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ORIGINAL PAPER

Interaction of heavy metal ions with an ion exchange resin obtained from a natural polyelectrolyte

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Abstract An ion exchange resin was synthesized by using a natural polyelectrolyte, sodium alginate, and barium ion as a cross-linker reagent. Resin was characterized by TGA and SEM. Equilibrium and kinetic experiments of Pb^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} ions uptake by barium alginate beads were carried out in batch-type experiments under different values of pH. The removal efficiency increases with increasing pH. The uptake of metal ions occurs rapidly in the first hour. Maximum retention capacity was also determined being Fe(II) > Fe(III) > Co(II) > Ni(II) > Pb(II) > Hg(II) in mmol/g dry beads basis. Elution from the loaded resins at maximum capacity was studied by using HCl and HNO_3 as eluents at different concentrations.

Keywords Ion exchange · Metal ions · Sodium alginate · Natural polyelectrolytes · Biopolymers

Introduction

The pollution of water bodies by toxic metal ions is a worldwide environmental concern [1, 2]. In this context, development of alternative technologies for an effective removal of these pollutants has been encouraged. One of the alternatives to uptake metals ions is to use natural polyelectrolytes as low-cost adsorbents. Among natural polyelectrolytes, alginates are those that comprise a family of polysaccharides which contain 1,4-linked β-D-mannuronic and α-L-guluronic acid residues arranged in a block-wise, non-regular order along the chain. This arrangement determines both

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cation specific affinity of the alginate gel as well as its fundamental physicochemical and rheological properties [3]. Alignment of two homopolymeric guluronic chains form coordination sites which easily accommodate calcium and other divalent cations according to the well known "egg-box model", which adhere to experimental evidence revealing that this model has to be regarded as substantially correct [4, 5]. Various results have been reported for the binding mechanism of metals to alginate beads. Some studies show that mainly ion exchange is observed [3, 5–9] and other studies report sorption through complexation in addition to ion exchange [10–13].

The aim of this work is to investigate the heavy metal adsorption potentiality of the alginate in the form of beads prepared with barium ions as cross-linker because its greater stability than those obtained with calcium ions [14]. This article will report the uptake of Pb(II), Hg(II), Co(II), Ni(II), Fe(II), and Fe(III) from dilute solutions by using protonated alginate beads. The influence of pH and the contact time on the uptake is reported as well. Also, the maximum retention capacities (MRC) are determined as well as the elution behavior in acidic media. The thermal stability and morphological characteristics of these beads are also discussed.

Experimental section

Reagents

Analytical grade salts- of barium chloride dihydrate, lead(II) nitrate, mercury(II) chloride, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, iron(II) sulfate heptahydrate, and iron(III) chloride from Merck were used. Standard solutions (1,000 µg/mL) of each metallic ion at different pH values were prepared. Solutions of the analytical grade, nitric acid, hydrochloric acid, and sodium hydroxide from Merck were used for the pH adjustment of the metal solutions to a particular value. Solutions and dilutions were prepared by using purified deionized water in a Fistream III Glass Still, a high-purity water device (Barnstead, England). Alginic acid, sodium salt (low viscosity) from Sigma was used.

Measurements

Metal ions in the aqueous phase were measured by atomic absorption spectrometry (AAS) (Unicam Solaar M-Series). The pH measurements were carried out in a Beckman pH-meter (Model 4500). Stirring were performed in a mechanical shaker (Thys 2 MLW). The thermal stability was examined by a thermobalance STA 625. The surface morphology of the resins was visualized by a scanning electronic microscope ETEC Autoscan U-1 Model. The surface of the beads was coated with gold under vacuum to obtain about 150 Å thickness using an Edward S 150 Sputter coater.

Preparation of alginate beads

Alginate beads were obtained according to a method previously described by Yiacoumi et al. [10] with minor modifications. These were formed by adding dropwise 100 mL of 2% w/w sodium alginate into 100 mL of 0.10 mol L^{-1} $BaCl_2$ solution under stirring. Stirring was kept during 3 h in order to stabilize the obtained beads. Then, these were washed several times with deionized water to remove ions from the bead surface. Afterward, beads were activated for 3 h in 1.0 mol L^{-1} HCl or 1.0 mol L^{-1} HNO_3 solution to convert the corresponding carboxylate groups into the protonated form. Beads were washed repeatedly with deionized water up to remove the acid excess, and dried in vacuum until constant weight at 50 °C. Under these conditions, the mean diameter of dry beads was 1.5 mm.

Equilibrium experiments

Metal ions uptake

A batch-type equilibrium procedure was used to determine the metal ion uptake from aqueous solution by the alginate beads at different pHs, temperatures, and times. The pH of the aqueous solution was varied from 0 up to 6 depending on the metal ion. The two phases were shaken in a shaking water bath at 20 °C for 15, 30, 45, 60, 90, or 120 min. After shaking, the phases were separated, and the supernatant solution was analyzed for Pb(II), Hg(II), Co(II), Ni(II), Fe(II), or Fe(III) by AAS. The amount of metal ion in the supernatant subtracted from the initial amount added gave the amount of metal ion adsorbed on the beads. Usually, 100 mg of dry beads were contacted with 10.00 mL of 50 mg L^{-1} solution of the corresponding metal ion when kinetic studies were carried out as well as the study of the effect of pH on retention. Maximum capacity was determined by considering 500 mg of dry beads and 200 mg L^{-1} solution of the corresponding metal ion at the optimum retention pH.

