Fibers and Polymers 2008, Vol.9, No.3, 263-266

Column Study of Cadmium Adsorption onto Poly(vinyl alcohol)/ Hydroxyapatite Composite Cryogel

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(Received October 29, 2007; Revised March 15, 2008; Accepted March 25, 2008)

Abstract: Macroporous PVA/HAp composite cryogel was studied for cadmium removal in a fixed-bed column. The cryogel was made through a freeze-thawing process. The morphology of the cryogel was measured. The adsorption performance of the cryogel in the column was examined by varying bed height and HAp amount in PVA cryogel. The maximum adsorption capacity and exhaustion time were determined from the breakthrough curves. The experimental data was described using Adams-Bohart model. Bed height did not exert a large influence on the maximum adsorption capacity and exhaustion time. The kinetic rate constant and the adsorption capacity of the bed were found to be affected by HAp amount.

Keywords: Adsorption, Fixed-bed column, Cryogel, Hydroxyapatite, Adams-Bohart model

Introduction

The removal of heavy metals in wastewater has been an important issue for many years due to environmental harms. The industrial wastewater often contains larger amount of heavy metals than the maximum concentrations allowed, which are produced by many industries including the electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing industries. Cadmium is one of the major heavy toxic elements contaminating natural waters and industrial liquid wastes. Cadmium has toxic effects on organisms, populationas and communities [1,2].

Different methods have been employed to remove heavy metals, such as chemical precipitation, evaporation, electrolysis, adsorption and etc. Adsorption is one of the most effective and widely used methods and have been greatly searched recently [3,4].

Hydroxyapatite (HAp) with the structural formula of $Ca_{10}(PO_4)_6(OH)_2$ has the very marked ability to adsorb easily various heavy metal ions [5-9]. However, because of low mechanical reliability, especially in aqueous environments, HAp cannot be used for heavy load-bearing applications [10]. There are some limitations when used under aqueous condition. Thus, Polymer/HAp composite materials have been investigated [11,12].

Cryogels are gel matrices that are formed in moderately frozen solutions of polymeric or monomeric precursors. Cryogels are characteristic of interconnected macropores, allowing unhindered diffusion of solutes and mass transport of particles. Furthermore, the material and the process of manufacture have no environmental harm. Therefore, cryogels are promising carriers for environmental applications and other applications [13,14]. Among those cryogels, PVA cryogel is the most typical one and has been researched for many years. PVA itself is a nontoxic and readily available low-cost polymer [15,16]. Therefore, macroporous PVA cryogel can act as an effective substrate for HAp.

In this work, macroporous HAp/PVA composite cryogel was prepared. The removal of cadmium by HAp/PVA composite cryogel was investigated using the column method in order to test the practical applicability for real industrial wastewaters. The morphology and the effect of operating parameters were studied and the obtained breakthrough curves were analyzed using Adams-Bohart model.

Experimental

Materials

PVA with degree of hydrolysis of 87-89 % and degree of polymerization of 1700 was obtained from Kolon company. HAp was purchased from SAMJO Co., Ltd. Cadmium standard solution (1000 ppm) was purchased from KANTO chemical Co., Inc. Cadmium nitrate tetrahydrate was purchased from KANTO chemical Co., Inc.

Preparation

PVA/HAp blend solutions (10 wt% PVA, PVA/HAp=1:1, 1:1.5 and 1:2) were prepared by mixing two materials in water and heating at 85 ^{o}C for 2 h. HAp was dispersed in water by stirring for 2 h followed by addition of PVA and stirring for another 1 h. Petri dishes containing PVA/HAp solutions were placed into the freeze-drying instrument. The temperature decreased at a rate of about –0.6 ^{o}C/min until –20 ^{o}C was reached. Then –20 ^{o}C was maintained for 24 h. After the freezing process, they were allowed to gradually thaw at rates of 0.025-2.5 ^{o}C/min to approach 20 ^{o}C. Only one freezing-thawing cycle was applied.

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Morphology

The structures of the surface and cross-section of PVA/HAp composite cryogel were analyzed using a Field Emission Scanning Electron microscope (JEOLJSM-6500F).

