanoferrates, are required for ^{137}Cs removal from solutions containing large amount of Na^+ and K^+ [2,8,9]. However, the use of these ion exchangers is restricted to a narrow range of pH and metal ferrocyanides, in their usual form as fine powders, have posed practical difficulties as sorbents [8–10].

In recent years, increased attention has been directed on the use of biological technologies, as the cheap alternative to the non-biological processes, for the removal of toxic heavy metals and radionuclides from industrial wastes [2,11–19]. Microbial by-products from industrial fermentations (e.g. *Aspergillus niger* and S*accharomyces cerevisiae*), derived or excreted products from microorganisms (e.g. metallothioneins, siderophores, phytochelatins, melanins, polysaccharides and inorganic phosphates), and marine algae biomass have been applied for the removal of other toxic (heavy) metals [2,16,20–23]. Metal uptake by (micro)organisms can be occurred by metabolism-dependent and/or -independent processes [2,3,6,23,24]. Metal adsorption on nonliving marine algae is only mediated by metabolism-independent mechanisms (biosorption). It has been reported that energy-independent mechanisms play a minor role in Cs^+ accumulation by microorganisms, because the cesium ion is very weak Lewis acid and has a low tendency to interact with ligands [2]. Thus, in comparison with other alkali metals, Cs^+ binds very weakly to ligands in biosorptive processes. In bioaccumulative (metabolism-dependent) processes, Cs^+ can be taken up by K^+ transport system(s) [2–4]. In a biological metal removal process using living cells, the low toxicity of Cs^+ can be regarded as an advantage, but the radiolytical effects of the radioisotopes (^{134}Cs and ^{137}Cs) might be an important drawback to such a process. In addition, bioaccumulation of Cs^+ is a slow phenomenon occurring in a long time, and this is the other disadvantage of such a system [2,3,7].

The purpose of this work was to investigate the capability of the native and chemically modified marine algae to remove cesium from solution. The effect of different environmental parameters on biosorption of cesium by chemically modified biosorbents was also examined.

2. Materials and methods

2.1. Biomass

Brown algae (*Padina australis*, *Sargassum glaucescens*, *Dictyota indica*, *Nizimuddinia zanardini* and *Cystoseria indica*), green alga (*Ulva fasciata*) and red algae (*Gracilaria corticata*, *Scinaia carnosa*, *Melanothamnus somalensis* and *Hypnea valentiae*) were harvested in January and February from the Gulf of Oman on the coast of Chabahar, Iran. Marine algae were washed several times with tap and then distilled water, and sundried on the beach. Dried biomass was ground in a laboratory blender and sieved using a RETSCH analytical sieve shaker AS 200.

2.2. Chemical modification of biomass

2.2.1. Crosslinking

Crosslinking of marine algae biomass was achieved by using formaldehyde and glutaraldehyde [25].

2.2.2. Preparation of ferrocyanide biosorbents

For this purpose, a modified procedure of Lin et al. was followed [10]. Three grams of crosslinked and native dry biomass of each marine alga was added to 100 ml of 1 M ethylenediamine solution and placed on a rotary shaker at 30 °C, at 150 rpm, for 3 h. Next, each biomass was separated by filtration through the filter papers (Whatman No. 40 Ashless). Subsequent double distilled water (DDW) washing, the biomass was mixed with 100 ml of 60 mM $CuCl_2$ solution for 18 h. The biomass was then filtered and treated with 100 ml of 60 mM potassium hexacyanoferrate solution for 48 h. After filtration, the biomass was thoroughly washed with DDW and dried in an oven at 55 °C overnight. This kind of biosorbent derived from marine algae was called Ferrocyanide Algal Sorbent type 1 (FAS1).

Ferrocyanide biosorbent was prepared using the other protocol. In this method, 3 g of DDW washed and crosslinked biomass of each marine alga was added to 100 ml of 0.1 M $Ni(NO_3)_2$ solution and shaked at 150 rpm, at 30 °C, for 18 h. After filtration through the filter papers and washing with DDW, the biomass was added to 100 ml of 25 g/l potassium hexacyanoferrate solution and left at 30 °C, for 24 h under gentle mixing (shaking at 150 rpm). Eventually, the biomass was separated by filtration, washed with DDW and dried at 55 °C. This kind of biosorbent derived from marine algae was called Ferrocyanide Algal Sorbent type 2 (FAS2).

2.3. Cesium sorption experiments

2.3.1. Preparation of cesium solution

All cesium solutions were prepared by diluting of 1 g/l cesium standard solution (Fluka AG, Chemische Fabrik CH-9470 Buchs).

