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Screening of Marine Algae of Oman Gulf for Biosorption of Cobalt

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Abstract: Batch experiments were conducted to study the ability of marine algae collected from Oman Gulf, Iran, for sorption of cobalt from the metal nitrate solution. The biosorption experiments were performed using native and chemically pretreated sun-dried biomass of marine algae. Our finding indicated that $MgCl_2$ pretreated *Cystoseria indica*, *Sargassum glaucescens* and *Padina australis* had more sorption capacities, while the $CaCl_2$ pretreated ones showed lower capacity (comparing with non-treated native biomass). Also, a fall in the cobalt uptake capacity of *Nizimuddinia zanardini*, *Gracilaria corticata*, *G. arcuata*, *Botryocladia leptopoda*, *Scinaia carnosa*, *Hypnea valentiae*, *Ulva fasciata* and *Codium* sp. took place after treatment with chemicals, including $CaCl_2$ (0.1 M), $MgCl_2$ (0.1 M), $CaCl_2$ (0.1 M)/HCl (pH 2) and HCl (0.1 M). Biosorption of cobalt was rapidly took place onto algal biosorbents and most of the sorbed metal ion was bound in the first minutes of contact. Uptake of cobalt was pH-dependent and the most cobalt removal occurred at pH 4. In our screening investigations, brown algae (*Dictyota indica*, *N. zanardini*, *P. australis*, *S. glaucescens*, and *C. indica*) removed cobalt most efficiently from aqueous solution, respectively. The capability of marine algae for separation of ^{60}Co was tested and a high ^{60}Co removal was demonstrated.

Keywords: ***Cobalt biosorption, Marine algae, Algal sorbents, Chemical pretreatment, Kinetics, Oman, cobalt biosorption, cobalt***

1-Introduction

The use of biological materials (such as bacteria, fungi, yeasts, algae and plants) for the separation of (heavy) metal ions and radionuclides from solutions represents an alternative or replacement to existing technologies (e.g. precipitation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation and evaporation) [1-5]. Metal ion uptake by biosorbents can be mediated by: i) bioaccumulation, an energy-dependent process and ii) biosorption, an energy-independent phenomenon [6]. For industrial-scale application, biosorptive processes are more applicable because bioaccumulation phenomena require the addition of nutrients and the maintenance of a healthy (micro)organism population in presence of metal toxicity and other unfavorable environmental conditions [1].

The influence of different parameters on the biosorption of (heavy) metals and radionuclides has been demonstrated. For instance, pH of the metal solution can play an important role on the biosorption below or above which a decrease occurs [1,7]. Kinetics of metal binding to the biosorbent is also an effective parameter, in particular for sequestering metals and radionuclides in continuous flow processes [1]. It has been proved that chemical pretreatment of biosorbents can significantly influence their metal uptake capacities [8].

Cobalt is extraordinarly used in many industrial applications (e.g. in the production of satellite alloys, pharmacology and nuclear medicine) [9-11]. Thus, development of technologies for secondary recovery processes together with decontamination of effluents is considered. The objectives of this study were to determine potent species of marine algae for cobalt separation through biosorptive processes and to investigate the influence of different parameters on the biosorption of cobalt by marine algae.

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2- Materials and methods

2-1 Biomass

Brown algae (*Padina australis*, *Sargassum glaucescens*, *Dictyota indica*, *Nizimuddinia zanardini* and *Cystoseria indica*), green algae (*Ulva fasciata* and *Codium* sp.) and red algae (*Gracilaria corticata*, *G. arcuata*, *Scinaia carnosa*, *Botryocladia leptopoda*, *Melanothamnus somalensis* and *Hypnea valentiae*) were harvested from the Oman Gulf on the coast of Chabahar (a coast line of approximately 300 km, N2523.782 E5904.492 Meydani, N2503.684 E6125.324 Gwatr), Iran.

These algae were washed with water and then dried in exposure to sunlight. Dried biomass were ground in a blender and sieved in the range of 0.045–4 mm using the machinery sieve (RETSCH AS 200).

