Biosorption of stable cesium by chemically modified biomass of *Sargassum glaucescens* and *Cystoseira indica* in a continuous flow system

R. Dabbagh *, M. Ebrahimi, F. Aflaki, H. Ghafourian, M.H. Sahafipour

Nuclear Science Research School, Nuclear Science Technology Research Institute, Tehran, Iran

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ABSTRACT

Pretreatment of biosorbents have been suggested to modify the surface characteristics which could improve biosorption process. Stable cesium biosorption was studied in continuous fixed-bed column by chemically modified biosorbents. Two kinds of brown algae (*Sargassum glaucescens* and *Cystoseira indica*) were treated with chemical agents including formaldehyde (FA), glutaraldehyde (GA), potassium hexacyanoferrate (HCF), FA and HCF, and GA and HCF. The highest biosorption capacity (BC) was obtained from *C. indica* treated with FA (63.5 mg Cs/g biomass) and *S. glaucescens* treated with FA and HCF (62 mg Cs/g biomass). To study the effect of the best treatments on the BC, the concentration of each treatment agent was decreased. With decreasing FA agent for *C. indica* treatment, the BC dropped. Treatment of 1 g *S. glaucescens* biomass with 2.2 g FA and then 0.18 g HCF resulted in the highest BC (73.08 mg Cs/g dry biomass) which was 35.8 times higher than intact *S. glaucescens*.

1. Introduction

Heavy metals are toxic pollutants released into the environment as a result of industrial, mining, and agricultural activities [1,2]. Stable cesium (^{133}Cs), the rarest of the alkali metals, has little economic value and no essential biological role, although can be adsorbed by living organisms easily [3–5]. However, nuclear technology has resulted in the large amount release of radioactive cesium isotope into the environment. ^{137}Cs has been a matter of serious concern because of its long half-life of 30 years [6]. To date, the removal of Cs radioisotopes from radioactive waste effluents has relied largely on ion exchange methods (e.g. natural and synthetic zeolites); however, other monovalent cations, especially Na$^+$ and K$^+$ can considerably impede Cs$^+$ adsorption, using these methods [5].

The utilization of biological materials for removing and recovering heavy metals from contaminated industrial effluents has emerged as a potential alternative method to conventional techniques which are deemed expensive and ineffective [1,7]. Biosorption entails the use of living or dead (micro)organisms and/or their derivatives which complex metal ions using ligands or functional groups situated on the outer surface of the cell. This phenomenon has been directly compared with chemical ion-exchange processes [8,9]. Various biosorbents have been scrutinized for metal biosorption [10]; among these, the sorption performance of algae has been demonstrated to be higher than that of activated carbon and other types of biomass, and comparable to synthetic ion exchange resins [11].

Biosorption in algae has mainly been attributed to the cell wall. In brown algae, the largest amount of cell wall content consists of mainly alginate and some sulfated polysaccharides [12,13]. Alginates, usually calcium and sodium alginates are present in a gel form in the cell wall which appear very porous and easily permeable to small ionic species [10,14]. Biosorption of metals consists of several mechanisms. The mechanisms involve chelation, adsorption by physical forces, and binding to cell wall polysaccharides and proteins [15]. In as much as the biosorption process involves mainly cell surface sequestration, cell wall modification can greatly alter the binding of metal ions. Biomass could be given several physical and chemical treatments. The physical treatments include heating/boiling [16], freezing/thawing, drying and lyophilization [17]. Chemical treatments used for biomass modification include washing the biomass with detergents [18,19], cross-linking with organic solvents [20,21], and alkali or acid treatment [21]. The pretreatments have been suggested to modify the surface characteristics/groups either by removing or masking the groups or by exposing more metal-binding sites [13].

Biosorption of cesium by native and chemically modified marine algae in batch system has been reported previously [5]. The aim of this study was to investigate the effect of chemical treatments on the cesium biosorption performance of brown algae *Sargassum glaucescens* and *Cystoseira indica* in a continuous system.

* Corresponding author.
  E-mail address: rdabbagh@yahoo.com (R. Dabbagh).

2. Materials and methods

2.1. Biomass

The brown algae *S. glaucescens* and *C. indica* were harvested in May and June from the Oman Sea on the coast of Chabahar, Iran. The algae were washed with tap and then distilled water several times, and then Sun-dried on the beach for 3 days. The dried biomass was ground in a laboratory blender and was sieved using a RETCH analytical sieve shaker AS200 to obtain 1–2 mm particles.

