

Comparison of porous poly (vinyl alcohol)/hydroxyapatite composite cryogels and cryogels immobilized on poly (vinyl alcohol) and polyurethane foams for removal of cadmium

Xiao Wang^a, Byung Gil Min^{b,*}

^a School of Textile and Light Industry, Dalian Polytechnic University, Dalian 116034, China

^b School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Gumi 730-701, Republic of Korea

Received 14 August 2007; received in revised form 10 December 2007; accepted 10 December 2007

Available online 23 December 2007

Abstract

Three novel adsorbents of hydroxyapatite/poly (vinyl alcohol) (HAp/PVA) cryogel, HAp/PVA cryogel immobilized on PVA foam and HAp/PVA cryogel immobilized on polyurethane (PU) foam have been investigated to compare the morphology and sorption performances for removal of cadmium. The adsorption kinetics was interpreted by double-exponential model, pseudo-first-order model and pseudo-second-order models. The equilibrium time was found to be 36, 24, and 12 h for cryogel, cryogel immobilized on PVA foam and PU foam, respectively. The adsorption was found to follow Langmuir isotherm model and the maximum sorption capacity was estimated to be 53.3, 53.1 and 47.7 mg g⁻¹ for cryogel, cryogel immobilized on PVA foam and PU foam. The effects of HAp/PVA ratio and drying method on cadmium sorption were also studied. The difference of adsorption kinetics model and equilibrium time among the three adsorbents was suggested to be ascribed to different pore size. Oven-dried HAp/PVA cryogel immobilized on PU foam was preferable due to short equilibrium time and good sorption ability.

© 2008 Published by Elsevier B.V.

Keywords: Adsorption kinetics; Langmuir isotherm; Gel; Foam; Heavy metals

1. Introduction

Hydroxyapatite (HAp) with the structural formula of Ca₁₀(PO₄)₆(OH)₂, is the major inorganic component of human bones and teeth [1,2]. Although HAp has long been researched as biomaterials such as important bone substitute materials and artificial implant, HAp has the very marked ability to adsorb easily various ions, organic molecules and polymers [3]. Because of the high stability and flexibility of the apatitic structure, many cationic and anionic substitutions are possible [4]. HAp has shown a certain ability to retain Pb, Cd, Zn, U, As, Sb and V [5,6]. The interaction of Cd²⁺, Zn²⁺, Ni²⁺, Ba²⁺, Mg²⁺ with HAp has been studied [4,7]. The mechanisms are suggested to be ion exchange and complexation. Ca²⁺ can be substituted by monovalent, divalent and trivalent cations. OH⁻ and PO₄³⁻ can be replaced by some anions and can provide surface complexation as well [7]. Furthermore, HAp is abundant in nature,

available easily, low in cost and have minimal environmental impact for restoration or remediation of natural resources [6]. Therefore, HAp has been applied to the research related to the removal of heavy metals. However, because of low mechanical reliability, especially in aqueous environments, HAp cannot be used for heavy load-bearing applications [8]. The existence of powder also limits the applications under aqueous condition. Thus, new materials comprising organic and inorganic compounds have been investigated due to their improved mechanical, thermal, optical, or chemical properties. In our last research, HAp/PVA composite cryogel, characteristic of macroporous structure, clean physical manufacturing process, environment-friendly material, has been studied and maximum sorption capacity of 53.3 mg g⁻¹ was obtained [9]. Nevertheless, the time to reach sorption equilibrium was found to be 36 h. The long equilibrium time was ascribed to small size of macropores varying from 0.1 μm to several micrometers. Therefore, large macroporous matrix for HAp is considered to improve sorption efficiency in this work.

Polyurethane (PU) and poly(vinyl alcohol) (PVA) foams have become attractive materials for preconcentration, extraction and

* Corresponding author. Tel.: +82 54 478 7711; fax: +82 54 478 7710.

E-mail addresses: wangxiao@dlpu.edu.cn (X. Wang), bgmin@kumoh.ac.kr (B.G. Min).