Column Experiments

The fixed-bed columns were made of glass tube with 2 cm of internal diameter. The bed heights used in the experiments were 9 and 13 cm. The flow rate was controlled at 7 m*l*/min. In a typical experiment cadmium solution with about 50 mg/*l* was pumped at a fixed flow rate to the column filled with PVA/HAp composite cryogel of known bed height. The feed and effluent cadmium concentrations were measured by Atomic Absorption Flame Emission Spectrophotometer (AA-6701F).

Results and Discussion

Morphology

Figure 1(a) demonstrated that PVA cryogel was a porous material with high porosity and good interconnectivity. The pore size varied from 0.1 μm to several μm. It could be seen that HAp (Figure 1(b)) was well dispersed and immobilized in inner macroporous PVA cryogel (Figure 1(c)). However, when HAp amount increased, pore channels became stuffed with HAp agglomerates (Figure 1(d)).

Column Data Analysis

As the feed cadmium solution passes through the column, the adsorption zone (where the bulk of adsorption occurs) moves out of the column and the concentration of effluent increases with time. The breakthrough curve is used to investigate cadmium removal by PVA/HAp composite cryogel in the fixed-bed column, expressed in terms of the ratio of effluent cadmium concentration (C_t) to feed cadmium concentration (C_0) versus time (t). The area under the breakthrough curve can be used to calculate the maximum adsorption capacity (Q). Q can be obtained from the following equation:

$$Q = \frac{0.06 \cdot F}{m_{ads}} \int_{t=0}^{t=te} (C_0 - C_t) \cdot dt \qquad (1)$$

where F is the flow rate (ml/min), C_0 is the feed cadmium concentration and C_t is the effluent cadmium concentration (mg/l), m_{ads} is the mass of PVA/HAp composite cryogel (or HAp) (g), and t_e is the exhaustion time (h). t_e was selected as the time when C_t/C_0 approached unity [17].

Adams-Bohart model was used to describe the breakthrough curve [18]. The model was first based on reaction kinetics for the adsorption of chlorine on charcoal and it assumes that equilibrium is not instantaneous; therefore, the rate of the

