Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.749204

51 (2013) 3438–3444
April

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Removal of Cr(VI) from aqueous solution using alginate/polyvinyl alcohol–hematite composite

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Received 2 March 2012; Accepted 10 October 2012

ABSTRACT

The aim of this study was to investigate the removal of Cr(VI) from aqueous solution by alginate/PVA–hematite composite. Kinetic test showed that Cr(VI) sorption to the composite reached equilibrium after 24 h. Equilibrium test demonstrated that the maximum sorption capacity of the composite was 12.501 mg/g. Further experiments indicated that Cr(VI) removal was very sensitive to solution pH between 2.0 and 9.0—with the highest removal capacity at the highly acidic solution pH, decreasing sharply with increasing pH. The influence of $CO_3^{2-}$and HPO_4^{2-} on the removal of Cr(VI) was important due to their competition with Cr(VI) ions at the sorption sites. The impact of the anions on Cr(VI) removal was in the order of $NO_3^- < SO_4^{2-} < HPO_4^{2-} < CO_3^{2-}$. This study improves knowledge of potential applications of alginate/PVA–hematite composite as adsorbent for Cr(VI) removal in water treatment.

Keywords: Alginate/PVA–hematite composite; Calcium alginate; Chromium; Hematite; Polyvinyl alcohol; Sorption

1. Introduction

Chromium contamination of drinking water resources is a serious environmental problem around the globe. In many countries such as China, USA, Canada, Mexico, India, and Italy, chromium is present in groundwater at concentrations exceeding the guidelines of the World Health Organization (0.05 mg/L), causing serious health problems. Chromium can exist in oxidation states ranging from −2 to + 6. In aquatic environments, however, trivalent Cr(III) and hexavalent Cr(VI) are the major forms of chromium, and Cr (VI) is the more toxic and cancerous [1,2].

Various treatment methods have been used for the removal of chromium from water, including coagulation–precipitation, ion exchange, adsorption, and membrane technology. Because of cost-effectiveness and simplicity of operation, adsorption can be used widely for chromium removal. Various adsorbents such as activated carbon, iron oxide, aluminum oxide, layered double hydroxide, clays and coal/bone charcoal have been used for chromium removal [2]. The application of iron oxide/hydroxide (goethite, hematite, magnetite)

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to remove chromium has been investigated by several researchers [3–7]. For example, the researchers have observed the reduction of Cr(VI) by composite of pinus tar and synthetic hematite [8], Cr(VI) removal by montmorillonite-supported magnetite nanoparticles [9], chromate uptake by chitosan–magnetite nanocomposite loaded with iron(III) [10], and sorption of chromate to iron and aluminum (oxy)hydroxides under various pH and ionic strength conditions [11].

The immobilization of functional materials into calcium alginate hydrogels is widely applied for chromate removal because it is a simple and cost-effective technique [12,13]. Sodium alginate is a nontoxic and biodegradable natural polymer, which is composed of (1-4)-linked D-mannuronic and L-glucuronic acid repeat units. Calcium ions can chelate carboxylate groups, make cross-links between chains, and form insoluble hydrogels [14]. However, mechanical strength and chemical stability of alginate hydrogels are poor. It is, therefore, necessary to improve their properties through blending with polymers such as polyvinyl alcohol (PVA) [15]. The aim of this study was to investigate the removal of Cr(VI) from aqueous solution using alginate/PVA–hematite composite. The composite was prepared through immobilization of synthetic hematite (α-Fe_2O_3) powders into alginate/PVA blend hydrogels. Batch experiments were performed under various experimental conditions to examine the removal of Cr(VI) by the composite.

