Removal of hexavalent chromium from aqueous solution by barium ion cross-linked alginate beads

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Abstract Barium ion cross-linked alginate beads have shown great affinity to toxic hexavalent chromium ions in aqueous solution, in contrast to the traditionally used calcium alginate beads. Our adsorption experiments were carried out by the batch contact method. The optimal pH for removal was found to be pH 4. The equilibrium was established in 4 h, and the removal efficiency of chromium(VI) was found to be 95 %. The adsorption data were applied to Langmuir, Freundlich, Dubinin–Redushkevich (D–R), and Temkin isotherm equations. Both Langmuir and Freundlich isotherm constants indicated a favorable adsorption. The value of mean sorption energy calculated from D–R isotherm indicates that the adsorption is essentially physical. The high maximum chromium(VI) adsorption capacity was determined from the Langmuir isotherm as 36.5 mg/g dry alginate beads. The chromium(VI) adsorption data were analyzed using several kinetic models such as the pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models, and the rate constants were quantified. Our study suggests that barium alginate beads can be used as cost-effective and efficient adsorbents for the removal of chromium(VI) from contaminated waters.

Keywords Adsorption · Biopolymer · Chromium(VI) · Toxic ion · Uptake

Introduction

Chromium compounds are widely used in numerous industrial processes involving electroplating, leather tanning, wood preservatives, catalysts, dyes, and pigments, etc. Waste chromium from such industrial processes contaminates natural waters. Cr(III) is essential in human nutrition, but toxic in large doses. On the other hand, hexavalent chromium compounds are highly toxic and carcinogen for humans. Thus, the removal of Cr(VI) ions from waters has become an important environmental issue and research area. The adsorption processes with commercial activated carbons, ion exchange resins, and both synthetic and natural polymers have been effectively used for this purpose (Chowdhury 2009). Recently, natural biopolymers are competing with the conventional adsorbents, and studies have been increasing on the development of inexpensive, nontoxic, and biodegradable biopolymorphic matrixes. The efficient removal capacities of biopolymers have been reported for toxic metal ions. Moreover, immobilizing biomass, clay, nanoparticles, agricultural byproducts, etc., in a biopolymeric matrix, sorption capacities of these matrixes have been highly improved. Recent review articles compare the metal removal capacities of various biological materials (Babel and Kurniawan 2003; Davis et al. 2003; Miretzky and Cirelli 2010; Mohan and Pittman 2006; Owlad et al. 2009; Saha and Orvig 2010) and conventional adsorbents.

Alginate is a polysaccharide biopolymer obtained from marine brown algae. Commercially, considerable quantities of ultra pure alginate polymer are being marketed. Alginate polymers have been extensively used in food and pharmaceutical industries as nontoxic material (August et al. 2006; Brownlee et al. 2005; Valencia-Chammorro et al. 2011). A huge number of applications based on
alginate gel beads exists in the literature (Prasad and Kadokawa 2009). Alginate can be cross-linked with various metal ions; however, calcium alginate beads have been used by to this date for removal or release studies. The effective removals of toxic metal ions (Chen et al. 1997; Gotoh et al. 2004; Gök and Aytas 2009; Lagoa and Rodrigues 2009) including Cr(III) ions (Araujo and Teixeira 1997; Ibanez and Umetsu 2004) by calcium alginate beads have been reported. Calcium alginate beads can attract metal ions including chrome(III) ions from solutions due to the interactions of positively charged metal ions and negatively charged carboxyl groups of alginate. However, literature studies have revealed that negatively charged chromate ions do not show any attraction to the calcium alginate beads (Bai and Abraham 2003; Fiol et al. 2005; Wang et al. 2010). The adsorption capacity of calcium alginate beads was only increased toward Cr(VI) ions by immobilizing grape stalks (Fiol et al. 2005, 2011), goethite (Lazaridis and Charalambous 2005), banana skin (Park et al. 2008), iron (Nayak et al. 2007; Wang et al. 2010), fungi (Li et al. 2008), fungal biomass (Bai and Abraham 2003), algae (Gökhale et al. 2009), and cyanobacterium (Kiran et al. 2007) in CA beads or combining alginate with other polymeric materials like polyethyleneimine (Ronald et al. 2006), gelatin (Bajpai et al. 2004), and carboxymethyl cellulose (Dewangan et al. 2011). Recently, studies on the physical properties of alginate gels cross-linked with barium ions have revealed that barium alginate beads possess greater stability (Bajpai and Sharma 2004) and consequently increasing number of controlled drug release studies from barium alginate beads began to appear in the literature (Bajpai and Dubey 2007; Singh and Chauhan 2011; Torre et al. 2002). However, removal studies using barium alginate beads are still very rare. Recently, barium alginate beads were used for the removal of positively charged metal ions (Maturana et al. 2011). Ibanez and Umetsu tried barium alginate beads together with calcium alginate beads for the removal of Cr(III) ions. They reported that different divalent cross-linking ions do not affect the Cr(III) uptake process in aqueous solution, since the uptake of metal ions is due to their interaction with the COOH groups of the alginic acid (Ibanez and Umetsu 2004). Our study is the first report on the use of barium alginate beads against chromate ions, and we shown in the present work a favorite sorption and high removal capacity of barium alginate beads for chromate ions. We propose that barium ion cross-linked plain alginate beads could be efficient, low cost, and easily prepared adsorbent candidates for the hexavalent chromium species, because of the strong affinity between barium and chromium(VI) ions. This is the novel and significant part of our study, which was performed in Chemistry Department, Technical University of Istanbul, Turkey (2011–2012).