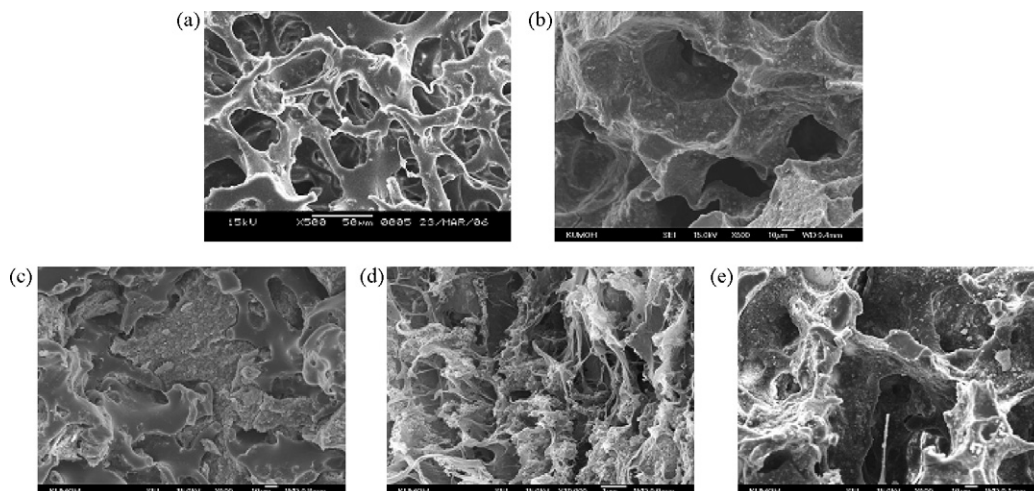


Fig. 1. SEM photographs of (a) porous PVA foam; (b) oven-dried HAp/PVA cryogel immobilized on PVA foam; (c) freeze-dried HAp/PVA cryogel immobilized on PVA foam; (d) freeze-dried HAp/PVA cryogel located on PVA foam; (e) coated PVA foam with HAp/PVA solution.

separation of a wide variety of inorganic and organic substances in different media because of low cost, high available surface area, high macroporosity, cellular structure and stability in acidic or basic media. Unloaded and loaded PU and PVA foams immobilized by functional species have been successfully applied to the sensitive detection, semiquantitative determination, selective collection, preconcentration and recovery of metal ions [10–15]. Of great interest to wastewater treatment is the potential of immobilizing functional reagents or microorganisms onto foams to remove heavy metals or degrade hydrocarbons and toxic wastes.

HAp can be immobilized in foams by coating with the help of PVA solution, but HAp particle is unstable and easy to release from foams. A new approach is suggested to immobilize HAp by forming HAp/PVA cryogel on PU and PVA foams. When HAp is anchored in foams through PVA cryogel, the entrapment of HAp in cryogel can make HAp difficult to release. Moreover, the intrinsic porous structure of foams remained, which can improve

sorption efficiency. In this study, the preparation, morphology and Cd^{2+} sorption abilities of HAp/PVA cryogel immobilized on PVA and PU foams were introduced. The sorption isotherm and kinetics were compared among cryogel, cryogel immobilized on PVA foam and cryogel immobilized on PU foam. The effects of HAp/PVA ratio and drying method were also studied.

2. Materials and methods

2.1. Materials

PVA with degree of hydrolysis of 99.5% and degree of polymerization of 1700 was obtained from Kolon company. HAp was purchased from SAMJO Co., Ltd. Cadmium nitrate tetrahydrate was purchased from KANTO chemical Co., Inc. PVA and PU foams were commercial products. The characteristics of porous foams were presented in SEM images (Figs. 1 and 2(a)) and Table 1.