2-2 Batch cobalt sorption experiments

Introductory cobalt sorption experiments were conducted applying various marine algae pretreated with solutions like double distilled water (DDW), $CaCl_2$ (0.1 M), $CaCl_2$ (0.1 M)/HCl (pH 2), $MgCl_2$ (0.1 M) and HCl (0.1 M). These experiments were carried out for determination of effective chemical treatment(s) and selection of efficient species. In these studies 100 mg of each alga was added to 50 ml of cobalt nitrate solutions in concentrations of 14.1 and 160 to 180 mg/l at pH 6 (pH of the solutions was adjusted using HNO_3 and NH_4Cl 0.1 M). After 3 h of exposure, biomass was separated by filtration. To determine the residual cobalt concentrations in solutions, the filtrates were analyzed by atomic absorption spectrophotometer (AAS) using a Varian Spectra AA-20 atomic absorption spectrophotometer at the wavelength of 240.7 nm.

2-3 Kinetics of cobalt sorption

Experiments for finding the equilibration time were conducted by adding 100 mg of dried algal biomass to 50 ml cobalt solutions (217 ppm and pH 6) in different contact times.

2-4 Effect of pH

The effect of pH on cobalt sorption was investigated in the pH ranges of 1-7.

2-5 Comparison of marine algae sorption performances

To compare the cobalt sorption capacities of marine algae, 100 mg of each algal biosorbent was added to 50 ml cobalt solutions bearing different concentrations of the metal (10-1200 ppm), with pH 5.5, for 3 h.

2-6 Batch cobalt sorption experiments using solutions containing different ^{60}cobalt concentrations

In this stage, 100 mg of dried biomass of algal sorbents were added to 100 ml of ^{60}cobalt solution with pH 6.6. Vials were sealed and shaked on an orbital shaker (150 rpm, for 3 h). The biomass was separated by filtration and the filtrates were evaluated with gamma spectroscopy analysis (MCA Spectrum Master Model 919 ORTEC, HPGe Detector) for residual ^{60}cobalt activity. The amount of collected ^{60}cobalt was determined. These experiments were performed using ^{60}cobalt solution in activities ranged between 4500 and 90000 Bequrel (Bq).

2-7 Calculation of the metal amount on biomass

The amount of the metal on biomass of marine algae calculated as follows:

$$q = v\,(C_i - C_f) / m$$

Where q is the metal uptake (mg metal/g of the biosorbent), v the liquid sample volume (l), 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 (g).

3- Results and discussion

Preliminary cobalt uptake studies on pretreated marine algae exhibited that treatment of *C. indica*, *S. glaucescens* and *P.australis* with $MgCl_2$ and $CaCl_2$ (0.1 M) respectively increased and decreased cobalt sorption in these algae when compared to non-treated virgin biomass. Treatment of *N. zanardini*, *G. corticata*, *G. arcuata*, *B. leptopoda*, *S. carnosa*, *H. valentiae*, *U. fasciata* and *Codium sp*. with

different chemicals resulted in a decrease in the algae sorption performances (Table 1). The influence of pretreatment of biomass on cobalt

Table 1. Biosorption of cobalt (mg metal/g dry mass) using various kinds of native and chemically pretreated marine algae biomass in different initial cobalt concentrations.