Materials and methods

Materials

Alginic acid sodium salt from brown algae, viscosity of 2 % solution at 25 °C ~ 250 cps (the label information of the commercial alginate product), and potassium dichromate were from Sigma (Steinheim, Germany). Barium chloride and calcium chloride were purchased from Baker (JT Baker, Holland). Chromium solutions were prepared by dissolving appropriate amounts of potassium dichromate (K2Cr2O7) in distilled water.

Preparation of beads

Barium alginate (BA) beads were prepared by dropwise addition of 2 % (w/v) sodium alginate solution in water into 20 % BaCl2 solution. Since alginate is a commercially purified natural material, the viscosity of alginate solutions changes based on the biomaterial source. In the experiments, we selected 2 % concentration for alginate solutions based on our previous studies with this product (Evingür et al. 2012; Tezcan et al. 2012). When the concentration increases further than 2 % for this product, the increase in viscosity prevents handling the solution. The physical properties of beads such as the mechanical strength, shrinkage, porosity depended on the guluronic and manuronic acids ratio of the used alginate type and the concentration of CaCl2 as the cross-linking agent (Martinsen et al. 1989). A wide range of CaCl2 concentrations has been used to obtain alginate beads in the literature for different applications. The use of BaCl2 as cross-linking agent has recently been increasing in controlled drug release applications. Here, also a wide range of BaCl2 concentrations has been used depending on the type of the used alginate and the purpose of study. Morshed et al. (2012) showed that when the BaCl2 concentration increased from 5 to 15 %, the entrapment efficiency of the drug increased considerably. In our work, we selected 20 % BaCl2 concentration as the cross-linking agent concentration after preliminary experiments. We observed very thin BaCrO4 precipitate particles in the solution when the BaCl2 concentration was kept in dilute concentrations. When the concentration of the BaCl2 solution increased, probably the diffusion rate of barium from the gels decreased due to greater cross-linking with sodium alginate. Thus, after this concentration, we did not observe any precipitate in the solution and all chromate ions were entrapped in the gel beads.

The resultant beads were allowed to stand in the mother liquor for 2 h at room temperature with constant stirring. Then, beads were filtered and kept in deionized water for a half an hour. The filtered beads were kept in fresh
deionized water for another half an hour in order to remove unbound Ba$^{2+}$ ions from the gels. BA beads were filtered and dried at room temperature. CA beads were prepared with the same procedure, using CaCl$_2$ solution instead of BaCl$_2$.

