ORIGINAL PAPER

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 isoterm 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

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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 biopolymeric 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

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alginate gel beads exists in the literature (Prasad and Ka-dokawa 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 Aytaş 2009; Lagoa and Ro-drigues 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 neg-atively charged carboxyl groups of alginate. However, lit-erature 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 bar-ium ions have revealed that barium alginate beads possess greater stability (Bajpai and Sharma 2004) and conse-quently 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 candi-dates 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 Uni-versity of Istanbul, Turkey (2011–2012).

Materials and methods

Materials

Alginic acid sodium salt from brown algae, viscosity of 2 % solution at 25 °C $\sim$ 250 cps (the label information of the commercial alginate product), and potassium dichro-mate 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 ($K_2Cr_2O_7$) 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 % $BaCl_2$ solution. Since alginate is a commercially purified natural material, the viscosity of alginate solutions changes based on the biomaterial source. In the experi-ments, 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 man-nuronic acids ratio of the used alginate type and the con-centration of $CaCl_2$ as the cross-linking agent (Martinsen et al. 1989). A wide range of $CaCl_2$ concentrations has been used to obtain alginate beads in the literature for different applications. The use of $BaCl_2$ as cross-linking agent has recently been increasing in controlled drug release applications. Here, also a wide range of $BaCl_2$ 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 $BaCl_2$ concentration increased from 5 to 15 %, the entrapment efficiency of the drug increased considerably. In our work, we selected 20 % $BaCl_2$ concentration as the cross-linking agent con-centration after preliminary experiments. We observed very thin $BaCrO_4$ precipitate particles in the solution when the $BaCl_2$ concentration was kept in dilute concentrations. When the concentration of the $BaCl_2$ solution increased, probably the diffusion rate of barium from the gels decreased due to greater cross-linking with sodium algi-nate. 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 $K_2Cr_2O_7$ 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:

$$\% \, \text{Removal} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

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:

$$\text{Removed amount} \left(\frac{mg}{g}\right) = \frac{(C_i - C_e)V}{m} \qquad (2)$$

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
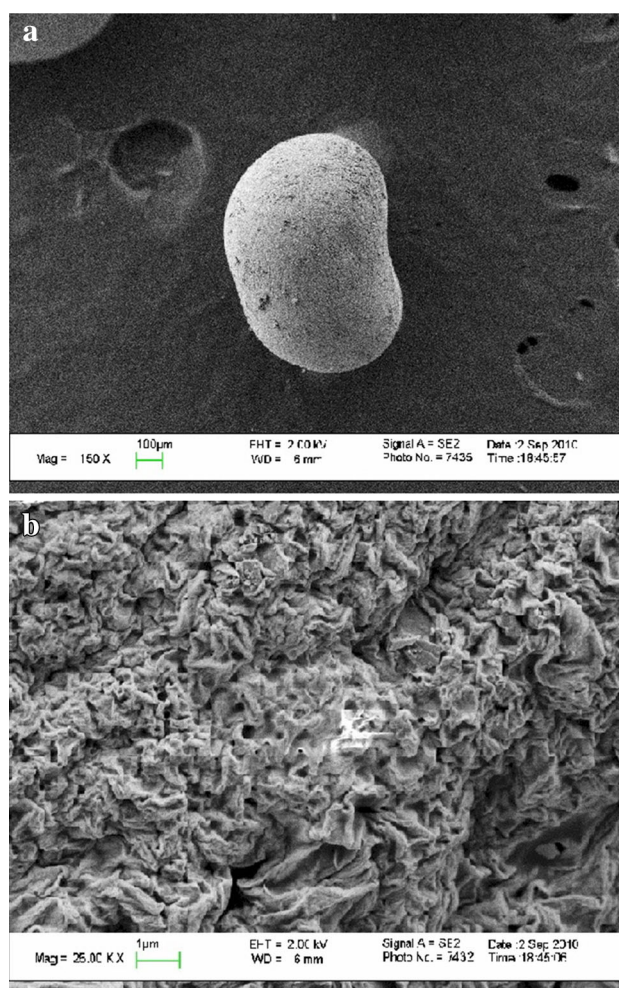