Sorbent type	Amount of cobalt sorption in initial cobalt concentrations of:				
	14.1 (ppm)	160 (ppm)	173 (ppm)	174 (ppm)	180 (ppm)
G. corticata		18.7			
G. corticata + $CaCl_2$ (0.1 M)		9.8			
G. corticata + $CaCl_2$ (0.1M)/HCl (pH 2)		10			
G. corticata + $MgCl_2$ (0.1M)		9.5			
G. corticata + HCl (0.1 M)		0.5			
B. leptopoda		27.5			
B. leptopoda + $CaCl_2$ (0.1 M)		12			
B. leptopoda + $CaCl_2$ (0.1M)/HCl (pH 2)		8			
B. leptopoda + $MgCl_2$ (0.1M)		13.5			
B. leptopoda + HCl (0.1 M)		0.5			
S. carnosa		21			
S. carnosa + $CaCl_2$ (0.1 M)		10.5			
S. carnosa + $CaCl_2$ (0.1M)/HCl (pH 2)		13			
S. carnosa + $MgCl_2$ (0.1M)		19.3			
S. carnosa + HCl (0.1 M)		5.7			
G. arcuata				7	14
G. arcuata + $CaCl_2$ (0.1 M)					8
G. arcuata + $CaCl_2$ (0.1M)/HCl (pH 2)					3
G. arcuata + $MgCl_2$ (0.1M)					4
G. arcuata + HCl (0.1 M)					0
H. valentiae					21
H. valentiae + $CaCl_2$ (0.1 M)					11.5
H. valentiae + $CaCl_2$ (0.1M)/HCl (pH 2)					10
H. valentiae + $MgCl_2$ (0.1M)					17
H. valentiae + HCl (0.1 M)					0
U. fasciata (0.1M)					17
U. fasciata + $CaCl_2$ (0.1 M)					7.5
U. fasciata + $CaCl_2$ (0.1M)/HCl (pH 2)					11
U. fasciata + $MgCl_2$ (0.1M)					14.5
U. fasciata + HCl (0.1 M)					5
***Codium* sp.**					10
Codium sp. + $CaCl_2$ (0.1 M)					2
Codium sp. + $MgCl_2$ (0.1M)					3
Codium sp. + $CaCl_2$ (0.1M)/HCl (pH 2)					3.5
Codium sp. + HCl (0.1 M)					1
P. australis + $CaCl_2$ (0.1M)/HCl (pH 2)	35				10
N.zanardini			7.85		24
N. zanardini + $CaCl_2$ (0.1 M)					15.5
N. zanardini + $MgCl_2$ (0.1M)					19.5
N. zanardini + HCl (0.1M)					3
N. zanardini + $CaCl_2$ (0.1M)/HCl (pH 2)					17.5
P. australis			15.5		16.2
P. australis + $CaCl_2$ (0.1 M)					12
P. australis + $MgCl_2$ (0.1M)					18
P. australis + HCl (0.1M)					3.5
C. indica	5.82		19.7	23.9	
C. indica + $CaCl_2$ (0.1M)/HCl (pH 2)				11	
C. indica + $MgCl_2$ (0.1M)				25.8	
C. indica + $CaCl_2$ (0.1M)				18.45	
C. indica + HCl (0.1M)				1.5	
S. glaucescens	5.03		19	22.8	
S. glaucescens + $CaCl_2$ (0.1M)/HCl (pH 2)				12.5	
S. glaucescens + $MgCl_2$ (0.1M)				27	
S. glaucescens + $CaCl_2$ (0.1M)				17.35	

S. glaucescens + HCl (0.1M)				8	
M. somalensis				5	

sorption has been studied previously. For example, it has been reported that cobalt uptake performance in *Pseudomonas halodenitrificans* was decreased after treatment with magnesium and calcium [8].

In studies to determine the kinetics of the cobalt sorption by marine algae (*C.indica*, *N. zanardini*, *P. australis* and *S. glaucescens*), most of the cobalt ions sequestered within the first 15 min of contact and the equilibration established in 3 h (Fig. 1).

In investigation of the effect of the solution pH on cobalt biosorption by *C. indica*, *N. zanardini*, *P. australis* and *S. glaucescens*, the maximum cobalt sorption was at pH 4. At pH 1, the cobalt sorption was low. At pH 5-7, the cobalt sorption was lower than that of at pH 4 (Fig. 2). In 1988, N. Kuyucak and B. Volesky reported that the marine alga *Ascophyllum nodosum* had the maximum cobalt sorption performance at pH about 4 [9].

The experiments for comparing cobalt sorption capacities of marine algae were done in different concentrations of cobalt, for 3 h. As illustrated in Fig. 3, while brown algae including *P. australis*, *N. zanardini*, *D. indica*, *S. glaucescens* and *C. indica* have high sorption capacities, red algae named *B. leptopoda*, *S. carnosa* and *G. corticata* show low sorption capacities. Brown algae *N. zanardini* and *D. indica* exhibited the maximum cobalt sorption between all investigated algal species (142.25 and 157 mg/g dry biomass, respectively). In 1988, N. Kuyucak and B. Volesky reported that the maximum cobalt sorption in brown alga *A. nodosum* was about 160 mg/g dry biomass [9].

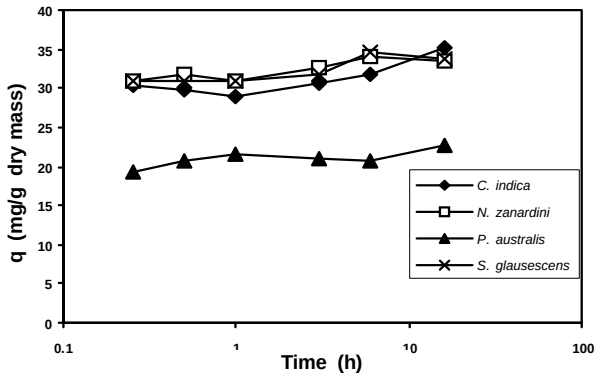

Fig. 1. Kinetics of cobalt binding to the biosorbents of marine algae at pH 6. Initial metal concentration 217 mg/l, biomass density 2 g/l, size of particles d = 0.2–0.5 mm and temperature 30 ˚C.