Sorption experiments

The batch mode was applied for the sorption studies. In order to find the removal % of the BA beads, 0.1 g of dried alginate beads was added into 10 mL of 1 mM K$_2$Cr$_2$O$_7$ solutions. The pH of each solution was adjusted by the addition of HCl or NaOH solutions before mixing the adsorbent. Since sufficient removal was observed at 25 °C in preliminary experiments, all experiments were performed at this temperature for energy-saving purposes. This is about the temperature of our laboratory, but sorption experiments were performed in a water-bath shaker with a controlled temperature facility at exactly 25 °C and at 200 rpm shaking rate. At determined time intervals, the Cr(VI) content of the samples was determined spectrophotometrically at 258 nm using a Shimadzu UV-1800 Spectrophotometer. Instead of taking fractions from shaking solutions, solutions were prepared in different bottles for every time interval. The percent removal of chromium from solutions by alginate beads was calculated as:

\[
\% \text{Removal} = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

where $C_i$ and $C_e$ are the initial and final equilibrium Cr(VI) concentrations in the solution, respectively. The initial metal concentration was taken as 10.4 mg/L for these experiments.

The effect of initial Cr(VI) concentration on the removal amount was investigated between 10.4 and 312 mg/L initial Cr(IV) concentrations. For these experiments, 0.05 g of dry beads was put into contact with 5 mL Cr(VI) solutions and shaken at 25 °C for 4 h. The amount of removed Cr(VI) was calculated as:

\[
\text{Removed amount} \left( \frac{\text{mg}}{\text{g}} \right) = \left( \frac{C_i - C_e}{m} \right) V
\]

where $C_i$ and $C_e$ are the initial and equilibrium concentrations of Cr(VI) solutions, respectively. $V$ is the volume of the solution, and $m$ is the mass of dry alginate beads.

SEM characterization

The surface morphology of the polymeric beads was examined using scanning electron microscopy (SEM) (JEOL-JSM-5919LV). The beads were dried in air at room temperature before being analyzed. Figure 1 shows the SEM images of the beads. Beads maintained some spherical shape after drying and indicated fairly smooth and porous morphology.

Results and discussion

Effect of pH

The effect of pH on the adsorption behavior of the system has been tested by varying the pH of 1 mM K$_2$Cr$_2$O$_7$ solution in the range between 2 and 7 at room temperature. While 5 % of the initial Cr(VI) solution was removed by alginate beads at pH 2, removal capacity increased to 95 % at pH 4. At pH 7, precipitate formation was observed in the solution. The change in adsorption behavior of BA beads can be explained with the swelling behaviors of BA beads in the media of varying pH. Bajpai and Sharma reported that when BA beads are immersed in the medium of pH 1, they exhibit minimum swelling, whereas when the beads
are transferred into a medium of pH 4.0, they demonstrate very high water uptake ratio (Bajpai and Sharma 2004). In accordance with the swelling ratio of beads, at pH 2 in our experiments, beads removed a very small percent of Cr(VI). However, while the swelling ratio increased, at pH 4, the negatively charged Cr(VI) species were attracted to the beads because of the mutual affinity of barium atom in the beads and negatively charged hexavalent chromium species in the solution. When the pH of the solution increased to pH 7, swelling increased, but as noted by Bajpai and Sharma, the alginate begins to dissolve, accompanied by leakage of Ba ions from the alginate core, which is responsible for the precipitation in the solution. Finally, pH 4 was selected as the optimal pH for the proceeding experiments.

Effect of shaking time

The sorption experiments were conducted at the pH 4 and 25 °C as explained in the experimental part. Similar experiments were performed with calcium alginate beads in the same experimental conditions. Figure 2 shows the effect of shaking time on the removal ratio of the beads. As seen from Fig. 2, in accordance with the previous studies (Bai and Abraham 2003; Fiol et al. 2005; Wang et al. 2010), the affinity of CA beads toward negatively charged Cr(VI) species is negligible. However, in contrast, BA beads showed great affinity toward Cr(VI) ions. From the experiments, 4 h was selected for optimal shaking time.

Effect of initial metal ion concentration and adsorption isotherms

In order to study the effect of initial Cr(VI) concentration on metal ion removal by BA beads, the experiments were performed with the solutions in which initial Cr(VI) concentrations changed within the range of 10.4–312 mg/L, at pH 4. The solutions were shaken with BA beads at 25 °C for 4 h. Figure 3 shows the adsorbed Cr(VI) amount per mass of alginate beads versus equilibrium Cr(VI) concentrations. The most common adsorption models, i.e., the Langmuir–Freundlich, Dubinin–Redushkevich (D–R), and Temkin models were applied to the experimental data. The linear form of Langmuir equation (Langmuir 1916) used was:

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} b} \quad (3)
\]

where \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) is the amount of Cr(VI) adsorbed at equilibrium (mg/g), \( q_{max} \) is the maximum adsorption capacity of adsorbent (mg/g), and \( b \) (L/mg) is a constant related to the free energy of adsorption. The linear form of Freundlich equilibrium was applied to data according to the equation (Freundlich 1906):

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)
\]

where \( K_F \) and \( n \) are Freundlich constants, which relate to the relative adsorption capacity of the adsorbent and the intensity of the adsorption, respectively.