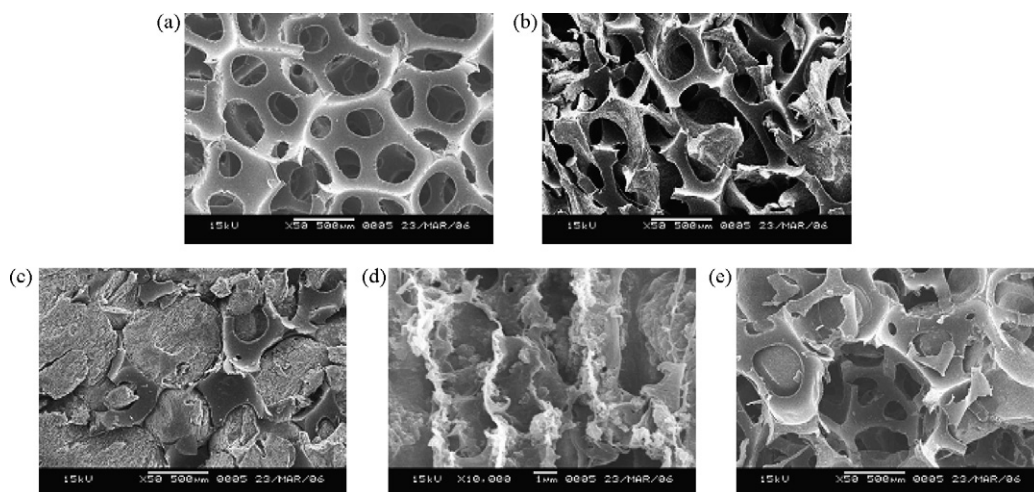


Fig. 2. SEM photographs of (a) porous PU foam; (b) oven-dried HAp/PVA cryogel immobilized on PU foam; (c) freeze-dried HAp/PVA cryogel immobilized on PU foam; (d) freeze-dried HAp/PVA cryogel located on PU foam; (e) coated PU foam with HAp/PVA solution.

Table 1

Characteristics, kinetic models, isotherm constants and correlation coefficients for Cd²⁺ sorption on HAp/PVA cryogel, cryogel immobilized on PVA and PU foams

Adsorbents	Material for Cd ²⁺ adsorption	Pore size (μm)	Sorption kinetic model	Equilibrium time (h)	Cd ²⁺ sorption capacity (mg g ⁻¹)	Langmuir constant (L mg ⁻¹)	Coefficient
HAp/PVA cryogel	HAp	~10	Double-exponential	36	53.3	0.091	0.991
Gel on PVA foam	HAp	25–100	Double-exponential	24	53.1	0.048	0.989
Gel on PU foam	HAp	100–200	Pseudo-first and second order	12	47.7	0.114	0.998

2.2. Preparation process

HAp/PVA blend solution (10 wt% PVA; HAp/PVA = 1) was prepared by mixing two materials in water and heating at 85 °C for 2 h. PU and PVA foams were immersed into the pre-made HAp/PVA blend solution. Following that, PU and PVA foams fully impregnated with HAp/PVA blend solution were frozen and thawed according to the process mentioned in HAp/PVA cryogel manuscript at rates of -0.6 and 0.025 °C min⁻¹. Thus, the HAp/PVA cryogel were immobilized on PU and PVA foams. Finally, the PU and PVA foams were freeze-dried and oven-dried, respectively. The coated sample was also made by oven-drying of PU foam impregnated with HAp/PVA blend solution without cryogelation.

2.3. Morphology observation

The HAp/PVA cryogels and cryogels immobilized on foams were analyzed using a field emission scanning electron microscope (JEOL JSM-6500F). Freeze-drying was applied to dry the specimen to remain the original structure. The surface and cross-section were observed after cutting. The distribution of HAp particles in cryogels and the porous structure of cryogels were investigated.

2.4. Sorption experiments

Batch sorption experiments were performed at a constant temperature of 20 °C on a shaker at 150 rpm using 100 ml conical flasks. Sorption kinetics data were obtained by contacting HAp/PVA cryogels and cryogels immobilized on foams with 50 ml cadmium solution at a concentration of about 100 mg L⁻¹ at the interval from 5 min to 36 h. The isotherm experiments were carried out in 50 ml cadmium solution at varying concentrations from about 10 to 400 mg L⁻¹. After sorption, the solutions were filtered by filter paper. All experiments were run in triplicate. The initial and final concentrations were measured by an atomic absorption flame emission spectrophotometer (AA-6701F).