2.3.2. Comparison of sorbents

For this purpose, 100 mg (dry mass) of native and modified biomass of various marine algae was added to 100 ml Erlenmeyer flasks containing 50 ml cesium solutions with pH 5.5, at different initial metal concentrations (between 20 and 500 mg cesium/l). The flasks placed on a rotary shaker with shaking at 150 rpm, at 30 °C, for 3 h. The biomass was separated from each metal solution by filtration through the filter papers. The filtrates, after appropriate diluting with DDW, were analyzed by atomic absorption spectrophotometery (AAS) using a Varian Spectr AA–20 at the wavelength of 852.1 nm. Metal-free and biosorbent-free blanks were used as controls.

2.3.3. Equilibration time

Experiments to determine the kinetics of cesium sorption were carried out in 100 ml Erlenmeyer flasks by adding 100 mg (dry mass) of ferrocyanide algal sorbents type 1 (FASs1) derived from *S. glaucescens* and *P. australis* to 50 ml of 370 mg/l cesium solutions with initial pH 5.5, at different contact time intervals between 2 min and 24 h, at 30 °C, and on a rotary shaker with shaking at 150 rpm. The biomass was separated from the metal solutions as described above and the filtrates were analyzed by AAS.

2.3.4. Effect of pH

The influence of initial pH values of the metal solution, ranged between 1 and 10, on biosorption of cesium was studied. HCl and NH_4OH were used to adjust the pH (no buffer used).

2.3.5. Effect of K^+ and Na^+ cations

The effect of K^+ and Na^+ cations on cesium biosorption was investigated by adding K^+ and/or Na^+ (0.5 and 1 mM) to solutions containing 0.1 and 1 mM cesium.

2.3.6. Effect of particle size

The influence of biosorbent size on cesium biosorption was evaluated in different particle sizes (0.045–4 mm).

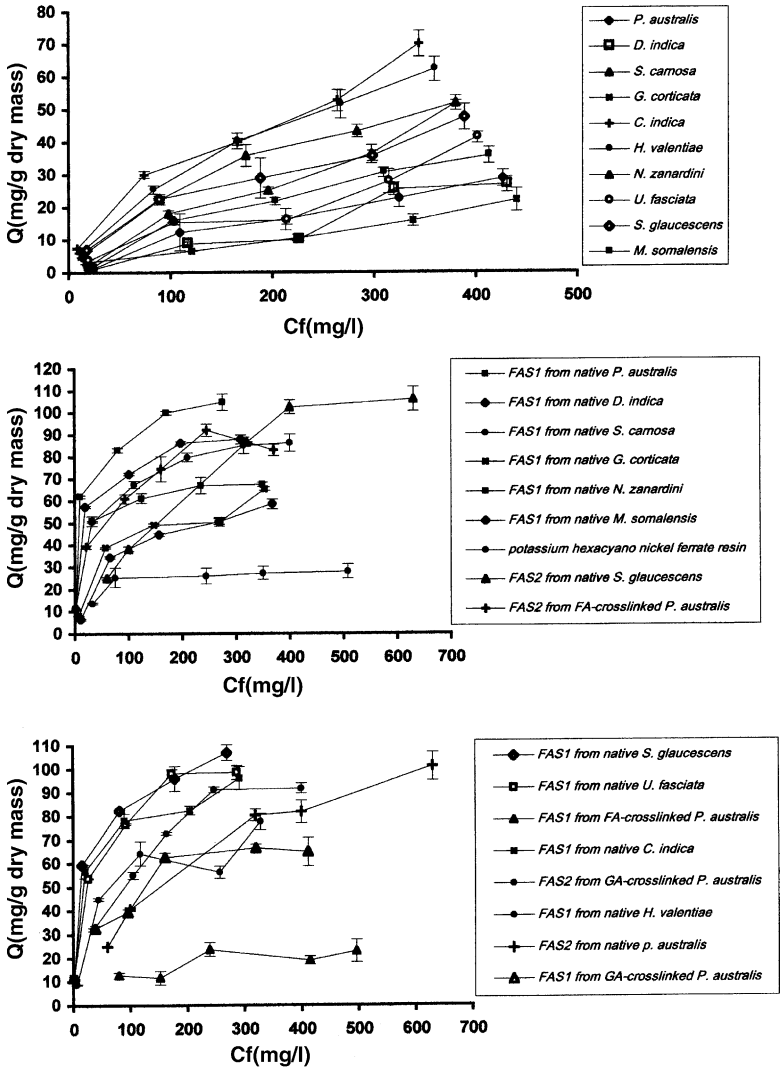

Fig. 1. Comparison of the cesium binding properties of the different sorbents at various residual concentrations, pH 5.5, contact time 3 h, biomass density 2 g/l, size of particles d = 0.2–0.5 mm and temperature 30 °C. Each point is the mean of three data and the error bars represent the standard deviation.

2.3.7. Desorption of cesium and reutilization of biomass

Recovery of cesium from the metal-laden biomass (100 mg dry mass) was examined using 15 ml of different concentrations of HNO_3, H_2SO_4, HCOOH, HCl, CH_3COOH, EDTA, $CaCl_2$, NaOH and KOH in a batch experiment on a rotary shaker (120 rpm) for 15 min, at 30 °C. The biomass was separated from each eluant solution by filtration and concentration of the metal released into the eluant solution was determined by AAS. The unloaded biomass on the filter paper was extensively washed with DDW and then used in an other sorption cycle. The sorption–desorption experiments were performed in nine cycles.