The linear form of Dubinin–Redushkevich (D–R) equilibrium was applied to data according to the equation (Dubinin 1960):

\[
\ln q_e = \ln q_m - B_D e^2 \quad (5)
\]

where \( q_e \) is the amount of chromate adsorbed onto per unit dosage of Ba-alginate bead (mmol/g), \( q_m \) is the theoretical monolayer sorption capacity (mmol/g), and \( B_D \) is the constant of the sorption energy.

\( \varepsilon \) is Polanyi potential, which is described as

\[
\varepsilon = RT \ln(1 + 1/C_e) \quad (6)
\]

where \( R \) is the gas constant equal to 8.314 J/mol K, \( T \) is the solution temperature (K), and \( C_e \) is the equilibrium concentration (mmol/L).
The value of mean sorption energy, \( E \) (kJ/mol), is described as
\[
E = \frac{1}{(2BD)^{1/2}}
\] (7)
The constant, \( BD \), is related to the mean free energy of sorption per mole of the sorbate (Hasany and Chaudhary 1996). The value of mean sorption energy gives information about chemical and physical sorption.

The linear form of Temkin isotherm was applied to the adsorption data according to the following equation (Temkin and Pyzhev 1940):
\[
q_e = B \ln A + B \ln C_e
\] (8)
where \( B = RT/b \) is the Temkin constant related to heat of sorption, \( A \) is the Temkin isotherm constant (L/mg), \( R \) is the gas constant (8.314 J/mol K), and \( T \) is the temperature (K).

Figure 4 shows the Langmuir, Freundlich, D–R, and Temkin adsorption isotherms, respectively. The Langmuir, Freundlich, D–R, and Temkin adsorption parameters calculated from the corresponding isotherms with the correlation coefficients are given in Table 1. Experimental data fit well to each adsorption models. The maximum Cr(VI) adsorption capacity was found from the Langmuir isotherm as 36.5 mg/g dry alginate beads. This value is well matched with experimental results and high and comparable with the reported adsorption capacities for many natural adsorbents (Babel and Kurniawan 2003; Davis et al. 2003; Mohan and Pittman 2006; Owlad et al. 2009; Saha and Orvig 2010). The dimensionless constant \( R_L \) calculated from \( b \) constant according to following equation also give an idea on the favorable adsorption:
\[
R_L = \frac{1}{1 + bC_0}
\] (9)
where \( C_0 \) is the initial Cr(VI) concentration. The \( R_L \) value was calculated for the first and last experimental initial concentrations of the \( \text{K}_2\text{CrO}_4 \) solution, i.e., 10.4 and 312 mg/L, and was found as 0.064 and 0.67, respectively. Since \( R_L \) values from experimental data lie between 0 and 1, the adsorption can be accepted favorable (Liu et al. 2010).

Accordingly, the high value of the Freundlich constant \( (K_F) \) is an indication of the high adsorption capacity, while the \( 1/n \) value smaller than unity indicates favorable adsorption.

The value of mean sorption energy \( (E) \) was calculated as 4.1 kJ/mol from \( BD \) constant of D–R isotherm. This value gives information about chemical or physical sorption. The

Fig. 4 Linearized, a Langmuir, b Freundlich, c Temkin, and d Dubinin–Radushkevich isotherms for the adsorption of chromium(VI) on BA beads
The $E$ value is lower than 8 kJ/mol for physical sorption and from 8 to 16 kJ/mol for chemical sorption (Kilislioglu and Bilgin 2003). The $E$ value (4.1 kJ/mol) indicates that the adsorption is essentially physical.

### Adsorption kinetics

In order to determine the rate of uptake of Cr(VI) ions from Ba-alginate beads, the pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich kinetic models were applied to the experimental data.