3. Results and discussion

3.1. Morphology of cryogels and cryogels immobilized on foams

Figs. 1 and 2(a) showed the SEM photographs of untreated foams with big interconnected macropores. PVA foam possessed smaller pore sizes than PU foam. The porous structure in

Figs. 1 and 2(b) of oven-dried HAp/PVA cryogel immobilized on foams presented that about half of the big intrinsic interconnected macropores of foams remained after oven-drying. The PU pores were found to be entangled with HAp/PVA cryogel to get a stable structure, whereas cryogel adhered to the wall of PVA foam. Figs. 1 and 2(c) displayed the SEM images of freeze-dried HAp/PVA cryogel immobilized on PU foam. Freeze-dried foams were stuffed with HAp/PVA cryogel and the intrinsic big macropores were full of HAp/PVA cryogel. Nevertheless, the HAp/PVA cryogel exhibited small macroporous structure (Figs. 1 and 2(d)), as discussed in the manuscript of HAp/PVA cryogel [9]. HAp was well distributed in pore channels of PVA cryogel. In addition, the macroporous structure was not affected largely by coating PU foam with HAp/PVA solution (Figs. 1 and 2(e)). HAp/PVA solid was easy to fall off from PU foam due to large pores, while it clung to the wall of PVA foam relatively strongly in consequence of smaller pores.

3.2. Sorption kinetics

Three kinetics models were involved to evaluate the efficiency of HAp/PVA cryogel immobilized on foams on Cd²⁺ sorption and understand the sorption behavior of HAp/PVA cryogel immobilized on foams towards Cd²⁺, which are pseudo-first-order, pseudo-second-order [16] and double-exponential models [17] with the equations:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

$$q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \quad (2)$$

$$q_t = q_e - \frac{D_1}{m_{\text{ads}}} \exp(-K_{D1} t) - \frac{D_2}{m_{\text{ads}}} \exp(-K_{D2} t) \quad (3)$$

where q_e is the sorption capacity at equilibrium (mg g⁻¹), q_t is sorbed amount at any time t (mg g⁻¹), k_1 is the first-order rate constant (h⁻¹), k_2 is the second-order rate constant (g mg⁻¹ h⁻¹), D_1 and D_2 are sorption rate constants of the rapid and the slow steps (mg L⁻¹), K_{D1} and K_{D2} are constants controlling the mechanism (h⁻¹), and m_{ads} is the adsorbent amount in the solution (g L⁻¹).

Figs. 3 and 4 illustrated the sorption kinetics curves of Cd²⁺ on HAp/PVA cryogel immobilized on foams and the experimental data were fit by these models. It was found in the case of PVA foam that the double-exponential model ($R^2 = 0.996$) demonstrated best agreement compared with the pseudo-first-order ($R^2 = 0.871$) and pseudo-second-order models ($R^2 = 0.959$). Formerly, the pristine HAp/PVA cryogel was

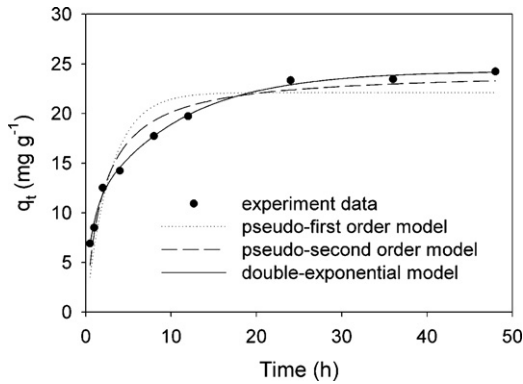


Fig. 3. Sorption kinetics of Cd^{2+} on HAp/PVA cryogel immobilized on oven-dried PVA foam by pseudo-first-order, pseudo-second-order and double-exponential models.

found to be well described by double-exponential model [9]. The sorption data of PVA foam fit the double-exponential model best, but pseudo-second-order model also represented high correlation, which was disagreeable with gel. In addition, the coefficients of pseudo-first-order ($R^2 = 0.974$) and pseudo-second-order models ($R^2 = 0.983$) suggested that both models were suitable for sorption kinetics of PU foam. Furthermore, to take into account the equilibrium time of sorption, the duration was examined to be 36, 24 and 12 h for cryogel, PVA foam and PU foam, respectively. The reason for the discrepancies of sorption model and equilibrium time among the three adsorbents may lie in obviously different pore size (Table 1). It was elicited that larger macropores caused faster one-stage sorption and quicker sorption equilibrium, whereas longer time and two stages were undertaken to approach sorption equilibrium as to smaller macropores.