All sorption experiments were accomplished in triplicate.

2.4. Data evaluation

The amount of the metal uptake within the biomass was calculated from the difference between initial metal concentration (C_i) and final metal concentration (C_f) in the solution, as it has been previously reported [16].

Langmuir and Freundlich sorption models were used to describe the experimental data.

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

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

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

where k and n are Freundlich constants. k and n are related to the sorption capacity and the sorption intensity, respectively. C_f is the final metal concentration in both Langmuir and Freundlich models.

F test was applied to determine the significant level of the regression coefficient (R^2) [26] and to indicate if the experimental and calculated data are fitted.

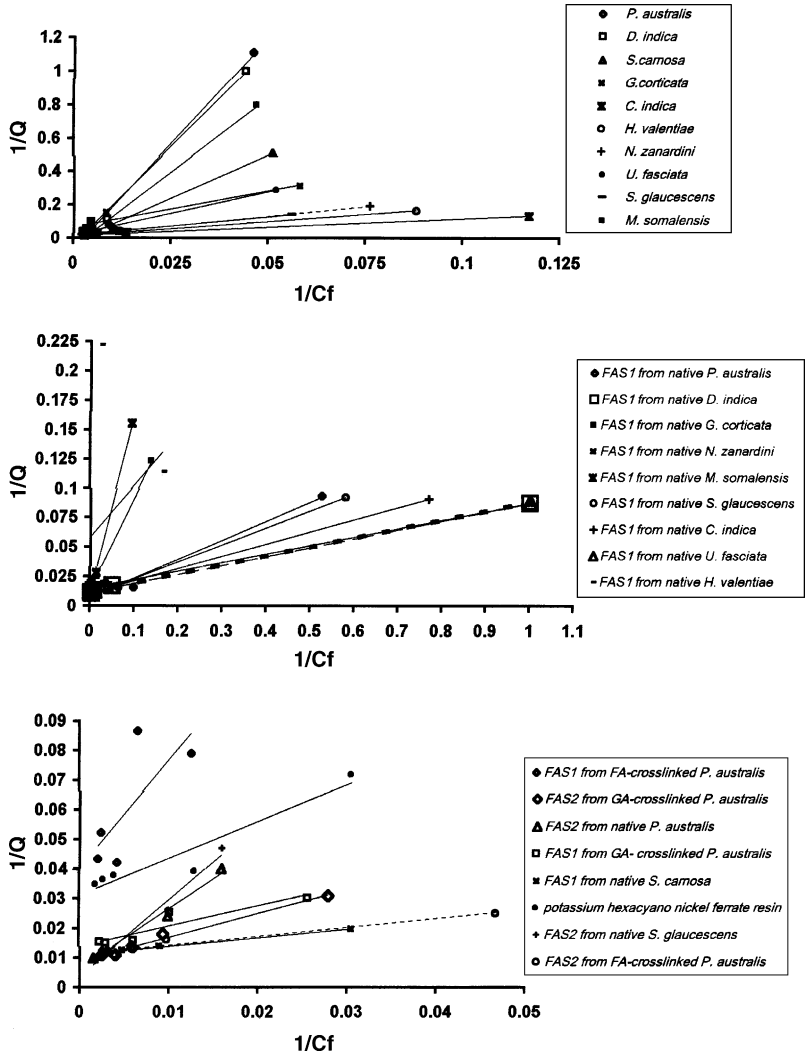

Fig. 2. The linearized Langmuir model for cesium uptake by different sorbents as represented by regression lines.

3. Results and discussion

3.1. Comparison of sorbents

In order to compare the sorption capacities of the biosorbents, equilibrium sorption experiments were carried out for 3 h. Sorption isotherms were plotted between the metal uptake (q) and the final residual concentration in the solution (C_f) (Fig. 1). These experimental data were mathematically represented by linearized Langmuir and Freundlich sorption models (Figs. 2 and 3 and Table 1).

The Langmuir model is being widely used to describe the relationship because it contains the two important parameters of the sorption system (q_{max} and b). q_{max} is attributable to the maximum metal uptake upon complete saturation of the sorbent and b is a coefficient attributed to the affinity between the sorbent and sorbate [27]. The sorption performances of the different biosorbents were compared by their respective q_{max} values calculated from fitting the Langmuir isotherm to the experimental data. Based on the q_{max} values in Table 1, the sorption performances of FASs1 derived from *P. australis*, *D. indica*, *M. somalensis*, *S. carnosa*, *H. valentiae*, *G. corticata*, *U. fasciata*, *C. indica* and *S. glaucescens* and ferrocyanide algal sorbents type 2 (FASs2) derived from *S. glaucescens* and *P. australis* are higher than that of the virgin biosorbents. The differences between sorption behaviours of various FASs, derived from different marine algae chemically modified in the same procedure, can be explained by varying content of their cell wall constituents bearing metal sorption sites.

