ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim., **2010**, *55*(8), 443-447

COLUMN STUDY OF CADMIUM ADSORPTION ONTO POLYACRYLONITRILE/HYDROXYAPATITE COMPOSITE BEAD

Xiao WANG,[a] Byung Gil MIN,[b]* Won-Seok LYOO,[c]
Viorel CHIHAIA,[d] Mariuca GARTNER,[d] Tionica F. STOICA,[e]
Jae Young BAE [f] and Soong-Hyuck SUH [f]

[a] School of Textile and Light Industry, Dalian Polytechnic University, Dalian 116034, China
[b] Department of Nano-Bio Textile Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea
[c] School of Textiles, Yeungnam University, Gyeongsan 712-749, Korea
[d] Institute of Physical Chemistry, "I.G. Murgulescu" Roumanian Academy, Splaiul Independentei 202, Bucharest 060021, Roumania
[e] National Institute of Materials Physics, Atomistilor str. 105 bis, P.O.B Mg. 7, Bucharest-Magurele, 077125, Roumania
[f] Department of Chemistry and Chemical Engineering, Keimyung University, Daegu 704-701, Korea

Received September 25, 2008

Macroporous polyacrylonitrile/hydroxyapatite (PAN/HAp) composite bead was studied for cadmium removal in a fixed-bed column. The morphology of PAN/HAp composite bead was measured. The adsorption performance of PAN/HAp composite bead in the column was examined by varying bed height and HAp amount in PAN bead. The maximum adsorption capacity and the exhaustion time were determined from the breakthrough curves. Experimental data was described using the Adams-Bohart model. Bed height did not exert large influence on the maximum adsorption capacity and the exhaustion time. The kinetic rate constant and the adsorption capacity of the bed were found to be affected by the total HAp amount.

INTRODUCTION

Environmental pollution due to heavy metals in wastewater has been one of the most concerned problems in the world. Heavy metals are associated with myriad adverse health effects, including allergic reactions, neurotoxicity, nephrotoxicity, and cancer.[1] Humankind are often exposed to heavy metals in various ways; mainly through the intake of metals in polluted water, or through the ingestion of food that contains high levels of heavy metals. Cadmium has not known vital or beneficial effect on organisms, and its accumulation over time in the bodies of mammals can cause serious illness. Cadmium has many commercial applications including electroplating and the manufacture of batteries. Exposure to cadmium can occur in the workplace or from contaminated foodstuffs and can result in emphysema, renal failure, cardiovascular disease, and perhaps cancer.[2,3]

Different methods have been employed to remove heavy metals, such as chemical precipitation, evaporation, electrolysis, adsorption, etc. Adsorption is one of the most effective and widely used methods and has been greatly searched recently.[4] Hydroxyapatite (HAp) with the structural formula of $Ca_{10}(PO_4)_6(OH)_2$ has very marked ability to adsorb various heavy metal ions significantly.[5-9] However, the adsorption properties can be limited due to the existence of powder type.[10] Moreover, polyacrylonitrile (PAN) beads could be fabricated in porous type when dispersing PAN polymer solution into coagulation bath. The porous structure could be realized in several ways such as the thermally induced phase-separation process, the PAN polymer solution mixed with mineral oil coagulated in cool mineral oil, and the polyacrylonitrile/dimethylformamide solution dropped into water.[11-13] Porous PAN bead can act as an effective substrate for HAp.

* Corresponding author: bgmin@kumoh.ac.kr

In this work, macroporous HAp/PAN composite bead was prepared. The removal of cadmium by HAp/PAN composite bead 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