Fig. 2. Uptake of cobalt from solution by marine algae at various pH values. Initial metal concentration 154 mg/l, biomass density 2 g/l, size of particles d = 0.2–0.5 mm, contact time 3 h and temperature 30 ˚C.

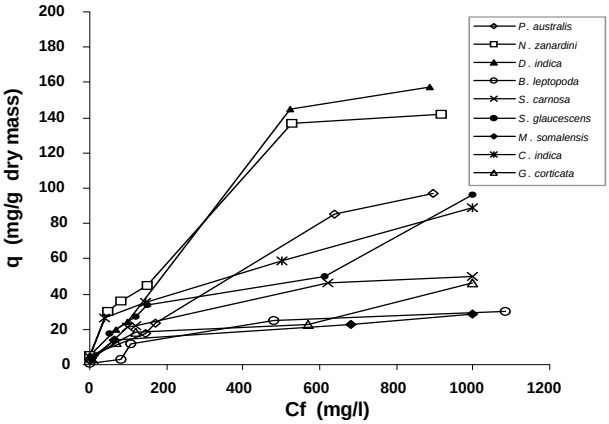

Fig. 3. Comparison of the cobalt sorption properties of the different biosorbents of marine algae at various residual concentrations, pH 5.5, contact time 3 h, biomass density 2 g/l, size of particles d = 0.2–0.5 mm and temperature 30 ˚C.

Our results show that the cobalt sorption efficiency in brown algae of Iran is as high as that of species reported around the world.

^{60}Co sorption experiments (batch type) were performed in activities 4500-90000 Bq. As shown in Fig. 4, marine algae of Oman Gulf have a considerable capability for separation of ^{60}Co from solution. For instance, the most efficient algal species were able to sequester 95% of ^{60}Co in the mentioned range of activity. According to Fig. 4, brown algae (*S. glaucescens*, *D. indica*, *N. zanardini*, *C. indica*

and *P. australis*), are the most effective biosorbents for this purpose, while red algae (*S. carnosa*, *B. leptopoda*, *G. arcuata* and *H. valentiae*) and green alga (*U. fasciata*) have a lower sorption properties.

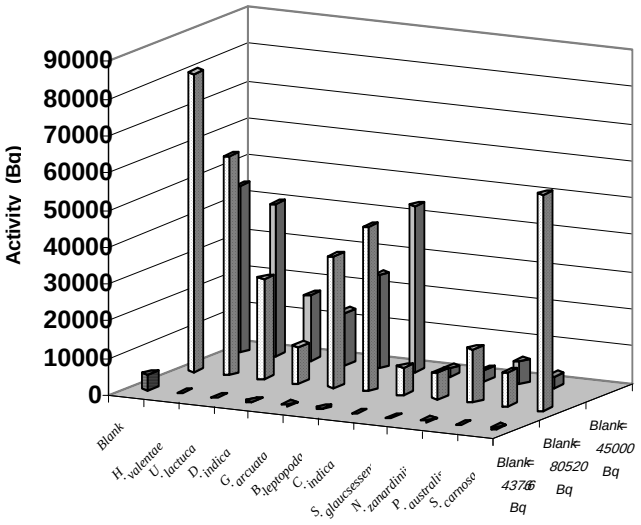

Fig. 4. Biosorption of ^{60}Co by various biomass of marine algae at different ranges of initial activity, at pH 5.5, contact time 3 h, biomass density 2 g/l, size of particles d = 0.2–0.5 mm and temperature 30 ˚ C.

4- Conclusions

The results of this work show that algae, namely *S. glaucescens, C. indica, N. zanardini, P. australis, G. corticata, B. leptopoda, S. carnosa and H. valentiae* were more effective in sequestering cobalt from solutions than other investigated species. The influence of chemical treatments on biosorbent performance was not the same in marine algae, and it seems that varying cell wall material content of marine algae causes these fluctuations. Marine algae of Oman Gulf sequestered cobalt from solution rapidly. The external pH significantly influenced biosorption of cobalt on algal biomass and the removal phenomenon was more efficient at pH 4. Brown algae were more efficient in removing cobalt from solution than other experimented species. Biosorbents derived from marine algae were highly efficient for separation of ^{60}Co from solution containing low and high activities. The present work shows that the biosorbent originated from marine algae could be considered for separation of cobalt ions. Investigations for sequestering cobalt from aqueous solution in continuous flow processes are underway.

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