2.2. Chemical modification

2.2.1. Cross-linking

Cross-linking of the biomass was carried out using formaldehyde (FA) and glutaraldehyde (GA) [22]. To obtain FA treated biomass, a mixture of 17 ml FA 30% and 33 ml HCl 0.1 M was added to 2.5 g sieved biomass (2.2 g FA/g biomass dry weight). The mixture was left at room temperature with gentle mixing. After 1 h, the biomass was filtered and washed with distilled water. Having been immersed in 100 ml 0.2 M sodium carbonate solution for 15 min, the biomass was filtered, washed with distilled water and dried overnight at 80 °C.

For GA treatment, 2.5 g sieved biomass was added to 0.5 M solution of GA in 100 ml HCl 0.1 M (2 g GA/g biomass dry weight) and left at room temperature with gentle mixing. After 72 h, the biomass was filtered and washed with distilled water. Having been soaked in 100 ml 0.5% (w/v) sodium carbonate solution for 15 min, the biomass was eventually filtered, washed with distilled water and dried overnight at 80 °C.

2.2.2. Potassium hexacyanoferrate treatment

Ferrocyanide biosorbents were prepared using the method previously reported for preparation of Ferrocyanide Algal Sorbet type 2 (FAS2) [5], with difference in the volume of 0.1 M Ni(NO$_3$)$_2$ solution. For this purpose, 3 g of intact or cross-linked algae were added to 50 ml of Ni(NO$_3$)$_2$ 0.1 M and placed on an orbital shaker at 150 rpm and 30 °C for 18 h. After filtration and washing with distilled water, the biomass was added to 100 ml of 2.5% potassium hexacyanoferrate (K$_4$[Fe(CN$_6$)]) (HCF) solution (0.73 g HCF/g biomass dry weight). The mixture was shaken at 150 rpm and 30 °C for 24 h. Finally, the biomass was separated by filtration, washed with distilled water and dried overnight at 80 °C.

As a result of chemical treatment, particles attached to each other after drying. In order to separate particles, the biosorbent was ground gently and was used in two ways: (1) was not sieved again, (2) sieved again to obtain entire 1–2 mm particles.

2.3. Column biosorption experiments

Continuous biosorption experiments were conducted in glass columns (2.7 cm inner diameter) filled with 10 g dry biomass of the chemically modified marine algae, and a movable stopper was put on top of the bed. The bed was washed with distilled water for 30 min with 2.5 ml/min/cm^2 loading rate. Cesium Chloride solution with the initial concentration of 70 mg/l and pH 5.5 was pumped upward through the column at desired flow rate by a peristaltic pump (Watson–Marlow 205U). Samples were collected from outlet of the column at defined time intervals and analyzed for determination of cesium concentration by atomic absorption spectrophotometry (AAS) using a Varian Spectr AA-220 at the wavelength of 852.1 nm. Metal-free and biosorbent-free blanks were utilized as controls.

The biosorption performance was evaluated based on the plot of the outlet metal ion concentration to initial metal concentration (C_e/C_0) as a function of process time. Biosorption capacity (BC) of
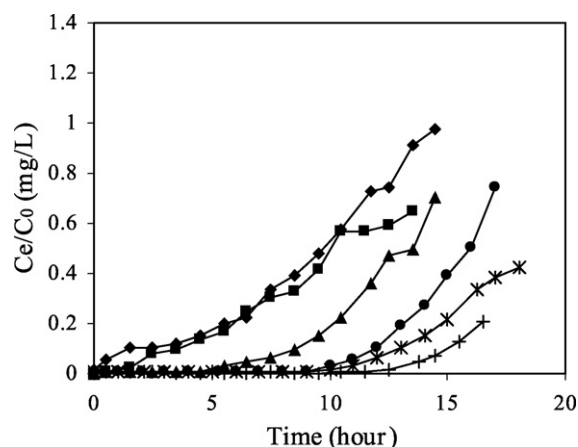

Fig. 1. Breakthrough curves for intact *S. glaucescens* (■) and *S. glaucescens* treated with GA (▲), FA (♦), HCF (×), FA and HCF (+), GA and HCF (●). Feeding cesium concentration 70 mg/l, residence time 2 min, biomass dry weight 10 g and pH 5.5.

the column was calculated from the total quantity of the metal mass bound by the biomass in the column prior to the breakthrough point (1 mg/l) divided by the biosorbent dry weight [1]. Cesium removal percent was calculated from the area above the breakthrough curve divided by the total amount of cesium passed through column up to saturation point, multiply by 100.

3. Results and discussion

Various chemically modified biosorbents originated from *S. glaucescens* and *C. indica* without sieving after treatment were studied in a continuous up-flow fixed-bed column system in which the cesium solution was passed through with 2 min residence time. Biosorption column breakthrough curves have been shown in Figs. 1 and 2, where the C_e/C_0 in the column outlet is plotted vs. the process time. Almost all biosorbents derived from treated *S. glaucescens*, except the one treated with FA, had more removal capacity than the intact biomass. Among the biosorbents derived from *S. glaucescens*, the ones treated with FA–HCF and GA–HCF had the highest sorption performance. All biosorbents originated from treated *C. indica* showed more removal capacity than the intact biomass; among which, the ones treated with FA and GA showed the highest performance, respectively. These results suggest that the different chemical treatments have disparate effects on increasing the cesium sorption capacity of various marine algae.