The Cs uptake by inorganic exchange materials, including composite ion exchangers of redox type, ammonium hexacyano cobaltous ferrate (pH 12, q_{max}: 35 mg Cs/g), potassium hexacyano nickel ferrate (pH 10, q_{max}: 30 mg Cs/g), zirconium phosphate (pH 7, q_{max}: 100 mg Cs/g), titanium phosphate (pH 7, q_{max}: 15 mg Cs/g), antimony pentoxide (pH 2, q_{max}: 30 mg Cs/g) and titanium oxide (pH 7, q_{max}: 1 mg Cs/g) has been previously reported [9,28]. In this work, the performance of potassium hexacyano nickel ferrate resin

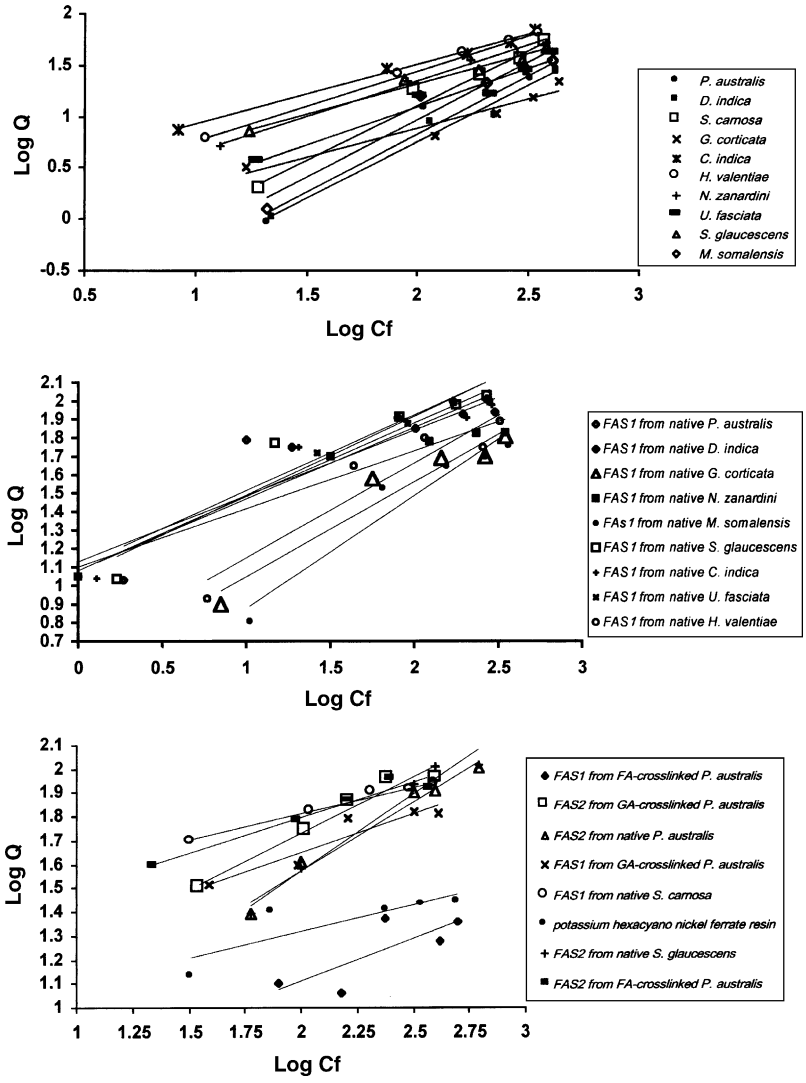

Fig. 3. The linearized Freundlich model for cesium uptake by different sorbents as represented by regression lines.