#### Pseudo-first-order model

The linear form of the pseudo-first-order kinetic model of Lagergren is defined with the following function (Lagergren 1898):

$$\log\left(\frac{q_e}{q_t}\right) = k_1 t + \log\left(\frac{1}{k_1}\right)$$

where $q_e$ and $q_t$ are the amounts of solute adsorbed at equilibrium and at any time, respectively, per unit weight of adsorbent (mg/g), $k_1$ is the adsorption constant (min$^{-1}$), and $t$ is contact time (min).

#### Pseudo-second-order model

For the pseudo-second-order kinetic model, the following Eq. (11) was used (Hamadi et al. 2001):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} \frac{1}{q_e} t$$

### Table 1

| Isotherms             | Parameters          |
|-----------------------|---------------------|
| Langmuir              |                     |
| $q_m$ (mg/g)          | 36.5                |
| $b$ (L/mg)            | 0.047               |
| $R^2$                 | 0.988               |
| Freundlich            |                     |
| $K_f$ (mg/g)          | 2.50                |
| $1/n$                 | 0.631               |
| $R^2$                 | 0.957               |
| Temkin                |                     |
| $B$                   | 7.89                |
| $A$ (L/g)             | 0.490               |
| $R^2$                 | 0.992               |
| Dubinin–Radushkevich |                     |
| $q_m$ (mg/g)          | 31.0                |
| $B_D$                 | $3.00 \times 10^{-8}$ |
| $R^2$                 | 0.994               |

**Fig. 5** Different kinetic models, a first-order; b second-order; c intraparticle diffusion; and d Elovich for the adsorption of chromium(VI) on BA beads.
Intraparticle diffusion model

In the intraparticle diffusion model, the rate-determining step is controlled in the liquid systems by diffusion of ions within the adsorbent. This kinetic model is expressed by the following equation:

\[ q_t = k_{id} t^{1/2} \]  

where \( k_{id} \) is the rate constant (mg g\(^{-1}\) min\(^{-1/2}\)). The intraparticle diffusion rate constant is determined from the linear segment of the plot \( q_t \) versus \( t^{1/2} \) (Weber and Morris 1963).

Elovich model

The Elovich model (13) is expressed as

\[ q_t = \left( \frac{1}{\beta} \right) \ln(\alpha \beta) + \left( \frac{1}{\beta} \right) \ln t \]  

where \( \alpha \) and \( \beta \) are constants (Chien and Clayton 1980).

Figure 5 gives the plots of the four applied kinetic models. Table 2 summarizes the rate constants of the kinetic models and their corresponding correlation coefficients. As seen from correlation coefficient values, experimental data are compatible with all four kinetic models. However, comparing first-order and second-order kinetic models, the experimental \( q_e \) value was found closer to the theoretical \( q_m \) value obtained from the first-order-kinetic approach. The adsorption kinetic of biopolymeric beads depends on the physical and chemical characteristics of beads. As the electrostatic attraction between barium ions and chromate ions is expected to have a significant influence on the adsorption mechanism, the uptake rate might be controlled both by the mass transfer rate of chromium ions from the bulk solution to the surface and by the diffusion within the adsorbent. The high correlation constant for the intraparticle model is the sign of the contribution of diffusion on the rate limiting step.

**Conclusion**

Alginate biopolymer beads cross-linked with barium ions were effectively used for the removal of chromium(VI) ions from aqueous solution. Contrary to traditionally used calcium alginate beads, barium alginate beads showed a high affinity to hexavalent chromium ions. The batch experimental data fitted to the Langmuir, Freundlich, Dubinin–Redushkevich (D–R), and Temkin isotherms. The adsorption capacity of beads for chromium(VI) ions was found as 36.5 mg Cr(VI)/g dry bead from the Langmuir equation, which is a quite high value and comparable with the published capacities of many biosorbents (Babel and Kurniawan 2003; Davis et al. 2003; Mohan and Pittman 2006; Owlad et al. 2009; Saha and Orvig 2010). The Langmuir and Freundlich constants indicated a favorable adsorption model. The value of mean sorption energy (\( E \)) calculated from D–R isotherm indicates that the adsorption is essentially physical. The preparation of plain barium alginate beads is a very easy process, and the use of beads for hexavalent chromium removal from water is proposed as a time- and cost-effective method.

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