2. Materials and methods

2.1. Preparation of alginate/PVA–hematite composite

All chemicals used for the experiments were purchased from Sigma Aldrich. Hematite was prepared by precipitation method. A solution of sodium hydroxide (NaOH) was added dropwise into 500 mL solution of 0.25 M iron chloride ($FeCl_3$ $6H_2O$) with intensive stirring until pH 8.0, at room temperature. The resulting precipitates were aged at 60˚C for 18 h, and then washed thoroughly with deionized water to remove excess sodium. The washed precipitates were oven-dried again at 150˚C for 18 h and then pulverized in a ball mill. The mineralogical and crystalline structural properties were examined using X-ray diffractometry (XRD, D8 Advance, Bruker, Germany) with a Cu Kα radiation of 1.5406 Å at a scanning speed of 0.6˚/s. The XRD pattern of the synthesized particles showed the characteristics of hematite (Fig. 1), indicating the peaks corresponding to hematite (JCPDS 87–1,166, 2θ = 24.149, 33.159, 35.632, 40.863, 49.464, 54.070, 62.438, 64.002). The surface area of hematite (98.0 m^2/g) was determined by N_2 adsorption–desorption isotherms and Barrett-Joyner-Halenda analysis using an ASAP 2010 instrument (Micromeritics, USA). The zeta potentials of hematite were measured at various pH values, which were obtained using dilute HNO_3 and NH_4OH. The point of zero charge (pH_{pzc}) of hematite was determined from the zeta potentials.

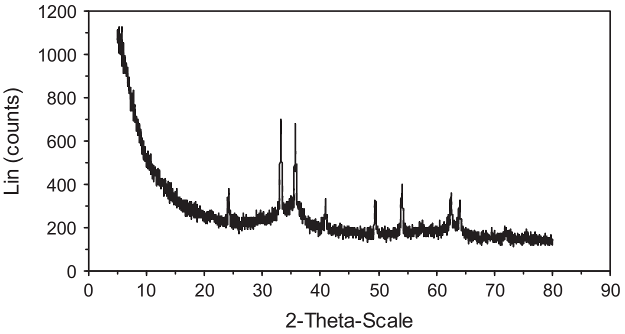

Fig. 1. X-ray diffraction pattern of hematite powders synthesized in the laboratory.

Alginate/PVA–hematite composite was prepared by entrapping a powdered form of hematite in alginate and PVA blend hydrogels. Preliminary tests indicated that alginate/PVA hydrogels were not dismantled in both acidic (5% acetic solution) and basic (0.1 M NaOH) solutions while about 5% of alginate hydrogels were dismantled in both solutions. PVA (20 g) and sodium alginate (2 g) were dissolved in 200 mL of distilled water and agitated on a magnetic stirrer at 70˚C for 5 h. Then, 16 g of hematite (8% w/v) was added to 200 mL alginate/PVA solution under intensive stirring

Fig. 2. Alginate/PVA-hematite composite used in the experiments.

to obtain the homogeneous suspension. The suspension was dropped into a stirred reservoir containing 500 mL solution of 0.3 M calcium chloride ($CaCl_2$) in order to form alginate/PVA–hematite composite using a syringe pump. The composite was allowed to cure in the same $CaCl_2$ solution for 24 h under stirring and then rinsed with deionized water to remove excess Ca^{2+}. Before use, the washed composite was oven-dried at 60˚C for 24 h to obtain 0.68 ± 0.04 mm alginate/PVA–hematite composite (Fig. 2).

2.2. Batch experiments

The desired Cr(VI) solution was prepared by diluting the stocking Cr(VI) solution (1,000 mg/L), which was made from potassium dichromate ($K_2Cr_2O_7$). All batch experiments were performed in 50 mL polypropylene conical tubes without pH adjustment except the experiments of pH effect. Note that pH of 50 mg/L Cr (VI) solution was 4.5. Batch experiments were conducted to examine the Cr(VI) removal under different dosages of alginate/PVA-hematite composite. The experiments were conducted at an initial Cr(VI) concentration of 50 mg/L (pH = 4.5) with the composite doses ranging from 0.02 to 0.3 g in 30 mL solution (from 0.67 to 10.00 g/L). The tubes were shaken at 25˚C and 100 rpm using a shaking incubator (DAIHAN Science, Korea). The samples were collected after 24 h of equilibration, and filtered through a 0.45 μm membrane filter. The total Cr concentration was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (ICP-1000 IV, Shimadzu Co., Japan) and Cr(VI) by UV–vis spectrophotometer (Helios, Thermo, USA) using diphenylcarbazide method.