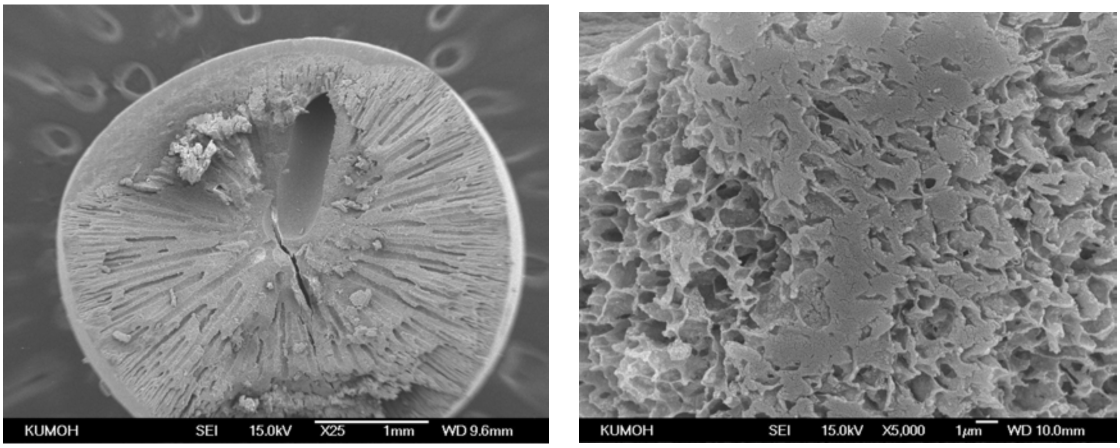
Polyacrylonitrile with degree of copolymer of 88% (ww) was obtained from Tae Kwang Industry Co., Ltd. HAp was purchased from Samjo Co., Ltd. Dimethylformamide (DMF) was supplied by Daejung Chemicals & Metals Co., LTD. Cadmium standard solution (1,000 ppm) was purchased from Kanto chemical Co., Inc. Cadmium nitrate tetrahydrate was purchased from Kanto chemical Co., Inc.

PAN/HAp mixer solution with 15 wt% PAN was prepared by mixing two materials in DMF. HAp was dispersed in DMF by sonication for two hours. The mixtures were stirred at 30-minute intervals for 10 minutes during sonication and then PAN was dissolved in the mixtures at 60 ℃ for two hours. The composite bead was made when PAN/HAp mixer solution was dropped into water that was employed as the coagulation bath.

The fixed-bed columns were made of glass tube with 2 cm of internal diameter. The bed heights used in the experiments were 9, 13.5 and 27 cm, respectively. The flow rate was controlled at 7 ml/min. In the typical experiment cadmium solution with about 50 mg/L was pumped at a fixed flow rate to the column filled with PAN/HAp composite bead of known bed height. The feed and effluent cadmium concentrations were measured by Atomic Absorption Flame Emission Spectrophotometer (AA-6701F).

RESULTS AND DISCUSSION

The structures of the surface and cross-section of PAN/HAp composite bead were analyzed using a Field Emission Scanning Electron microscope (JEOLJSM-6500F) are displayed Fig. 1. As can be seen in this figure, HAp was well dispersed and immobilized inside inner macroporous PAN bead. The bead consisted of channels of 30-100 μm, distributed with the small pores of about 1 μm.



(a) **(b)**

Fig. 1 – SEM micrograph of PAN/HAp composite bead: (a) low magnification; (b) high magnification.

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 increasing time. The breakthrough curve is used to investigate cadmium removal by PAN/HAp composite bead in the fixed-bed column, expressed in terms of the ratio of effluent cadmium concentration to feed cadmium concentration versus time. The area under the breakthrough curve can be used to calculate the maximum adsorption capacity, *Q*, which can be obtained from the following equation:

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

where F is the flow rate, C_0 is the feed cadmium concentration, C_t is the effluent cadmium concentration, m_{ads} is the mass of PAN/HAp composite bead (or, HAp), and t_e is the exhaustion time which was selected as the time when C_t/C_0 approached to unity. [14]

The Adams-Bohart model was used to describe the breakthrough curve. [15] This model was first based on the reaction kinetics for the adsorption of chlorine on charcoal, and it assumes that equilibrium does not occur instantaneously. Under those conditions the rate of the sorption, which is proportional to the fraction of sorption capacity, still remains on the sorbent. The resulting equation is given by:

$$\frac{C_1}{C_0} = \frac{1}{1 + \exp[(N_0 kH / v) - kC_0 t]} \tag{2}$$

where N_0 is the adsorption capacity of the bed, k is the rate constant, H is the bed height and v is the linear flow rate obtained from dividing the flow rate by the column section area. Eq. (2) can describe the sigmoid shape of the breakthrough curve well.

In the range of low ratios of C_t/C_0, particularly when C_t/C_0 is much lower than unity, Eq. (2) can be rearranged into:

$$\ln \frac{C_t}{C_0} = kC_0 t - N_0 kH / v \tag{3}$$

A straight line can be attained by plotting *ln* (C_t/C_0) against t, consequently giving the values of k and N_0.[16, 17]

The breakthrough curves at different bed heights were displayed in Fig. 2. It could be found that the breakthrough curve became less steep as the bed height increased, which could be ascribed to broaden the mass transfer zone. The exhaustion time as in Table 1 was observed to increase until a certain bed height was reached. In addition, the maximum adsorption capacity in Table 1 increases slightly, and then remains constant with the smallest bed height. Conclusively, at the flow rate of 7 ml/min, bed height did not exert large influences on the maximum adsorption capacity and the exhaustion time.