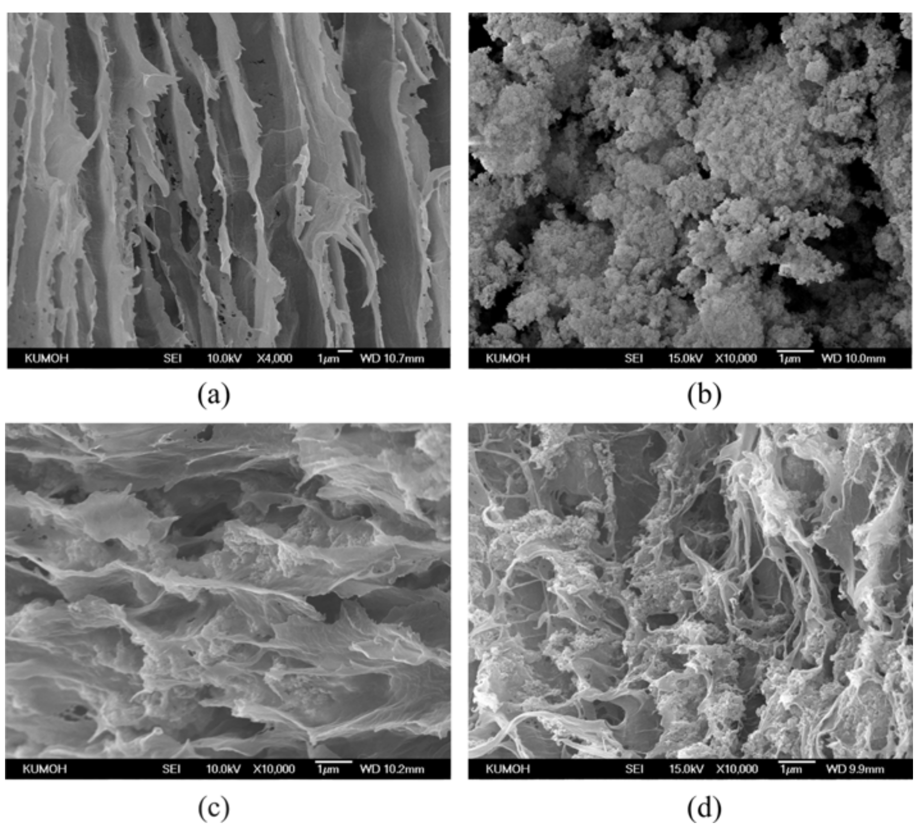

Figure 1. SEM micrograph of PVA cryogel, HAp powder and PVA/HAp composite cryogel; (a) PVA cryogel, (b) HAp powder, (c) PVA/HAp cryogel (1:1), and (d) PVA/HAp cryogel (1:1.5).

sorption is proportional to the fraction of sorption capacity which still remains on the sorbent. The equation is given by:

$$\frac{C_t}{C_0} = \frac{1}{1+\exp[(N_0kH/v)-kC_0t]} \quad (2)$$

where N_0 is the adsorption capacity of the bed (mg/*l*), k is the rate constant (*l*/mg h), H is the bed height (cm) and v is the linear flow rate (cm/h) obtained by dividing the flow rate by the column section area. Equation (2) could describe the sigmoid shape of the breakthrough curve well.

In the range of low ratios of C_t/C_0, considering that C_t/C_0 is much lower than unity, equation (2) can be rearranged into:

$$\ln\frac{C_t}{C_0} = kC_0t - N_0kH/v \quad (3)$$

A straight line can be attained by plotting $\ln(C_t/C_0)$ against t, giving the values of k and N_0 [19,20].

Effect of Bed Height

The breakthrough curves at different bed heights were displayed in Figure 2. It could be found that the breakthrough curve became less steeper as the bed height increased, which could be ascribed to broadened mass transfer zone. The exhaustion time (Table 1) was observed not to change. In addition, the maximum adsorption capacity (Q) (Table 1) decreased slightly. Conclusively, at the flow rate of 7 m*l*/min, bed height did not exert a large influence on maximum adsorption capacity and exhaustion time.

Effect of HAp Amount

Figure 3 illustrated breakthrough curves at different amounts of HAp. The curves demonstrated less sharper change in trend when more HAp was added. The maximum adsorption capacity (Table 1) decreased with HAp amount increasing. No obvious change of exhaustion time was found. Although the number of adsorption sites increased due to growing amount of HAp, the possibilities of attainment of adsorption sites did not increase accordingly due to more difficult diffusion of Cd^{2+} among HAp agglomerates and particles, which has been shown in SEM images. The sorption amount can be improved by better dispersion of HAp and decreasing HAp particle size.

The Adams-Bohart model (equation (3)) was adopted to correlate the experimental data in the initial part of the breakthrough curves (C_t/C_0<0.05) at different HAp amounts. The experimental and theoretical results were exhibited in Figure 4. The model parameters were listed in Table 2. The high correlation coefficients indicated that the experimental data fit Adams-Bohart model well. The kinetic rate constant (k) presented a increasing dependency on HAp amount, which implied that increasing adsorption sites could improve

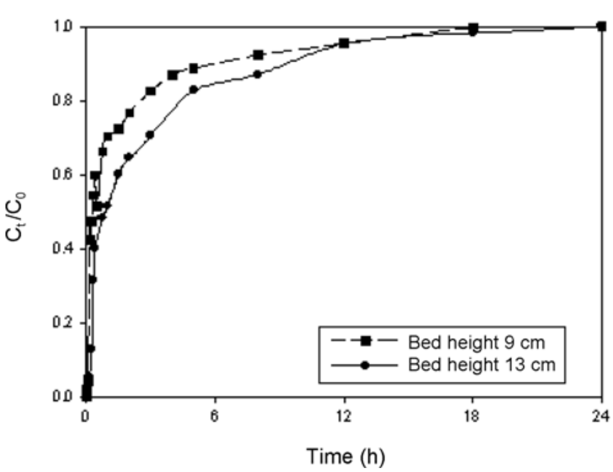

Figure 2. Breakthrough curves at different bed heights.