Next, kinetic batch experiments were performed at the initial Cr(VI) concentration of 50 mg/L and the composite dose of 0.1 g in 30 mL solution (adsorbent dose = 3.33 g/L). In the experiments, the samples were taken at 0.5, 1, 1.5, 2, 4, 6, 12, 24, and 48 h post-reaction. Equilibrium batch experiments were conducted with different concentrations of Cr(VI) solution. The composite (0.1 g) was added to 30 mL chromate solution (adsorbent dose = 3.33 g/L; initial concentration = 10–200 mg/L). The samples were collected 24 h post-reaction. In the pH experiments, 0.1 M NaOH and 0.1 M HCl solutions were used for adjusting the pH from 2.0 to 9.0. The pH was measured with a pH probe (9107BN, Thermo Scientific, USA). In the competing anion experiments, the competing anions (NO_3^-, SO_4^{2-}, HPO_4^{2-}, and CO_3^{2-}) were added to Cr (VI) solution to achieve the desired anion concentrations (1, 10 mM). All experiments were performed in triplicate.

2.3. Data analysis

The equilibrium data were analyzed using the following Langmuir and Freundlich isotherm models:

$$q_e = \frac{Q_m K_L C}{1 + K_L C} \tag{1}$$

$$q_e = K_F C^n \tag{2}$$

where C is the concentration of Cr(VI) in the aqueous solution at equilibrium (mg/L), K_L is the Langmuir constant related to the binding energy (L/mg), Q_m is the maximum mass of Cr(VI) removed per unit mass of alginate/PVA–hematite composite (removal capacity) (mg/g), K_F is the distribution coefficient (L/g), and n is the Freundlich constant. Values of K_L, Q_m, K_F, and n can be determined by fitting the Langmuir and Freundlich models to the observed data.

The kinetic data were analyzed using the following pseudo first-order and pseudo second-order models [16,17]:

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{3}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

where q_t is the amount of Cr(VI) removed at time t (mg/g), q_e is the amount of Cr(VI) removed at equilibrium (mg/g), k_1 is the pseudo first-order rate constant (h^{-1}), and k_2 is the pseudo second-order velocity constant (g/mg/h). In addition, the kinetic data were analyzed with the following intra-particle diffusion model (Weber-Morris equation) [10]

$$q_t = k_i t^{1/2} + I \tag{5}$$

where k_i is the intra-particle diffusion rate constant ($mg/g/h^{1/2}$), and I is the intercept (mg/g) related to the thickness of the boundary layer.

3. Results and discussion

3.1. Cr(VI) sorption in alginate/PVA–hematite composite

The Cr(VI) sorption in alginate/PVA–hematite composite (initial Cr(VI) concentration = 50 mg/L) under different dosages of adsorbents is presented in Fig. 3. The removal percentage increased from 3.1 to 56.5% with increasing the composite doses from 0.67 to 10.00 g/L. Meanwhile, adsorption capacity increased from 2.45 to 4.71 mg/g with increasing the

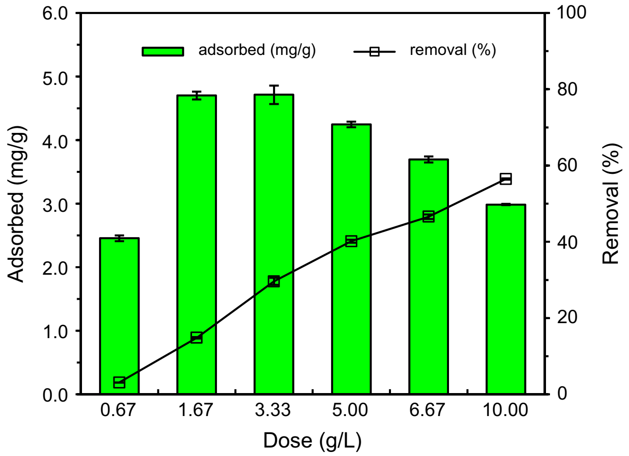

Fig. 3. Cr(VI) removal in alginate/PVA-hematite composite under different dosages of adsorbents (initial chromate concentration = 50 mg/L).