Table 1
Calculated cesium uptakes by different types of sorbent materials

Sorbent type	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	$b(\times 100)$	R^{2a}	K	n	R^{2a}
Native Biomass						
P. australis	16.2	0.24	0.988**	0.035	0.88	0.951**
S. glaucescens	55.2	0.73	0.924*	2.614	2.12	0.928*
D. indica	30.6	0.14	0.994**	0.033	0.89	0.967**
M. somalensis	21.9	0.25	0.987**	0.052	0.88	0.946**
S. carnosa	54.9	0.18	0.993**	0.095	0.94	0.975*
G. corticata	14.5	1.6	0.916*	0.56	1.76	0.9319**
H. valentiae	71.9	8.06	0.9983**	1.2	1.47	0.9978**
U. fasciata	45.6	0.43	0.646ns	0.5	1.43	0.768ns
N. zanardini	67.5	0.63	0.99**	0.93	1.45	0.99**
C indica	63.29	1.5	0.995**	2.23	1.73	0.99**
FAS1 derived from						
P. australis[b]	139.4	4.4	0.987**	12.7	2.43	0.823*
D. indica[b]	85.1	15	0.999**	13.5	2.8	0.928**
M. somalensis[b]	88.8	0.74	0.999**	1.85	1.63	0.993**
S. carnosa[b]	89.8	3.9	0.994**	22.3	4.3	0.993*
H. valentiae[b]	88.4	1.8	0.996**	4.3	1.94	0.887*
G. corticata[b]	71.4	1.78	0.998**	3.4	1.93	0.933**
U. fasciata[b]	85.2	15.3	0.995**	12.1	2.5	0.982**
C. indica[b]	88.4	10.9	0.999**	12.07	2.57	0.927**
N. zanardini [b]	65.2	2.3	0.998**	12.69	3.18	0.944**
S. glaucescens[b]	112.3	6.2	0.998**	11.5	2.3	0.897**
P. australis[c]	72.4	2	0.865*	10.1	3.1	0.875*
P. australis[d]	24.5	1.1	0.558ns	2.56	2.84	0.612ns
FAS2 derived from						
S. glaucescens[b]	198.7	0.23	0.996**	1.8	1.52	0.971**
P. australis[b]	158.7	0.31	0.986**	2.48	1.7	0.977**
P. australis[c]	112.8	1.1	0.98**	4.4	1.825	0.99**
P. australis[d]	89.4	3.7	0.95*	13.4	2.93	0.989**
Potassium hexacyano nickel ferrate resin[e]	33	2.3	0.916*	7.37	4.42	0.684 ns

All values obtained from Figs. 2 and 3. ns: not significant.
[a] F test was used to determine the level of significance.
[b] Prepared by chemical modification of DDW washed marine algae.
[c] Prepared by chemical modification of glutaraldehyde-crosslinked marine algae.
[d] Prepared by chemical modification of formaldehyde-crosslinked marine algae.
[e] State Unitary Enterprise–MosNPO "Radon", 7th Rostovsky Lane, 2/14, Moscow, Russia.
* $p = 0.05$.
** $p = 0.01$.

(d = 0.5–0.8 mm) was also studied by the same procedure as biosorption. The results of the present work indicated that the cesium uptake performance of FASs was much more than that of the inorganic exchange material (Table 1).

The magnitude of k and n, the Freundlich constants, indicates easy separation of ions from solution and high adsorption capacity of sorbent [29]. n value greater than 1.0 shows that the plot of q versus C_f is convex to the final concentration axis and the sorption is favourable [30]. It is impossible that biosorption capacity increases with equilibrium concentration exponentially at high concentrations because biosorption saturation is physically reasonable [12]. Thus, n value lower than unity in Table 1, that occurs when previously sorbed ions modified the surface in such a way that further sorption is favoured, shows unfavourable equilibrium adsorption isotherm. As shown in this table, the k and n values of chemically modified marine algae, except FAS2 derived from *S. glaucescens*, increased and this rise indicates that the FASs are better biosorbents. The lower k and n values of FAS2 derived from *S. glaucescens*, in comparison with those of the native one, were in conflict with data calculated from the experiments. This means that the Freundlich model is not suitable for representing the experimental data of FAS2 derived from *S. glaucescens*.

Crosslinking of the biosorbent material improves its mechanical stability and pressure resistance required for sorption column applications [31]. Formaldehyde and glutaraldehyde crosslink hydroxylic and amino groups of the prolonged carbon chain, respectively, and after these modifications, biomass has a lower expansion because of its more rigid structure [25]. However, this kind of chemical modification does not necessarily increase metal uptake and it has been shown that crosslinking may positively or negatively affect the biosorption performance [25,31]. In this work, formalde-

Table 2
Biosorption of cesium from dilute metal solution (7000 μg/l) by different biosorbents of marine algae at pH 5.5, biomass density 2 g/l, size of particles d = 0.2–0.5 mm, contact time 3 h and temperature 30 °C

Biosorbent type	Amount of cesium adsorbed from the solution (μg/l)	S.D.
D. indica[a]	400	100
C. indica[a]	5180	25
N. zanardini[a]	3560	230
S. glaucescens[a]	5400	100
P. australis[a]	1240	57
G. corticata[b]	6250	90
D. indica[b]	6990	3
C. indica[b]	6760	100
S. glaucescens [b]	6984	28
P. australis[b]	6670	60
P. australis[c]	6670	57
P. australis[d]	6954	30

S.D. = standard deviation.
[a] Native biosorbents of marine algae.
[b] FAS1 derived from DDW washed marine algae.
[c] FAS1 derived from glutaraldehyde-crosslinked marine algae.
[d] FAS1 derived from formaldehyde-crosslinked marine algae.

hyde and glutaraldehyde crosslinking resulted in decrease of the cesium q_{max} values in FAS1 and FAS2 derived from *P. australis* when compared with the capacities of the non-crosslinked ones, and negative effect of the formaldehyde crosslinking was much more than that of the glutaraldehyde crosslinking (Table 1). It seems that crosslinking of marine algae with glutaraldehyde and formaldehyde in particular destroys or changes the cesium binding sites.