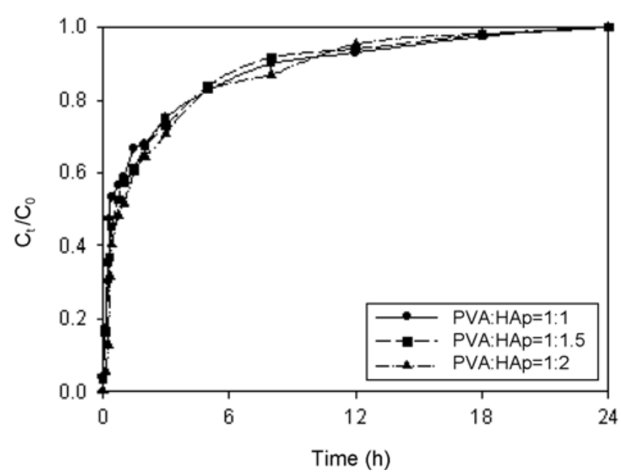

Figure 3. Breakthrough curves at different HAp amounts.

Table 1. Column data and parameters at different bed heights and HAp amounts

PVA/HAp ratio	Bed height (cm)	Flow rate (ml/h)	m_{ads} (cryogel) (g)	m_{ads} (HAp) (g)	Q (mg/g cryogel)	Q (mg/g HAp)	t_e (h)
1:1	9	7	11	5.5	7.148	14.297	24
1:1.5	9	7	14	8.4	8.392	13.967	24
1:2	9	7	14	9.33	5.307	7.961	24
1:1	13	7	7.5	3.75	6.815	13.64	24
1:1.5	13	7	7.5	4.5	5.033	8.388	24
1:2	13	7	7.5	5	4.826	7.238	24

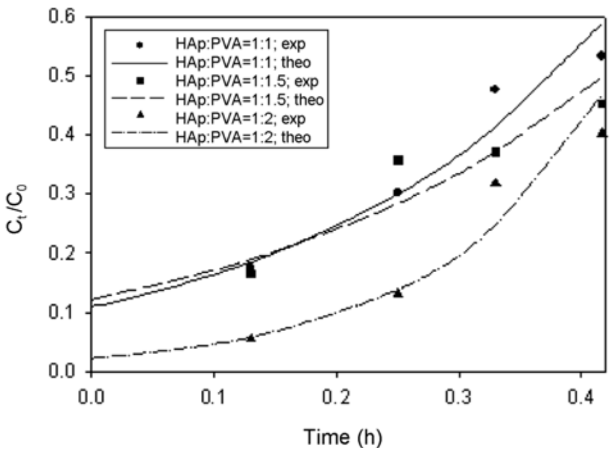

Figure 4. Comparison of the experimental and model fit breakthrough curves at different HAp amounts.

Table 2. The calculated constants of Adams-Bohart model at different HAp amounts

PVA/HAp ratio	Bed height (cm)	Flow rate (m*l*/h)	*K* (*l*/mg h)	N_0 (mg/*l*)	R^2
1:1	13	7	0.062	370.5	0.959
1:1.5	13	7	0.076	305.9	0.872
1:2	13	7	0.132	295.6	0.964

the removal efficiency of cadmium and the overall system kinetics could be affected by HAp amount. The decreasing adsorption capacity of the cryogel (N_0) at higher HAp amount should be ascribed to certain agglomeration of HAp in PVA cryogel.

Conclusion

Macroporous PVA/HAp composite cryogel was investigated for the removal of cadmium in a fixed-bed column. HAp was well dispersed and immobilized in inner macroporous PVA cryogel. Larger and more HAp agglomerates were found at higher amount of HAp. Bed height was not an important factor for maximum adsorption capacity and exhaustion time at the flow rate of 7 m*l*/min. The experimental data fit to Adams-Bohart model well in the initial part of breakthrough curves. The kinetic rate constant and adsorption capacity depended on HAp amount in PVA cryogel.

Acknowledgement

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE).

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