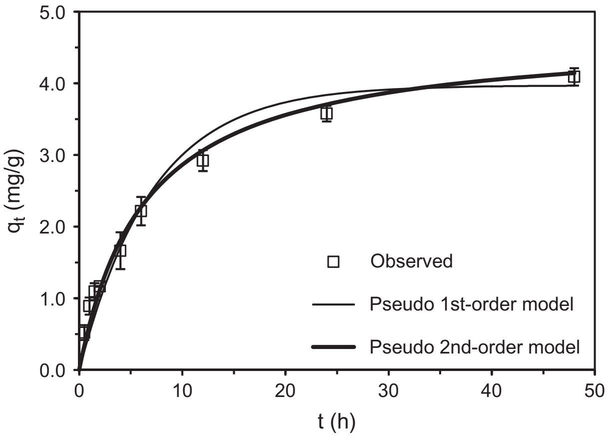

Fig. 4. Kinetic batch data and model fit for Cr(VI) removal in alginate/PVA-hematite composite (adsorbent dose = 3.33 g/L; initial chromate concentration = 50 mg/L). Kinetic model parameters are provided in Table 1.

composite dose from 0.67 to 3.33 g/L. Then, it decreased from 4.71 to 2.99 mg/g with increasing the composite dose from 3.33 to 10.00 g/L. Results indicated that adsorption capacity of the composite was the maximum at the adsorbent dose of 3.33 g/L at the given experimental conditions.

At pH 2–6, dominant species of Cr(VI) are $HCrO_4^-$ and $Cr_2O_7^{2-}$, depending on concentration. During the experiments, Cr(VI) ions in aqueous solution could diffuse into alginate/PVA-hematite composite through the pores in the composite. Then, Cr(VI) ions could come in contact with the entrapped hematite particles and subsequently be removed from aqueous phase to solid phase (hematite). The adsorption of Cr(VI) ions to hematite surfaces could be described by ligand exchange mechanism. In the adsorption process, Cr (VI) ions could replace hydroxyl ions (OH^-) on the surfaces of hematite, forming inner-sphere complexes [4,18]. Additionally, when hematite becomes positively charged at highly acidic pH, electrostatic attraction could occur between negatively-charged Cr(VI) ions and positively-charged surfaces of hematite [3]. Note that the pH_{pzc} of hematite was determined to be 6.3. The pH_{pzc} is the pH where net surface charge is equal to zero. A particle carries a positive charge below the pH_{pzc} but a negative charge above it.

3.2. Kinetics and isotherms of Cr(VI) sorption

The adsorption kinetics of Cr(VI) in alginate/PVA-hematite composite (initial Cr(VI) concentration = 50 mg/L) is shown in Fig. 4. The sorption reached equilibrium after 24 h of reaction time. Model parameters for the pseudo first-order and pseudo second-order models obtained from the kinetic experiments are provided in Table 1. In the pseudo first-order model, the value of q_e was 3.970 mg/g while the value of k_1 was 0.141 h^{-1}. The value of q_e from the pseudo second-order model was greater than that from the pseudo first-order model. The value of q_e was 4.693 mg/g, while the values of k_2 was 0.033 g/mg/h. The correlation coefficients (R^2) indicated that the pseudo second-order model described the kinetic data better than the pseudo first-order model.

In Fig. 5, the intra-particle diffusion model was applied for the kinetic sorption data for Cr(VI) removal in alginate/PVA-hematite composite. The plots were composed of two line segments. The model was fitted well with the data with the coefficient of determination (R^2) of 0.993 (first line) and 0.971 (second line). According to Weber and Morris [10], the first line in the plots indicates boundary layer adsorption while the second line describes the intra-particle diffusion. The values of k_i for the first and second lines were 0.865 and 0.331 mg/g/$h^{1/2}$, respectively.

Table 1
Kinetic model parameters obtained from model fitting to experimental data

Pseudo first-order model			Pseudo second-order model		
q_e (mg/g)	k_1 (1/h)	R^2	q_e (mg/g)	k_2 (g/mg/h)	R^2
3.970	0.141	0.962	4.693	0.033	0.986

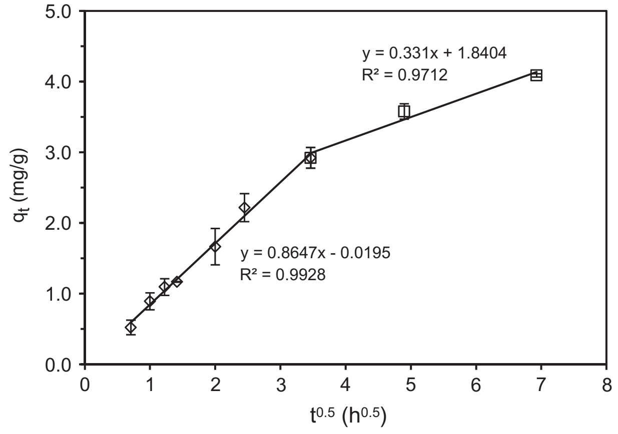

Fig. 5. Intra-particle diffusion model for Cr(VI) removal in alginate/PVA-hematite composite.