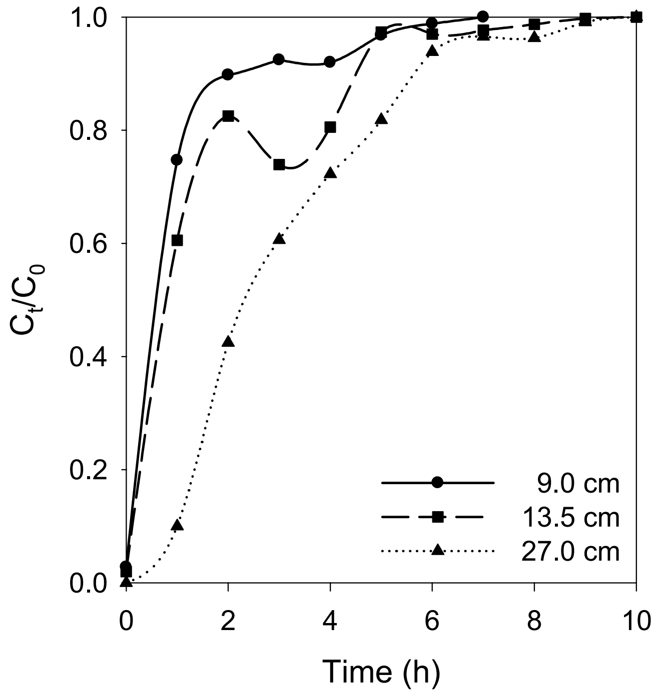


Fig. 2 – Breakthrough curves at different bed heights.

Table 1

Column data and parameters at different bed heights and HAp amounts

HAp [wt%]	H [cm]	F [ml/h]	m_{ads} (bead) [g]	m_{ads} (HAp) [g]	Q [mg/g bead]	Q [mg/g HAp]	t_e [h]
50	9	7	7	3.5	3.892	7.784	7
50	13.5	7	10	5	4.193	8.385	10
50	27	7	20	10	3.918	7.836	10
60	9	7	8.5	5.1	5.070	8.440	15
70	9	7	9.6	6.72	6.120	8.740	18

Fig. 3 illustrated breakthrough curves at different amounts of HAp. The curves demonstrated less sharp change in its shape when more HAp's were added. Moreover, both the maximum adsorption capacity and the exhaustion time (see, Table 1) increased with the total HAp amount increasing. This could be attributed to an increment in the number of adsorption sites due to the growing amount of HAp. At the same residence time, i.e., the time for cadmium solution to fill the column, more HAp's naturally led to an enhancement in the removal ability of cadmium.

The Adams-Bohart model in Eq. (3) was adopted to correlate the experimental data of the initial part of the breakthrough curves (C_t/C_0<0.035) at the different amounts of HAp. The experimental and theoretical results were exhibited in Fig. 4. The model parameters were also listed in Table 2. The high correlation coefficients indicated that the experimental data fit the Adams-Bohart model well. The kinetic rate constant, *k*, illustrated an increasing dependency on HAp amount, which implied that more developed adsorption sites could improve the removal efficiency of cadmium and the overall system kinetics could be affected by the total HAp amount. The decreasing adsorption capacity of the bead, N_0, at higher HAp amounts was observed partly due to a certain agglomeration of HAp in PAN bead.

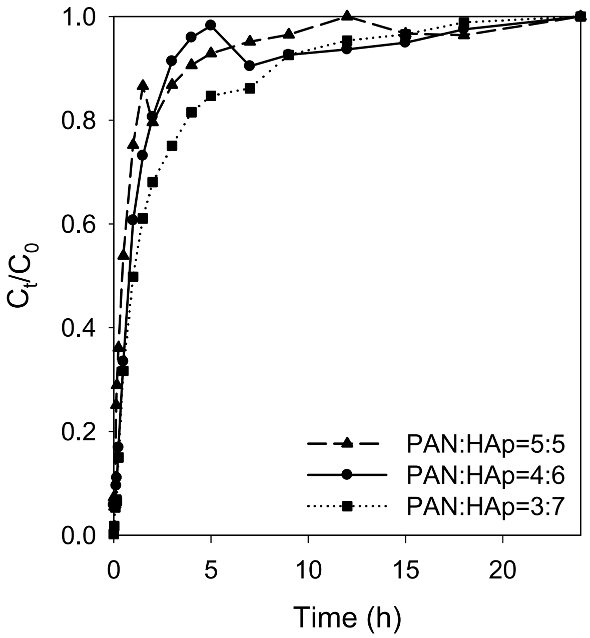


Fig. 3 – Breakthrough curves at different HAp amounts.