Biosorption of cesium by FASs1 from solutions containing low concentration of the metal was remarkably efficient (Table 2). The best performing biosorbents, FASs1 and FASs2 were chosen for further studies.

3.2. Equilibration time

In the biosorption of cesium by FASs1 originated from *S. glaucescens and P. australis*, most of the cesium ions were sequestered from solution within 2 min and the equilibrium was established in 30 min (Fig. 4). Equilibrium time is a function of many factors, such as type of biomass (number and kind of biosorption sites), size and form of biomass, physiological state of biomass (active or inactive, free or immobilized), and the metal involved in the biosorption system [32]. Lu and Wilkins have shown that equilibrium time for heavy metals (Cu^+, Cd^+ and Zn^+) removal by native and immobilized cells of *S. cerevisiae* was reached after 5–10 min and 24 h, respectively [12]. It has been reported that recovery of ^{137}Cs by a bioaccumulation system using cells of *Rhodococcus erythropolis* CS98 was completely achieved after 24 h [3]. The results of our previous work have indicated that the equilibrium time for removal lead by the same biosorbents of marine algae was 3 h [16].

3.3. Effect of pH

The pH of the solution can play a key role on bioaccumulation and adsorption of cesium [7–9]. Inorganic exchange materials have shown high cesium sorption values only for certain pH ranges [9]. In this study, as illustrated in Fig. 5, biosorption of cesium by FASs1 derived from *P. australis* and *C. indica* was efficient at pH values ranged between 1 and 10, though the highest removal of cesium occurred at pH 4.

3.4. Effect of K^+ and Na^+ cations

High concentrations of Na^+ and K^+ in waste effluents can seriously affect Cs^+ adsorption to most zeolites [2]. It has been demonstrated that potassium ions reduced the cesium accumulation by *Chlorella pyrenoidosa*, *Synechocystis* sp. strain PCC 6803, *C. emersonii* and *Rhodococcus* strains [4,7,33,34]. Results of this research demonstrated that no considerable decrease in the cesium uptake performance of the biosorbents observed in the presence of various combinations of cesium, sodium and potassium (Table 3).

3.5. Effect of particle size

In the present work, the sorption of the smallest (0.045–0.25 mm) and the biggest (2–4 mm) particles of FAS2

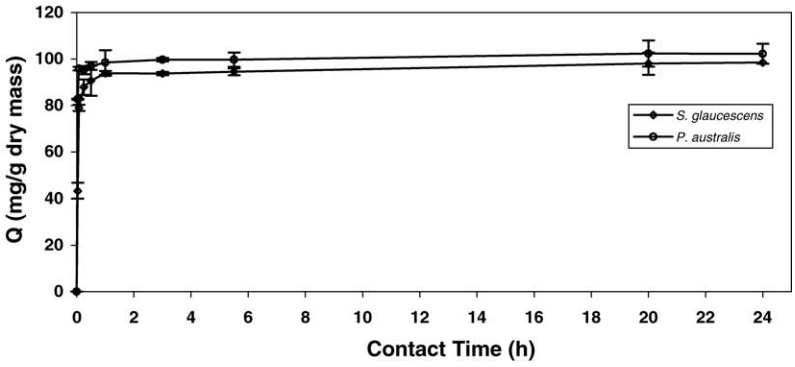

Fig. 4. Kinetics of cesium binding to the FASs1 derived from *S. glaucescens* and *P. australis* at pH 5.5, initial metal concentration 370 mg/l, biomass density 2 g/l, size of particles d = 0.2–0.5 mm and temperature 30 °C. Each point is the mean of three data and the error bars represent the standard deviation.

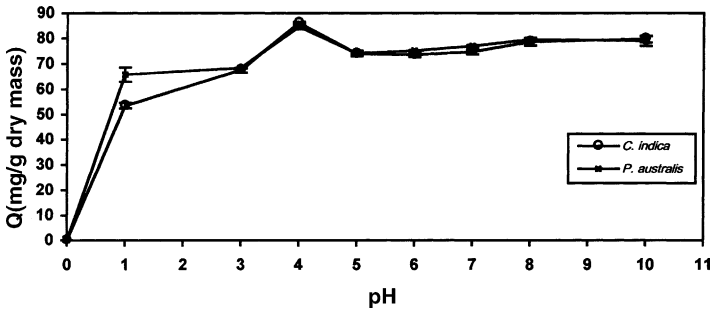

Fig. 5. Uptake of cesium from solution by FASs1 derived from *C. indica* and *P. australis* at various pH values, initial metal concentration 270 mg/l, biomass density 2 g/l, size of particles d = 0.2–0.5 mm, contact time 3 h and temperature 30 °C. Each point is the mean of three data and the error bars represent the standard deviation.