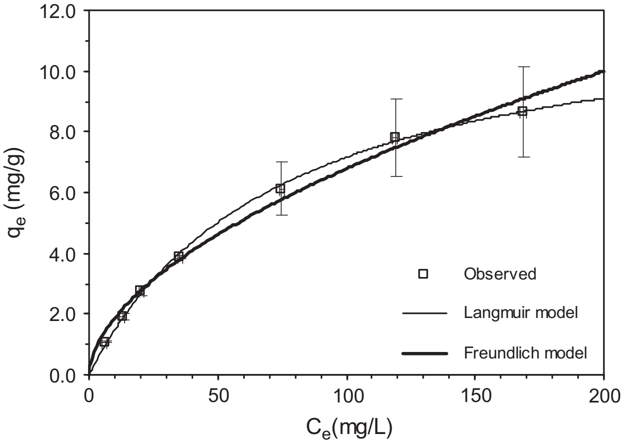

Fig. 6. Equilibrium batch data and model fit for Cr(VI) removal in alginate/PVA-hematite composite (adsorbent dose = 3.33 g/L). Equilibrium isotherm model parameters are provided in Table 2.

The equilibrium isotherm of Cr(VI) in alginate/PVA-hematite composite is presented in Fig. 6. The equilibrium isotherm constants are summarized in Table 2. In the Freundlich model, the distribution coefficient (K_F) was 0.521 L/g, while the Freundlich constant (n) was 0.558. In the Langmuir model, the Langmuir constant (K_L) was 0.013 L/mg, while the removal capacity (Q_m) was 12.501 mg/g. The correlation coefficient (R^2) of the Langmuir model was slightly greater than that of the Freundlich model. In our experiments, the maximum adsorption capacity for Cr(VI) was determined to be 12.501 mg per one gram of the composite, which was in the range of the removal capacity for polymer-based composites reported in the literature (Table 3).

3.3. Influence of pH and anions on Cr(VI) sorption

The influence of initial solution pH on Cr(VI) in alginate/PVA-hematite composite is shown in Fig. 7. The removal capacity at pH 2.0 was 10.94 mg/g and decreased to 7.63 mg/g at pH 3.0. As the solution pH further increased, the removal capacity decreased sharply and arrived at 1.15 mg/g at pH 9.0. Results demonstrated that Cr(VI) removal in the composite was sensitive to solution pH changes between 2.0 and 9.0 with the highest removal capacity at the highly acidic solution pH. Note that the reduction of Cr(VI) to Cr(III) did not occur during the experiments for Cr(VI) removal in alginate/PVA-hematite composite at the highly acidic solution pH. Our results conform well with the report of Singh et al. [4] who showed the maximum removal of Cr(VI) to hematite particles in pH 2.0–3.0. This phenomenon could be attributed to the protonation of hematite surfaces at acidic pHs, resulting in the electrostatic attraction between positively-charged hematite surfaces ($S–OH_2^+$) and negatively-charged chromium ions ($HCrO_4^-$).

The effect of anions on the removal of Cr(VI) in alginate/PVA-hematite composite is presented in Fig. 8. Nitrate (NO_3^-), monovalent anion, showed minimal effect on the removal of Cr(VI) in the composite at concentrations ranging from 1 to 10 mM. Also, sulfate (SO_4^{2-}) had relatively low impact on the removal of Cr(VI) in the composite. This result agreed well with the report of Wei et al. [23], showing that the effect of NO_3^- and SO_4^{2-} on Cr(VI) removal in magnetic iron-nickel oxide was minimal. Meanwhile, divalent anions such as phosphate (HPO_4^{2-}) and carbonate (CO_3^{2-}) profoundly interfered with the removal of Cr(VI) in the composite. HPO_4^{2-} and CO_3^{2-} influenced the removal due to their competition