Fig. 1 SEM images of barium alginate beads

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 $K_2Cr_2O_7$ 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
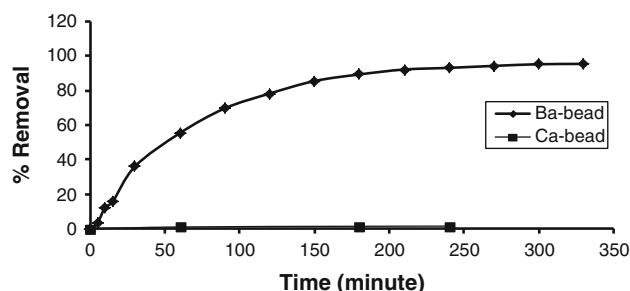
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Fig. 2 Uptake % of Cr(VI) ions as a function of the contact time. Initial Cr(VI) concentration 10.4 mg/L; sorbent concentration 10 g/L; pH 4; temperature 25 °C; agitation rate 200 rpm

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
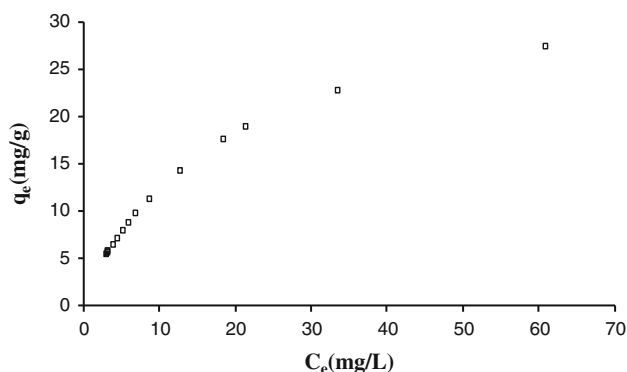

Fig. 3 The effect of initial concentration on the sorption amount. Initial Cr(VI) concentration 10.4–312 mg/L, sorbent concentration 10 g/L; pH 4, temperature 25 °C, agitation time 4 h, agitation rate 200 rpm

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:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} b} \qquad (3)$$

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):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (4)$$

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).

$$\ln q_e = \ln q_m - B_D \varepsilon^2 \qquad (5)$$

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.

ε is Polanyi potential, which is described as

$$\varepsilon = RT \ln(1 + 1/C_e) \qquad (6)$$

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

$$E = 1 \Big/ (2B_D)^{1/2} \tag{7}$$

The constant, B_D, 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):

$$q_e = B \ln A + B \ln C_e \tag{8}$$

where $B = RT/b$, 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:

$$R_L = \frac{1}{1 + bC_0} \tag{9}$$

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 K_2CrO_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 B_D constant of D–R isotherm. This value gives information about chemical or physical sorption. The
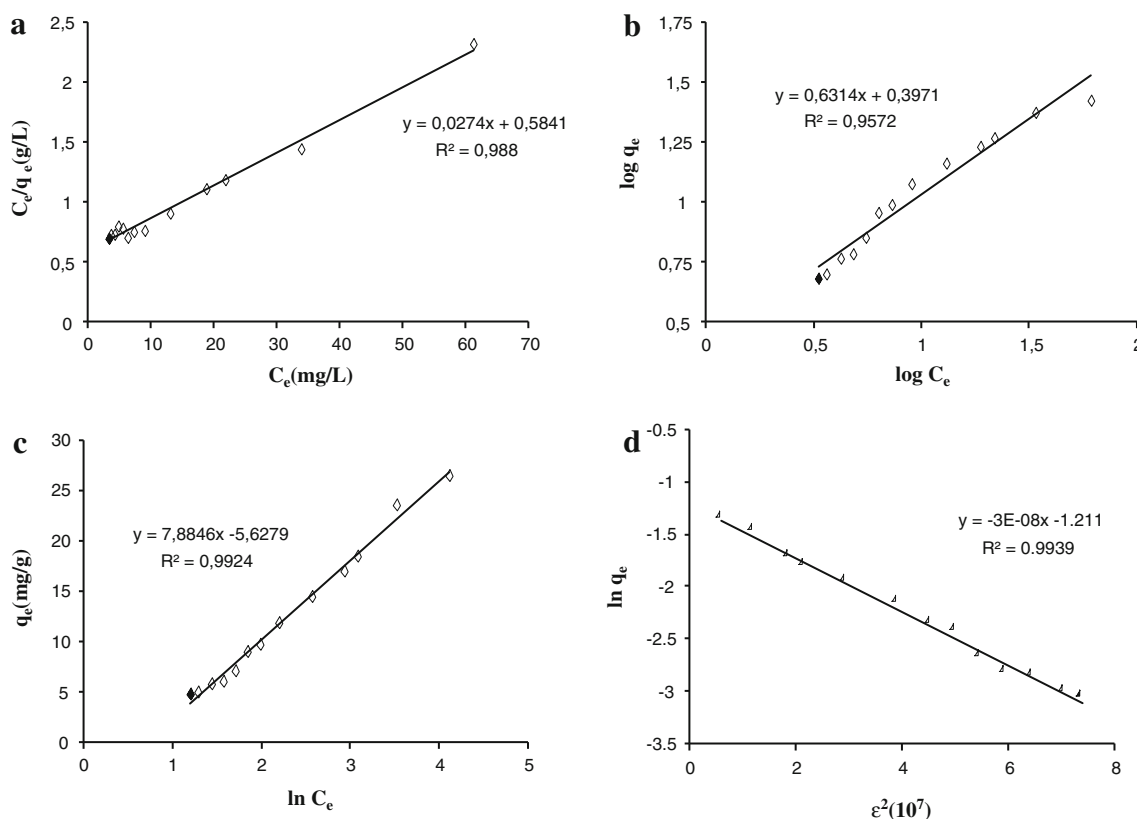