Elution of metal ions

Alginate beads at maximum capacity were dried until constant weight in order to evaluate the possibility of regeneration of beads in acidic media. In this context, 0.1 g ± 0.1 mg of dry beads loaded at maximum capacity were contacted with 10.00 mL of 1 mol L^{-1} up to 5 mol L^{-1} solutions of HCl or HNO_3 as eluents to be assayed depending on the metal ion. After shaking for a 1 h period, beads were filtrated and washed with type I water. All filtrate were collected in a 50.00 mL volumetric flask and made up to volume. Analyses were performed by AAS.

Results and discussion

Effect of pH on metal sorption

Figure 1 shows the removal of Hg(II), Ni(II), Co(II), Fe(II), Fe(III), and Pb(II) from 50 mg L^{-1} solution after 1 h at solution pH values of 1 and 2 for Fe(III), of 1, 2, 3, 4, and 5 for Fe(II) and Pb(II), of 1, 2, 3, 4, 5, and 6 for Ni(II), Co(II), and Hg(II). The optimal metal ion removal occurred at a solution pH of 2 for Fe(III) and 3 for Pb(II).

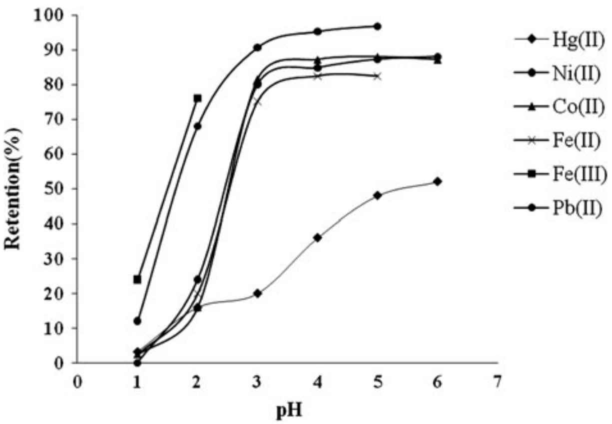

Fig. 1 Uptake of heavy metal ions by protonated alginate beads at several values of pH at 20 °C

The remaining metal ions reached the equilibrium at the maximum solution pH value considered. It is known that the ionization constants for different carboxylic acid groups were around 3–4. Consequently, when the pH is higher than 4 the carbonyl groups are deprotonated, and therefore, negatively charged and able to bind positively charged metal ions. When a solubilized specie is dissociated in a lower extent, as $HgCl_2$, the acid–base behavior is modified because of the higher stabilization of Hg(II); then no precipitation of the oxide occurs until a pH close to 7 [15]. Therefore, at pH 6 mercury precipitation as oxide is not a possible retention mechanism.

Kinetic study

Metal ions uptake by barium alginate beads occurs rapidly in the first hour, followed by a slow uptake process. As it has been seen previously from the equilibrium study, the solution pH plays a very important role in the kinetics. Figure 2 shows that most of the metal ions assayed reach the equilibrium about 1 h at their corresponding optimum pHs.

Maximum retention capacity (MRC)

Maximum retention capacity of the alginic beads was determined by considering the optimum retention pH for each metal ion assayed. Table 1 shows the results obtained in evaluating this analytical parameter. MRC values of nickel(II) and cobalt(II) are higher than those obtained in a previous work [5], differences may be attributed to the synthesis procedure and to the drying process.

However, we should expect that the adsorbed metal ions will constantly decrease with an increasing of ionic strength of the media because of similar types of results which have been reported elsewhere [16].

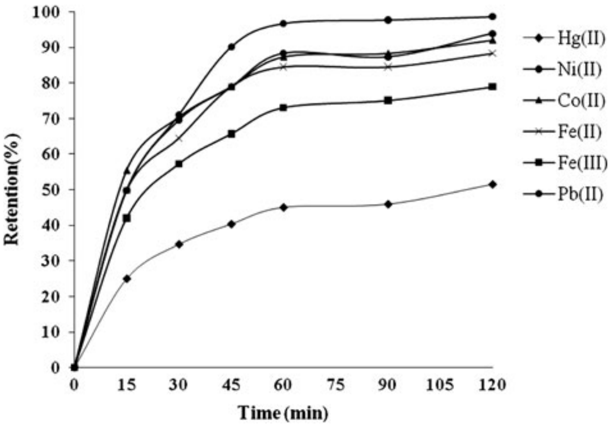

Fig. 2 Uptake of heavy metal ions at optimum pH by protonated alginate beads at different contact time at 20 °C

Table 1 Maximum retention capacity of alginic beads at optimum pH for: Pb(II), Hg(II), Ni(II), Co(II), Fe(II), and Fe(III)