derived from *S. glaucescens* differed by 12 mg Cs/g biomass and particles of 2–4 mm exhibited the highest uptake (Fig. 6). The biosorption of heavy metals has been observed to depend on the sorbent particle size. For example, It has been confirmed that biosorption of Cd, Ni, Cu, Pb, Zn, and Co ions by large particles of marine algae biomass was higher than that by smaller particles [25,35]. On the other hand, Al-Asheh and Duvnjak and Jha et al. have shown that the maximum cadmium adsorption was obtained using very fine particles of pine bark and chitosan, because of an increase of the surface area per weight of the sorbents with a decrease of their particle sizes [13,36]. Leusch et al. have reported that architecture may play an important role in the binding of heavy metals cations [35]. The nanoengineered sorbents, namely self-assembled monolayers on mesoporous supports (SAMMS), manufactured by immobilization of the copper(II) ferrocyanide on the surface of the silica, and ammonium molibdatophosphate (AMP–1) ion exchanger have been proven to remove cesium very efficiently within <2 min and at high concentrations of sodium and potassium. However, for large-scale applications, these sorbents have posed practical difficulties because of their fine and microcrystaline structures [8–10]. Thus, when larger (bio)sorbents have a higher metal uptake than smaller ones, they are more favourable for large-scale applications.

3.6. Desorption of cesium and reutilization of biomass

Recovery of metal from loaded biomass without damaging the capacity of the biosobent is a very important factor for the success of the biosorbent technology development [2,16]. Relatively harsh treatments are required for cesium desorption from biomass where metabolism-independent cesium adsorption occurs [2]. In this investigation, harsh and gentle treatments were used to release the adsorbed cesium on FASs1 derived from *P. australis*, *S. glaucescens* and *D. indica*. As shown in Table 4, no efficient desorption was observed applying acids, EDTA and $CaCl_2$ (0.01–1 M). The desorption efficiency of 0.1 M NaOH and KOH was not considerable (26 and 39.8%, respectively), whereas 78.5–100% cesium recovery was achieved using 0.5 and 1 M NaOH and KOH. These results show that a complete desorption of cesium ions could only be obtained by using 0.5 and 1 M NaOH and KOH.

Repeated use of the FASs1 derived from *C. indica* and *S. glaucescens* in several times in sorption–desorption pro-

Table 3
Effects of cation concentrations on cesium biosorption by FASs1 derived from *S. glaucescens* and *P. australis*

Biosorbent type	Ion added to the medium	Concentration (mM)	Cs^+ concentration in algae[a] (μmol/g dry mass) in presence of:	
			0.1 mM Cs^+[b]	1 mM Cs^+[b]
FAS1 (*S. glaucescens*)	None		46 ± 0.019	392 ± 0.007
	K^+	0.5	46 ± 0.026	368 ± 0.015
	K^+	1	46 ± 0.011	353 ± 0.007
	Na^+	0.5	46 ± 0.035	368 ± 0.007
	Na^+	1	46 ± 0.019	353 ± 0.015
	K^+, Na^+	0.5	46 ± 0.011	370 ± 0.019
	K^+, Na^+	1	44 ± 0.007	360 ± 0.007
FAS1 (*P. australis*)	None		47 ± 0.011	372 ± 0.007
	K^+	0.5	46 ± 0.078	336 ± 0.035
	K^+	1	45 ± 0.037	332 ± 0.026
	Na^+	0.5	47 ± 0.083	362 ± 0.004
	Na^+	1	45 ± 0.008	319 ± 0.019
	K^+, Na^+	0.5	46 ± 0.008	349 ± 0.011
	K^+, Na^+	1	45 ± 0.056	329 ± 0.026

[a] Mean value ± standard deviation.
[b] Concentrations of Cs^+ added to the medium.

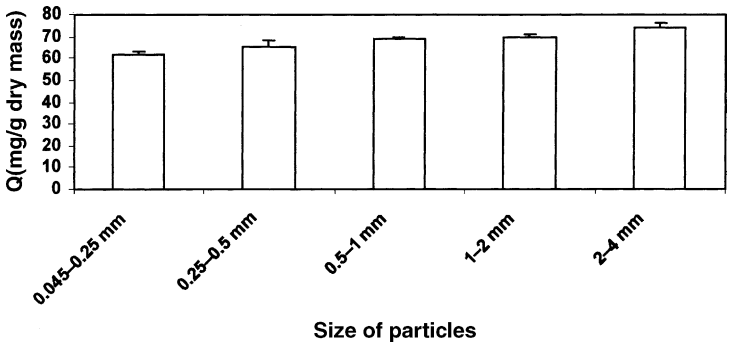

Fig. 6. Cesium biosorption as a function of particle size for FAS2 derived from *S. glaucescens* at pH 5.5, initial metal concentration 315 mg/l, biomass density 2 g/l, contact time 3 h, and temperature 30 °C. Each point is the mean of three data and the error bars represent the standard deviation.