Biosorption capacity and removal percent of the various biosorbents was calculated (Table 1). As shown in the table, FA–HCF
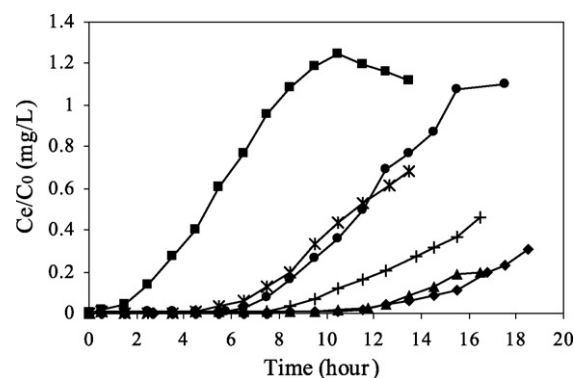

Fig. 2. Breakthrough curves for intact *C. indica* (■) and *C. indica* treated with GA (▲), FA (♦), HCF (×), FA and HCF (+), GA and HCF (●). Feeding cesium concentration 70 mg/l, residence time 2 min, biomass dry weight 10 g and pH 5.5.

Table 1

Biosorption capacity and percent removal of different biosorbents (breakthrough point 1 mg/l)

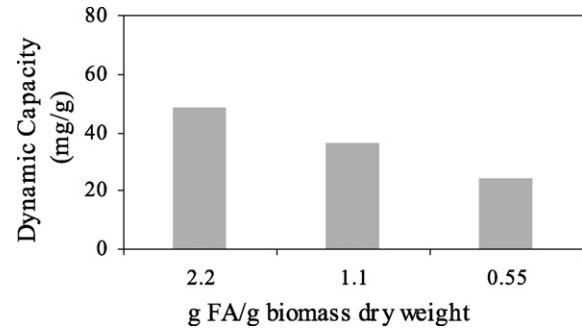|	Biosorption capacity (mg Cs/g dry biomass)	Percent removal (%)
S. glaucescens		
Native	2.04	71.5
FA treated	0.08	61.5
GA treated	31.7	84.1
HCF treated	49.4	91.2
FA and HCF treated	62	94.6
GA and HCF treated	56.5	88.3
C. indica		
Native	2.2	28.6
FA treated	63.5	94.9
GA treated	60.4	96
HCF treated	37.3	64.5
FA and HCF treated	37.2	89.2
GA and HCF treated	39.7	63.1

Fig. 3. The biosorption capacity of *C. indica* treated with different ratios of FA/biomass (w/w).
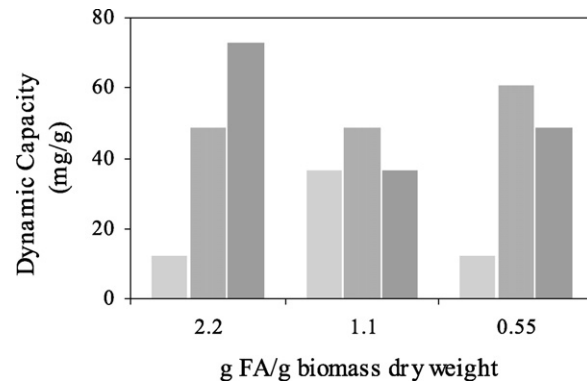

Fig. 4. The biosorption capacity of *S. glaucescens* treated with different amounts of formaldehyde (g FA/g biomass dry weight), then treated with different amounts of potassium hexacyanoferrate; 0.73 (▢), 0.36 (▨) and 0.18 (■) (g HCF/g biomass dry weight).

treated *S. glaucescens* and FA treated *C. indica* have the highest biosorption performance among the biosorbents.

Formaldehyde modification is a chemical cross-linking between adjacent chemical groups, preferably hydroxyl groups of two adjacent polysaccharide molecules of the cell wall. Glutaraldehyde cross-links chemical groups (mainly amino groups), which are more distant from each other because of the prolonged carbon chain. It has been evinced that cross-linking may positively or negatively influence the biosorption performance [5,22]. As illustrated in Table 1, *S. glaucescens* treated with FA showed very low biosorption capacity and removal percent in comparison with intact one.