Fig. 4 Linearized, **a** Langmuir, **b** Freundlich, **c** Temkin, and **d** Dubinin–Radushkevich isotherms for the adsorption of chromium(VI) on BA beads

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Table 1 Langmuir, Freundlich, Temkin, and the D–R isotherm constants and correlation coefficients for sorption of chromate on barium alginate beads

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	3.00×10^{-8}
R^2	0.994

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):

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \qquad (10)$$

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):

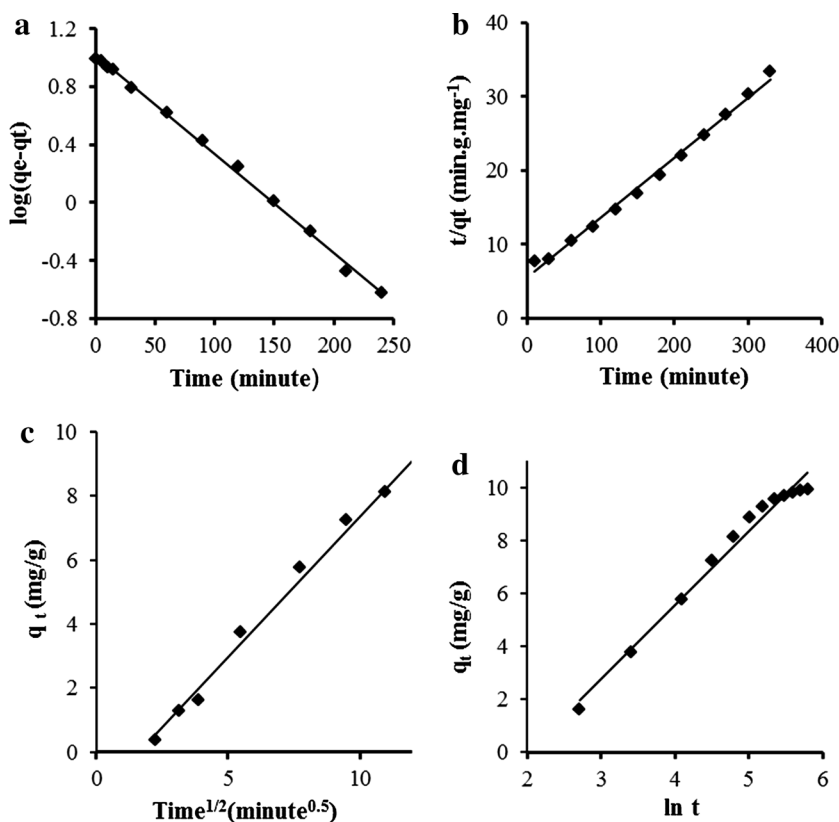$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} \frac{1}{q_e} t \qquad (11)$$

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

Table 2 Rate constants of the kinetic models and their corresponding correlation coefficients

Kinetic models and its parameters	
Pseudo-first-order kinetic	
q_e (mg/g)	10.56
$k_1 \times 10^{-3}$ (min^{-1})	15.90
R^2	0.9968
Pseudo-second-order kinetic	
q_e (mg/g)	13.21
$k_2 \times 10^{-3}$ (g mg^{-1} min^{-1})	0.9581
R^2	0.9938
Intraparticle diffusion model	
$k_{id} \times 10^{-3}$ (mg/g min$^{1/2}$)	0.7835
R^2	0.9807
Elovich model	
α	0.4060
β	0.3581
R^2	0.9932

where k_2 (g mg^{-1} min^{-1}) is the second-order rate constant.