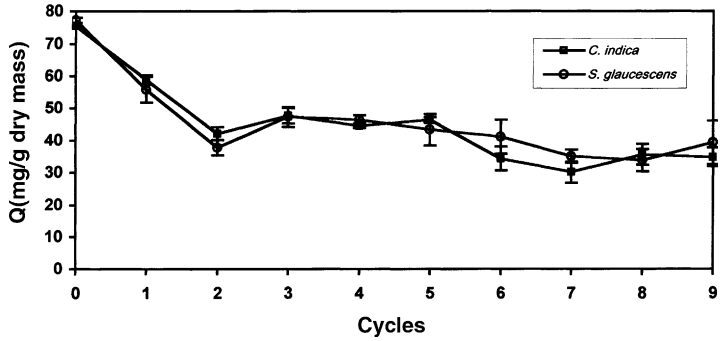

Fig. 7. Amount of cesium bound per cycle by FASs1 derived from *S. glaucescens* and *C. indica*, initial metal concentration in each step 225 mg/l, pH 5.5, biomass density 2 g/l, size of particles d = 0.2–0.5 mm, contact time in each sorption step 45 min, desorbent agent 1 M NaOH, desorption time 15 min and temperature 30 °C. Each point is the mean of three data and the error bars represent the standard deviation.

cesses indicated that recovery of the cesium adsorbed on the biosorbents was a destructive process and the cesium uptake capacities of the biosorbents after the 1st and 9th sorption–desorption cycle were 72–77% and 46–51%, respectively (Fig. 7). Although this drawback can be compensated by use of easily and massively available marine algae in the oceans, further research is needed to carry out on the cesium recovery and biosorbent regeneration.

Table 4
Recovery of cesium from Cs-loaded FASs1 using various concentrations of desorbent agents, q = 81.5, 80.7 and 76.7 mg/g whithin the sorbents derived from *P. australis*, *S. glaucescens*, and *D. indica*, respectively, initial metal concentration 240 mg/l, contact time with metal solution 45 min, volume of desorbent agents 15 ml, desorption time 15 min and temperature 30 °C

Desorbent agent	Metal desorption (%) from FAS1 derived from[a]		
	P. australis	*S. glaucescens*	*D. indica*
0.1 M HNO_3	26.7 ± 0.93	23.5 ± 2.03	
0.01 M HNO_3	25.9 ± 1.32	20.2 ± 2.9	
1 M HNO_3		34 ± 3.4	
1 M H_2SO_4		39 ± 0.74	
1 M HCOOH		42 ± 2.3	
1 M HCl		32.9 ± 1.65	
1 M CH_3COOH		41.4 ± 3.2	
0.1 M EDTA		27.9 ± 2.42	
1 M $CaCl_2$		30.2 ± 1.53	
0.1 M NaOH			26 ± 1.24
0.5 M NaOH	100 ± 4.3	100 ± 5.5	78.5 ± 0.89
1 M NaOH			100 ± 7.89
0.1 M KOH			39.8 ± 2.67
0.5 M KOH			100 ± 4.9
1 M KOH			100 ± 3.05

[a] Mean value ± standard deviation.

4. Conclusions

The feasibility of removal of cesium by various biosorbents derived from marine algae was successfully demonstrated. The values obtained from the experiments were described using Langmuir and Fruendlich sorption models and F test used to show whether the sorption models are in agreement with the experimental data. For biosorption of cesium from solutions containing low and high concentrations of the metal, the ferrocyanide biosorbents, including FASs1 and FASs2, were considerably more efficient than native biomass. Formaldehyde and glutaraldehyde crosslinking of *P. australis* decreased the adsorption capacities of FAS1 and FAS2 derived from the alga. In view of kinetic aspects, the cesium sorption by FAS1 derived from *S. glaucescens* and *P. australis* was a fast process and equilibrium was reached during the first 30 min of contact. The ferrocyanide biosorbents were found to be suited for removal of cesium at different pH values between 1 and 10. At sodium and/or potassium concentrations of 0.5 and 1 mM, no decrease in cesium sorption capacities observed. This work shows that size of biosorbent

particles plays an important role on biosorption of cesium and the highest removal of cesium is obtained applying the big particles (2–4 mm). Cesium was completely released from the metal-loaded biosorbents using 0.5 and 1 M NaOH and KOH. Desorption process was destructive and resulted in decrease in biosorbent uptake capacities.

To the best of our knowledge, removal of cesium from effluents by biosorption process has not been promising yet. In the present work, we succeeded to produce the newest of the highly effective biosorbents, namely FAS1 and FAS2, by chemical modification of marine algae biomass, that are able to potentially remove cesium from solution. These kinds of biosorbents are introduced as good candidates for removing cesium from effluents.

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