The double-exponential model indicated a diffusion-controlled and a two-step mechanism. Two phases were included in this kinetics model: a rapid sorption stage and subsequently much slower stage before the equilibrium was established. A first rapid sorption step was realized involving external surface diffusion of Cd^{2+} and diffusion of Cd^{2+} into easily attainable pores. Consequently, the slow step was controlled by the further pore and internal diffusion and then the sorption reaches equilibrium. Dissimilarly, pseudo-first-order and pseudo-second-order mod-

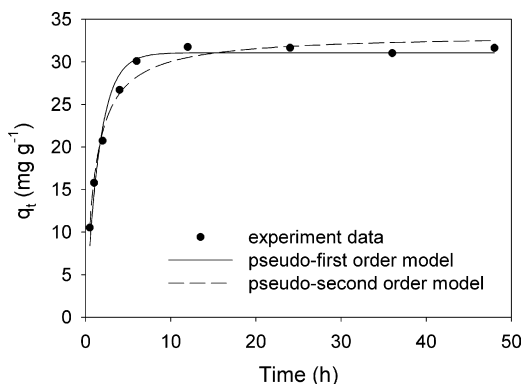


Fig. 4. Sorption kinetics of Cd^{2+} on HAp/PVA cryogel immobilized on oven-dried PU foam by pseudo-first-order and pseudo-second-order models.

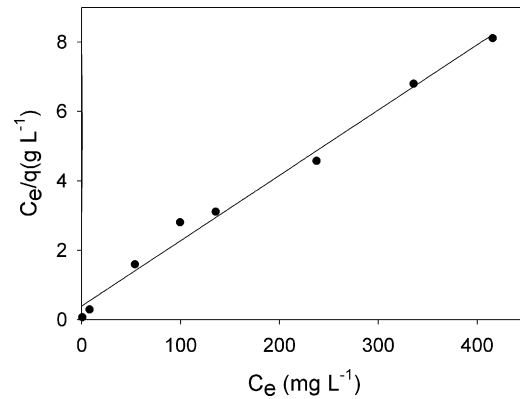


Fig. 5. Langmuir isotherm of Cd^{2+} adsorbed on oven-dried HAp/PVA cryogel immobilized on PVA foam.

els pointed out one-step mechanism. Only one fast sorption stage proceeded in terms of the two models before the equilibrium was obtained. Due to large macropores, Cd^{2+} was effortless to contact large surface area promptly and only one diffusion step was necessitated. The equilibrium was reached after one-step fast sorption.

3.3. Sorption isotherm

The experimental isotherm data of Cd^{2+} sorption onto HAp/PVA cryogel immobilized on PVA and PU foams were evaluated by extensively used Langmuir and Freundlich models [18–20]. The Langmuir isotherm was originally defined to account for the adsorption of gases on metal surfaces, and was derived by Langmuir on kinetic grounds. It has proved to be reasonably well suited to describe the sorption of a solute from a liquid solution. The Langmuir sorption model can be expressed as:

$$q = \frac{Q K_L C_e}{1 + K_L C_e} \quad (4)$$

where q is the sorption amount of metal ion by HAp in cryogel (mg g^{-1}), Q is maximum sorption capacity (mg g^{-1}), C_e is the final concentration of metal in solution when reaching equilibrium (mg L^{-1}) and K_L is the Langmuir constant (L mg^{-1}).

By rearranging the above equation to the linearised form:

$$\frac{C_e}{q} = \frac{1}{Q K_L} + \frac{C_e}{Q} \quad (5)$$

Q and K_L can be determined by the slope ($1/Q$) and intercept ($1/QK_L$) from the line of C_e/q versus C_e .

The classical work of Freundlich on sorption by animal charcoal led to the purely empirical conclusion that the sorption isotherm could be defined as:

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_F and n are Freundlich constants indicating sorption capacity and intensity, respectively. They can be obtained from linear plot of $\log q$ against $\log C_e$.