Metal ion	Optimum retention pH	MRC (mmol/g dry beads)	MRC (mg/g dry beads)
Pb(II)	4	1.10	228
Hg(II)	5	0.15	30
Ni(II)	4	1.53	90
Co(II)	4	1.60	94
Fe(II)	4	1.63	91
Fe(III)	2	1.61	90

Elution behavior

In order to evaluate the regeneration of the alginic beads at MRC, elution of the corresponding metal ions were carried out. The elution of the retained metal ions in acidic media by using hydrochloric acid and nitric acid from 1 mol L^{-1} up to 5 mol L^{-1} depending on the metal ion was performed in a batch experimental set-up. Factors as the extent of hydration of the metal ions and beads microstructure are mainly involved in metal ion elution. Nevertheless, a key factor appears to be the effect of the eluent concentration. As can be observed in Table 2, in all cases the elution percentage of all cations increases as the concentration of HCl or HNO_3 increases. These elution studies suggest a recovery higher than 90% when concentration of HCl or HNO_3 solutions are higher than 3 mol L^{-1}.

Thermal stability

Thermal stability of alginate beads were carried out in inactivated, activated, and loaded forms. Results are shown in Table 3. In spite of all samples are stable up to 100 °C within experimental error, the inactivated alginate beads (A) show a slightly

Table 2 Elution percentage in acidic media of Pb(II), Hg(II), Ni(II), Co(II), Fe(II), and Fe(III) from loaded alginic beads at optimum pH

Metal ion	Eluent									
	HCl (mol L^{-1})					HNO_3 (mol L^{-1})				
	1	2	3	4	5	1	2	3	4	5
Pb(II)	–	–	–	–	–	69	87	90	89	86
Hg(II)	70	83	87	90	90	–	–	–	–	–
Ni(II)	73	85	90	92	89	–	–	–	–	–
Co(II)	70	87	90	91	93	–	–	–	–	–
Fe(II)	69	76	89	95	95	–	–	–	–	–
Fe(III)	57	70	85	90	93	–	–	–	–	–

Table 3 Thermogravimetric analyses of inactivated alginate beads (A), activated alginate beads (B), and alginate beads loaded with cobalt(II) (C)

Sample	Weight loss at various temperatures (%)			
	100 °C	200 °C	300 °C	400 °C
A	2.2	8.3	42.0	51.9
B	0	22.1	50.3	59.1
C	1.1	17.1	51.9	61.3

higher stability than the activated (B) and loaded (C) alginate beads which in turn have not a substantial difference. These results demonstrate that these beads can be used up to 100 °C without a significant decomposition.

Morphology

The morphologies of unloaded and loaded beads were examined. Electron micrographs of non-activated beads (Fig. 3a), i.e. prior to acid treatment, show a surface less homogeneously distributed and corrugated nodules with a higher amount of cavities than the activated beads (Fig. 3b). On the other hand, beads at

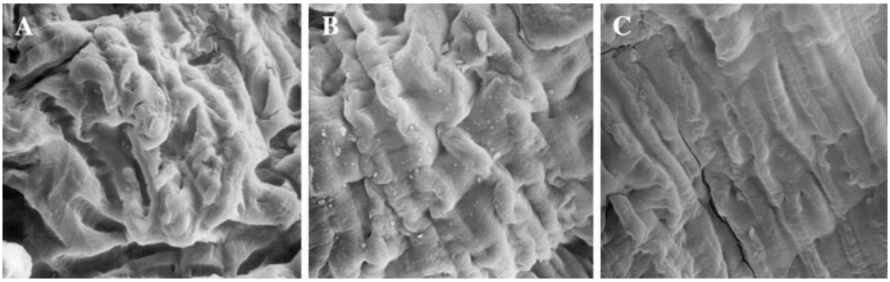

Fig. 3 Electron micrographs (800×) of alginate beads without activation (**a**), activated (**b**), and loaded at maximum capacity with cobalt(II) (**c**)

maximum retention capacity for cobalt(II) show a regular distribution of nodules and cavities which can be considered as a “macroscopic” manifestation of the egg-box junction structure mentioned elsewhere (Fig. 3c), which leaves free carboxylic functional groups in the H-form, which may interact with metal ions.

Despite loaded beads were obtained after three successive contacts with fresh solution, morphology seemed not to be affected in agreement to stability studies that have been reported elsewhere [14]. Nevertheless, further studies are necessary to determine the stability after successive reuses.

Conclusions

The ability of protonated barium alginate beads to uptake different heavy metal ions from dilute aqueous solutions was clearly confirmed. Uptake of metal ions occurs rapidly within the first 60 min. A clear implication of this work is in the development of cost-effective treatment technologies for waste streams containing metal ions. The widespread treatment processes like adsorption, precipitation, and ion exchange are usually effective, but not economic. Moreover, the disposal and reuse of adsorbents and ion exchange resins are energy consumers. Natural polyelectrolytes such as barium alginate beads can overwhelm these problems because of the low volume reached by them after drying. Moreover, loaded alginate beads, after being contacted with an acid solution of HCl or HNO_3, could be reused.

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