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:

$$q_t = k_{id} t^{1/2} \tag{12}$$

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

$$q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t \tag{13}$$

where α and β 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.

References

Araujo MM, Teixeira JA (1997) Trivalent chromium sorption on alginate beads. Int Biodter Biodegr 40:63–74

August AD, Kong HJ, Mooney DJ (2006) Alginate hydrogels as biomaterials. Macromol Biosci 6:623–633

Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater 97:219–243

Bai RS, Abraham TE (2003) Studies on chromium(VI) adsorption–desorption using immobilized fungal biomass. Bioresour Technol 87:17–26

Bajpai SK, Dubey S (2007) Dynamic release of vitamin B-2 from floating barium alginate beads for gastric delivery. J Macromol Sci A 44:1005–1011

Bajpai SK, Sharma S (2004) Investigation of swelling/degradation behaviour of alginate beads crosslinked with Ca^{2+} and Ba^{2+} ions. React Funct Polym 59:129–140

Bajpai J, Shrivastava R, Bajpai AK (2004) Dynamic and equilibrium studies on adsorption of Cr(VI) ions onto binary bio-polymeric

beads of cross linked alginate and gelatin. Colloid Surf A 236:81–90

Brownlee IA, Allen A, Pearson JP, Dettmar PW, Pavler ME, Atherton MR (2005) Alginate as a source of dietary fiber. Crit Rev Food Sci 45:497–510

Chen JP, Tendeyong F, Yiacoumi S (1997) Equilibrium and kinetic studies of copper ion uptake by calcium alginate. Environ Sci Technol 31:1433–1439

Chien SH, Clayton WR (1980) Application of Elovich equation to the kinetics of phosphates release and sorption in soils. Soil Sci Soc Am J 44:265–268

Chowdhury P (2009) Polymers for the extraction of chromium-role of polymers in the removal and recovery of chromium from wastewater. J Macromol Sci Pure Appl Chem 46:1030–1038

Davis AT, Volesy B, Mucci A (2003) A review of the biochemistry of heavy metal biosorption by brown algae. Water Res 37:4311–4433

Dewangan T, Tiwari A, Bajpai AK (2011) Removal of chromium(VI) ions by adsorption onto binary biopolymeric beads of sodium alginate and carboxymethyl cellulose. J Disper Sci Technol 32:1075–1082

Dubinin MM (1960) The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. Chem Rev 60:235–266

Evingür GA, Tezcan F, Erim FB, Pekcan Ö (2012) Monitoring the gelation of polyacrylamide–sodium alginate composite by fluorescence technique. Phase Transitions 85(6):530–541

Fiol N, Poch J, Villaescusa I (2005) Grape stalks wastes encapsulated in calcium alginate beads for Cr(VI) removal from aqueous solutions. Sep Sci Technol 40:1013–1028

Fiol N, Poch J, Villaescusa I (2011) Chromium(VI) uptake by grape stalks wastes encapsulated in calcium alginate beads: equilibrium and kinetics studies. Chem Spec Bioavailab 16:25–33

Freundlich HMF (1906) Uber die adsorption in Losungen. Zeitsch Phys Chem 57:385

Gök C, Aytaş S (2009) Biosorption of uranium(VI) from aqueous solution using calcium alginate beads. J Hazard Mater 168:369–375

Gökhale SV, Jyoti KK, Lele SS (2009) Modeling of chromium (VI) biosorption by immobilized Spirulina platensis in packed column. J Hazard Mater 170:735–743

Gotoh T, Matsushima K, Kikuchi KI (2004) Adsorption of Cu and Mn on covalently cross-linked alginate gel beads. Chemosphere 55:57–64

Hamadi NK, Chen XD, Farid MM, Lu MGQ (2001) Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. Chem Eng J 84:95–105

Hasany SM, Chaudhary MH (1996) Sorption potential of Hare River sand for the removal of antimony from acidic aqueous solution. Appl Rad Isot 47:467–471

Ibanez JP, Umetsu Y (2004) Uptake of trivalent chromium from aqueous solutions using protonated dry alginate beads. Hydrometallurgy 72:327–334

Kilislioglu A, Bilgin B (2003) Thermodynamic and kinetic investigation of uranium adsorption on amberlite IR-118H resin. Appl Radiat Isot 58:155–160