Figs. 5 and 6 depicted the linear fit curves of Langmuir isotherm. The values of isotherm constants were also listed

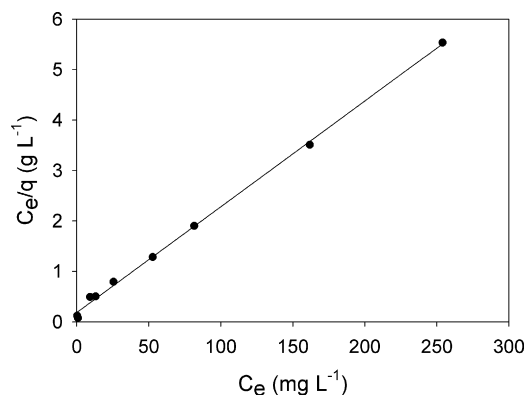


Fig. 6. Langmuir isotherm of Cd^{2+} adsorbed on oven-dried HAp/PVA cryogel immobilized on PU foam.

in Table 1. It was clearly seen that the experimental isotherm data of the three adsorbents fit well with the Langmuir model, whereas the Freundlich was comparatively less suitable. The maximum sorption capacity (Q) was estimated to be 53.3, 53.1 and 47.7 $mg\ g^{-1}$ for cryogel, PVA foam and PU foam, respectively. It was suggested from this similar sorption result that strong capacity could be obtained for all the three adsorbents. Based on the analysis of both sorption kinetics and isotherm, HAp/PVA cryogel immobilized on PU foam was preferred as a consequence of short equilibrium time and good sorption ability.

3.4. Effect of HAp/PVA ratio on Cd^{2+} sorption

Figs. 7 and 8 illustrated Cd^{2+} sorption of HAp/PVA cryogel immobilized on PVA and PU foams versus HAp/PVA ratio. More amount of HAp in foams led to increment of Cd^{2+} removal undoubtedly if the sorption was evaluated per foam. It was not expected that Cd^{2+} sorption per gram of HAp decreased with increasing HAp/PVA ratio, similar with cryogel. The reason should be in conformity with that for cryogel [9]. The HAp particles were not only distributed on the surface of pores, but also entrapped into the internal region of cryogel on the foams. When the HAp/PVA ratio increased, the attainable HAp amount did not increase accordingly. Moreover, the more difficult Cd^{2+} diffusion among HAp agglomerates due to large amount of HAp also resulted in inverse effect. The sorption amount per HAp can

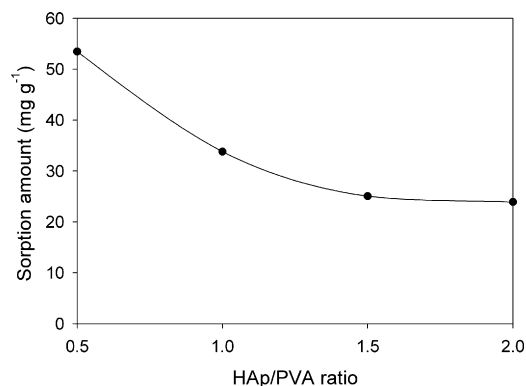


Fig. 7. Effect of HAp/PVA ratio on sorption amount of Cd^{2+} by oven-dried HAp/PVA cryogel immobilized on PVA foam.

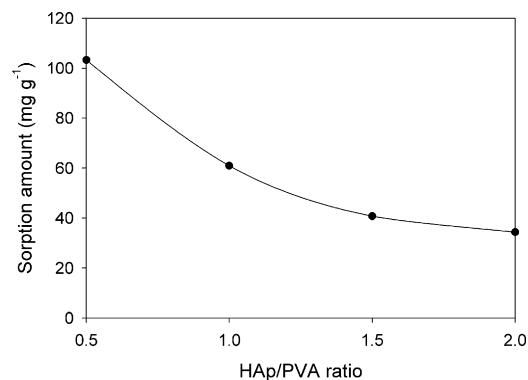


Fig. 8. Effect of HAp/PVA ratio on sorption amount of Cd^{2+} by oven-dried HAp/PVA cryogel immobilized on PU foam.