Table 2
Equilibrium isotherm model parameters obtained from model fitting to experimental data

Freundlich isotherm model			Langmuir isotherm model		
K_F (L/g)	n	R^2	K_L (L/mg)	Q_m (mg/g)	R^2
0.521	0.558	0.992	0.013	12.501	0.999

Table 3
Cr(VI) removal capacity of polymer-based composites reported in the literature

	Alginate goethite bead	Cross-linked magnetic chitosan bead	Biofunctional magnetic bead	Grafted chitosan bead	Biopolymeric beads of sodium alginate	Alginate/PVA hematite composite
Removal capacity (mg/g)	27.10	83.20	6.97	9.34	16.67	12.50
Reference	[12]	[19]	[20]	[21]	[22]	This study

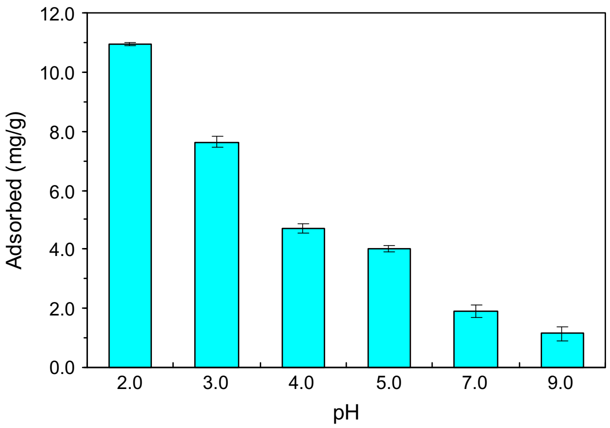

Fig. 7. Effect of initial solution pH on Cr(VI) removal in alginate/PVA-hematite composite (adsorbent dose = 3.33 g/L; initial chromate concentration = 50 mg/L).

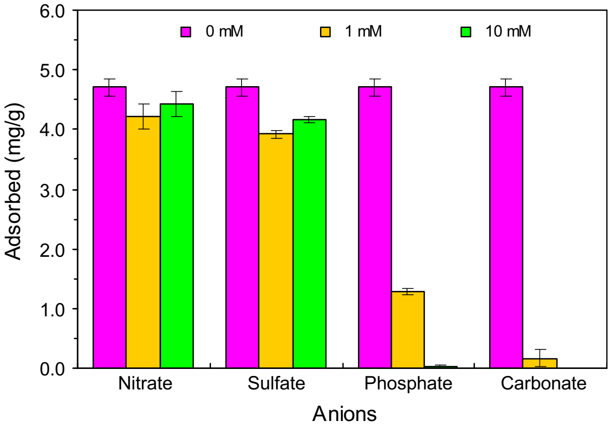

Fig. 8. Effect of anions on Cr(VI) removal in alginate/PVA-hematite composite (adsorbent dose = 3.33 g/L; initial chromate concentration = 50 mg/L).

with Cr(VI) ions at the sorption sites. Our results indicated that the removal of Cr(VI) in the composite was most affected by CO_3^{2-}. At the given experimental conditions, the impact of anions was in the order of $NO_3^- < SO_4^{2-} < HPO_4^{2-} < CO_3^{2-}$.

4. Conclusions

The removal of Cr(VI) by alginate/PVA-hematite composite was observed in this study. Kinetic test indicated that Cr(VI) sorption onto the composite reached equilibrium after 24 h. The composite was effective in the removal of Cr(VI) with the maximum sorption capacity of 12.501 mg/g. Results also demonstrated that Cr(VI) removal was very sensitive to solution pH between 2.0 and 9.0 with the highest removal capacity at the highly acidic solution pH, decreasing sharply with increasing pH. The influence of the anions on Cr(VI) removal was in the order of $NO_3^- < SO_4^{2-} < HPO_4^{2-} < CO_3^{2-}$. This study improves knowledge of potential applications of alginate/PVA-hematite composite as adsorbent for Cr(VI) removal in water treatment.

Acknowledgments

This research was supported by the National Research Foundation of Korea, funded by the Ministry of Education, Science and Technology, Republic of Korea (grant number 2011-0009688).

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