Kiran B, Kaushik A, Kaushik CP (2007) Response surface methodological approach for optimizing, removal of Cr(VI) from aqueous solution using immobilized cyanobacterium. Chem Eng J 126:147–153

Lagergren S (1898) About the theory of so called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens. Handlingar Band 24(4):1–39

Lagoa R, Rodrigues JR (2009) Kinetic analysis of metal uptake by dry and gel alginate particles. Biochem Eng J 46:320–326

Langmuir I (1916) The constitution and fundamental properties of solids and liquids. J Am Chem Soc 38(11):2221–2295

Lazaridis NK, Charalambous Ch (2005) Sorptive removal of trivalent and hexavalent chromium from binary aqueous solutions by composite alginate–goethite beads. Water Res 39:4385–4396

Li H, Liu T, Li Z, Deng L (2008) Low-cost supports used to immobilize fungi and reliable technique for removal hexavalent chromium in wastewater. Bioresour Technol 99:2234–2241

Liu Y, Li H, Tan GQ, Zhu X (2010) Fe^{2+} modified vermiculite for the removal of chromium (VI) from aqueous solution. Sep Sci Technol 46(2):290–299

Martinsen A, Skjakbraek G, Smidsrod O (1989) Alginate as immobilization material correlation between chemical and physical-properties of alginate gel beads. Biotechnol Bioeng 33(1):79–89

Maturana HA, Peric IM, Rivas BL, Pooley SA (2011) Interaction of heavy metal ions with an ion exchange resin obtained from a natural polyelectrolyte. Polym Bull 67:669–676

Miretzky P, Cirelli AF (2010) Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. J Hazard Mater 180:1–19

Mohan D, Pittman CU (2006) Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. J Hazard Mater 137:762–811

Morshed M, Mallick J, Nath AK, Uddin Z, Dutta M, Hossain A, Kawsarl H (2012) Effect of barium chloride as a cross linking agent on the sodium alginate based diclofenac sodium beads. Bengladesh Pharm J 15(1):53–57

Nayak D, Banerjee A, Roy S, Lahiri S (2007) Speciation dependent studies on chromium absorption using calcium alginate and iron doped calcium alginate biopolymer. J Radioanal Nucl Ch 274:219–224

Owlad M, Aroua MK, Ashri W, Daud W, Baroutian S (2009) Removal of hexavalent chromium-contaminated water and wastewater: a review. Water Air Soil Poll 200:59–77

Park D, Lim S, Yun YS, Park JM (2008) Development of a new Cr(VI)-biosorbent from agricultural biowaste. Bioresour Technol 99:8810–8818

Prasad K, Kadokawa J (2009) Alginate-based blends and nano/microbeads. In: Rehm BHA (ed) Alginates: biology and applications. Springer, Berlin

Ronald N, Makoto F, Masatoshi M (2006) Hybrid properties of alginate-PEI adsorbent for chromium (VI) removal from aqueous solutions. Sep Sci Technol 41:3619–3637

Saha B, Orvig C (2010) Biosorbents for hexavalent chromium elimination from industrial and municipal effluents. Coordin Chem Rev 254:2959–2972

Singh B, Chauhan D (2011) Barium ions crosslinked Alginate and Sterculia gum-based gastroretentive floating drug delivery system for use in peptic ulcers. Int J Polym Mater 60:684–705

Temkin MJ, Pyzhev V (1940) Recent modifications to Langmuir isotherms. Acta Physiochim 12:217–222

Tezcan F, Günister E, Özen G, Erim FB (2012) Biocomposite films based on alginate and organically modified clay. Int J Biol Macromol 50:1165–1168

Torre ML, Faustini M, Norberti R, Maggi L, Maffeo G, Conte U, Vigo D (2002) Barium alginate cell-delivery systems: correlation between technological parameters. Int J Pharm 242:389–391

Valencia-Chammorro SA, Palou L, del Rio MA, Perez-Gago MB (2011) Antimicrobial edible films and coatings for fresh and minimally processed fruits and vegetables: a review. Crit Rev Food Sci 51:872–900

Wang XS, Tang YJ, Chen LF, Li FY, Wan WY, Tan YB (2010) Removal of Cr(VI) by zero-valent, iron-encapsulated alginate beads. Clean—soil. Air Water 38:263–267

Weber WJ, Morris JC (1963) Kinetics of adsorption on carbon from solution. J Sanit Eng Div Am Soc Civ Eng 89:31–60