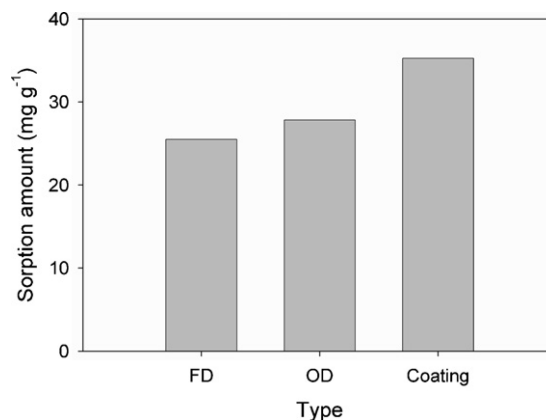


Fig. 9. Effect of drying methods on sorption amount of Cd^{2+} by HAp/PVA cryogel immobilized on PVA foam.

be improved by better dispersion of HAp and decreasing HAp particle size.

3.5. Effect of drying method on Cd^{2+} sorption

Figs. 9 and 10 demonstrate the comparison of Cd^{2+} sorption by oven-dried and freeze-dried HAp/PVA cryogel immobilized on PVA and PU foams and foams coated by HAp/PVA solution. The sorption ability seemed to be in sequence of

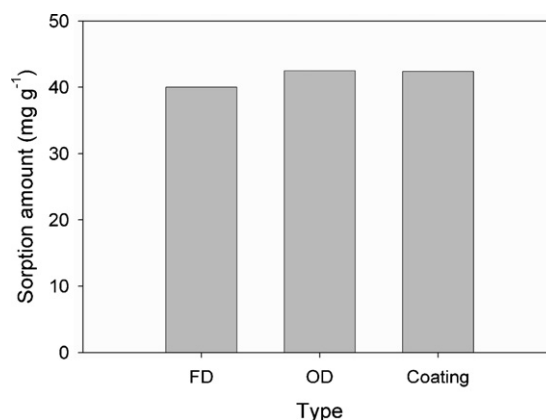


Fig. 10. Effect of drying methods on sorption amount of Cd^{2+} by HAp/PVA cryogel immobilized on PU foam.

coated, oven-dried and freeze-dried samples. Although coated foam presented better sorption amount, the unstably anchored HAp/PVA solids hindered the application. Oven-dried foam was found to be slightly better than freeze-dried specimen. Moreover, oven-drying method is more energy-saving compared with freeze-drying method.

4. Conclusions

In this study, the morphology and sorption performances of HAp/PVA cryogel, cryogel immobilized on PVA foam and PU foam were compared. The macropores of PU foams were found to be entangled with HAp/PVA cryogel, whereas cryogel adhered to the wall of PVA foam after oven-drying. Freeze-dried foams were stuffed with HAp/PVA cryogel and the intrinsic big macropores were full of HAp/PVA cryogel with small macropores. The adsorption data of cryogel immobilized on PVA foam fit the double-exponential model best, but pseudo-second-order model also represented high correlation, which was disagreeable with cryogel. Both pseudo-first-order and second-order models were suitable for sorption kinetics of cryogel immobilized on PU foam. In addition, the equilibrium time was examined to be 36, 24 and 12 h for cryogel, cryogel immobilized on PVA foam and PU foam, respectively. The difference of adsorption kinetics model and equilibrium time among the three adsorbents was suggested to be ascribed to different pore size. The adsorption was found to follow Langmuir isotherm model and the maximum sorption capacity was estimated to be 53.3, 53.1 and 47.7 mg g⁻¹ for cryogel, cryogel immobilized on PVA foam and PU foam. Higher ratio of HAp/PVA led to less amount of Cd²⁺, owing to larger HAp agglomerates and more difficult Cd²⁺ diffusion. Oven-drying method was better than freeze-drying. Therefore, oven-dried HAp/PVA cryogel immobilized on PU foam was preferable due to short equilibrium time and good sorption ability.

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).