As a result of chemical treatment, particles attached to each other after drying. In order to separate them, the biosorbent was ground gently which caused creating particles smaller than 1 mm along with remaining some particles greater than 2 mm. Consequently, a gradient of particle sizes was created with priority of 1–2 mm ones.

In order to obtain entire 1–2 mm particles, the algae were ground and sieved again after chemical treatment. As it can be seen in Table 2, the biosorption capacity of both FA–HCF treated *S. glaucescens* and FA treated *C. indica* decreased after second sieving. However FA–HCF treated *S. glaucescens* showed more decrease than FA treated *C. indica*. This phenomenon can be related to the particles shape. *S. glaucescens* particles are chip-like which increases surface attachment of particles in comparison with needle-like *C. indica* particles. This means that the particles sizes of *C. indica* remain more conserve than *S. glaucescens* ones after treatment.

The removal percent of both algae with and without second sieving were also calculated which showed about 1.1 times decrease. Since decreasing particle size causes increasing surface contact, it can be concluded that in biosorption process of biosorbent without second sieving, less than 1 mm particles play an important role during the first times of process and increase the biosorption capacity before the breakthrough point.

As mentioned earlier, FA–HCF treated *S. glaucescens* and FA treated *C. indica* showed the highest biosorption capacity (62 and 63.5 mg Cs/g dry biomass, respectively). The effect of these treat-

ments was also investigated by decreasing the weight ratio of each treatment agent in terms of dried biomass weight during the treatment process. For this purpose, 2.2, 1.1 and 0.55 g FA/g biomass dry weight and 0.73, 0.36 and 0.18 g HCF/g biomass dry weight were applied. The treated biosorbents were sieved again to obtain accurately 1–2 mm particles. The biosorption experiments were conducted in a continuous system with the same conditions mentioned earlier.

After treatment of *C. indica* with different amounts of FA, the BC diminished as the weight ratio of FA/biomass decreased (Fig. 3). It can be suggested that increasing FA concentration enhances the cross-linking of *C. indica* biomass; consequently, more active sites are exposed to the cesium ions. When *S. glaucescens* pretreated with 2.2 g FA was treated with different amounts of HCF, the BC raised as the weight ratio of HCF/biomass decreased (Fig. 4). This shows that the active sites may increase with decreasing HCF. Treatment of *S. glaucescens*, subsequent exposure to 1.1 g FA/g dry biomass, with different amounts of HCF caused no significant difference in BC. Following the treatment of *S. glaucescens* with 0.55 g FA/g dry biomass and different amounts of HCF, the lowest and highest BCs were obtained with 0.73 and 0.36 HCF/biomass (w/w), respectively. It is

Table 2

Comparing the biosorption capacity of sieved and not-sieved biosorbents (FA–HCF treated *S. glaucescens* and FA treated *C. indica*) after cross-linking (breakthrough point 1 mg/l)

Biosorbent	Biosorption capacity (mg Cs/g dry biomass)		Removal percent (%)	
	With second sieving	Without second sieving	With second sieving	Without second sieving
FA–HCF treated *S. glaucescens*	12.18	62	88.9	94.6
FA treated *C. indica*	48.7	63.5	90	94.9

evident from the results that these treatments have negative effect on each other in some concentrations. Overall, *S. glaucescens* treated with 2.2 g FA/g dry biomass as well as 0.18 g HCF/g dry biomass indicated the highest BC with the removal percent of 96.45%. Final cesium concentration at effluent after biosorption was 2.5 mg/l which is very low.

Current study was performed in laboratory scale using pure chemicals. All needed materials for chemical treatments are also industrially available with affordable price. Moreover, the treatment duration and the number of steps can be decreased by further investigations and the process practicality in pilot scale can be examined.

Regeneration of the biosorbent is also possible. Jalali-Rad et al. [5], used hexacyanoferrate treated *C. indica* and *S. glaucescens* several times in 9 sorption–desorption processes using 0.5 and 1 M NaOH and KOH. Uptake capacities of the biosorbents after the 1st and 9th sorption–desorption cycles were 72–77% and 46–51%, respectively.

4. Conclusions

In this study, two types of brown algae (*S. glaucescens* and *C. indica*) were treated with chemical agents including FA, GA, HCF, FA–HCF, and GA and HCF. In the first experiment, the highest BC was obtained from *C. indica* treated with FA and *S. glaucescens* treated with FA and HCF. Along with decreasing FA concentration for *C. indica* treatment, the BC reduced. Altering the ratio of FA and HCF agents for *S. glaucescens* treatment suggested that these chemicals may augment or attenuate their effects on each other. However, treating 1 g *S. glaucescens* with 2.2 g FA and then 0.18 g HCF, resulted in the highest BC (73.08 mg Cs/g biomass) which was 35.8 times higher than intact *S. glaucescens*.

Acknowledgement

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