References

- [1] M.I. Kay, R.A. Young, A.S. Posner, Crystal structure of hydroxyapatite, *Nature* 204 (1964) 1050–1052.
- [2] G.K. Lim, J. Wang, S.C. Ng, C.H. Chew, L.M. Gan, Processing of hydroxyapatite via microemulsion and emulsion routes, *Biomaterials* 18 (1997) 1433–1439.
- [3] M. Okazaki, Y. Yoshida, S. Yamaguchi, M. Kaneno, J.C. Elliott, Affinity binding phenomena of DNA onto apatite crystals, *Biomaterials* 22 (2001) 2459–2464.
- [4] K.J. Zhu, K. Yanagisawa, R. Shimanouchi, A. Onda, K. Kajiyoshi, Preferential occupancy of metal ions in the hydroxyapatite solid solutions synthesized by hydrothermal method, *J. Eur. Ceram. Soc.* 36 (2005) 509–513.
- [5] E.D. Vega, J.C. Pedregosa, G.E. Narda, P.J. Morando, Removal of oxovanadium(IV) from aqueous solutions by using commercial crystalline calcium hydroxyapatite, *Water Res.* 37 (2003) 1776–1782.
- [6] J.A. Gómez del Río, P.J. Morando, D.S. Cicerone, Natural materials for remediation of industrial effluents: comparative study of the retention of Cd, Zn and Co by calcite and hydroxyapatite, *J. Environ. Manage.* 71 (2004) 169–177.
- [7] C.C. Ribeiro, I. Gibson, M.A. Barbosa, The uptake of titanium ions by hydroxyapatite particles-structural changes and possible mechanisms, *Biomaterials* 27 (2006) 1749–1761.
- [8] R.E. Riman, W.L. Suchanek, K. Byrappa, C.W. Chen, P. Shuk, C.S. Oakes, Solution synthesis of hydroxyapatite designer particulates, *Solid State Ionics* 151 (2002) 393–402.
- [9] X. Wang, B.G. Min, Cadmium sorption properties of poly (vinyl alcohol)/hydroxyapatite cryogels: I. Kinetic and isotherm studies, *J. Sol-Gel Sci. Technol.* 43 (2007) 99–104.
- [10] M.F. El-shahat, E.A. Moawed, M.A.A. Zaid, Preconcentration and separation of iron, zinc, cadmium and mercury, from waste water using Nile blue a grafted polyurethane foam, *Talanta* 59 (2003) 851–866.
- [11] E. Quek, Y.P. Ting, H.M. Tan, *Rhodococcus* sp. F92 immobilized on polyurethane foam shows ability to degrade various petroleum products, *Bioresour. Technol.* 97 (2006) 32–38.
- [12] P. Fong, A. Chow, Extraction mechanism of monovalent ion-pairs by polyurethane foams, *Talanta* 39 (1992) 825–836.
- [13] A.B. Farag, M.S. El-Shahawi, Removal of organic pollutants from aqueous solution: V. Comparative study of the extraction, recovery and chromatographic separation of some organic insecticides using unloaded polyurethane foam columns, *J. Chromatogr.* 552 (1991) 371–379.
- [14] M.S. El-Shahawi, M.A. El-sonbati, Retention profile, kinetics and sequential determination of selenium(IV) and (VI) employing 4,4'-dichlorodithizone immobilized-polyurethane foams, *Talanta* 67 (2005) 806–815.
- [15] S. Palagyi, T. Braun, Separation and preconcentration of trace elements and inorganic species on solid polyurethane foam sorbents, *Analyst* 117 (1992) 1537–1541.
- [16] Y.S. Ho, C.C. Chiang, Sorption studies of acid dye by mixed sorbents, *Adsorption* 7 (2001) 139–141.
- [17] N. Chiron, R. Guilet, E. Deydier, Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherms and kinetic models, *Water Res.* 37 (2003) 3079–3086.
- [18] S. Al-Asheh, F. Banat, R. Al-Omari, Z. Duvnjak, Predictions of binary sorption. isotherms for the sorption of heavy metals by pine bark using single isotherm data, *Chemosphere* 41 (2000) 659–665.
- [19] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process Biochem.* 37 (2002) 1421–1430.
- [20] E.D. van Hullebusch, A. Peerbolte, M.H. Zandvoort, P.N.L. Lens, Sorption of cobalt and nickel on anaerobic granular sludges: isotherms and sequential extraction, *Chemosphere* 58 (2005) 493–505.