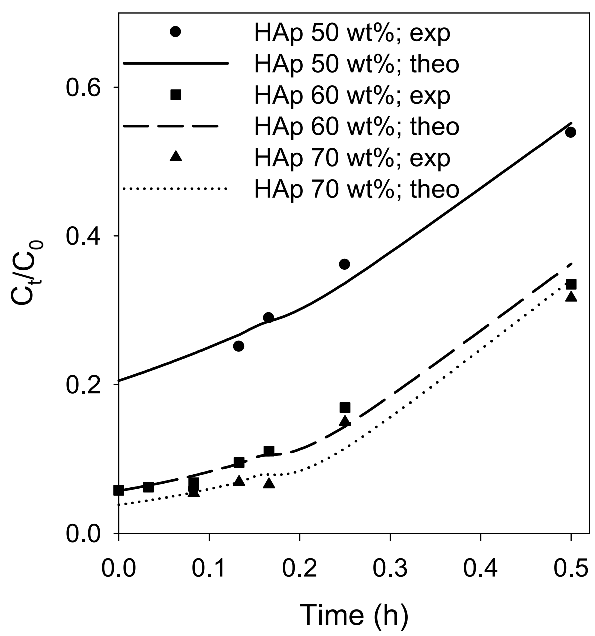


Fig. 4 – Comparison of breakthrough curves between the experimental data and the model fit at different HAp amounts.

Table 2

Calculated constants of the Adams-Bohart model at different HAp amounts

HAp [wt%]	*Bed height* [cm]	*Flow rate* [ml/h]	*k* [L/mg h]	N_0 [mg/L]	R^2
50	9	7	0.037	634.5	0.971
60	9	7	0.074	578.7	0.978
70	9	7	0.085	573.4	0.948

CONCLUSIONS

Macroporous PAN/HAp composite bead was investigated for the removal of cadmium in a fixed-bed column. HAp was well dispersed in pore channels of 30-100 μm in PAN bead. Bed height was not an important factor for the maximum adsorption capacity and the exhaustion time at the flow rate of 7 ml/min. A good agreement for experimental data fitted to the Adams-Bohart model was found in the initial part of breakthrough curves. The kinetic rate constant and the adsorption capacity strongly depended on the total HAp amount in PAN bead.

Acknowledgements: The study was supported by Kumoh Institute of Technology.

REFERENCES

1. R. A. Goyer, “Toxic Effects of Metals”, 5th Edition, McGraw-Hill, New York, 1996.
2. N. Chiron, R. Guilet and E. Deydier, *Water Res*., **2003**, 37, 3079.
3. A. Benhammou, A. Yaacoubi, L. Nibou and B. Tanouti, *J. Colloid Interf. Sci.*, **2005**, 282, 320.
4. L. A. Smith, J. L. Means, A. Chen, B. Alleman, C. C. Chapman, J. S. Tixier, Jr., S. E. Brauning, A. R. Gavaskar and M. D. Royer, “Remedial Options for Metals-contaminated Sites”, CRC Press, New York, 1995.
5. M. Okazaki, Y. Yoshida, S. Yamaguchi, M. Kaneno and J. C. Elliott, *Biomaterials*., **2001**, 22, 2459
6. K. J. Zhu, K. Yanagisawa, R. Shimanouchi, A. Onda and K. Kajiyoshi, *J. Eur. Ceram. Soc*., **2005**, 36, 509.
7. E. D. Vega, J. C. Pedregosa, G. E. Narda and P. J. Morando, *Water Res*., **2003**, 37, 1976.
8. J. A. Gómez del Río, P. J. Morando and D. S. Cicerone, *J. Environ. Manage*., **2004**, 71, 169.
9. C. C. Ribeiro, I. Gibson and M. A. Barbosa, *Biomaterials*, **2006**, 27, 1749.
10. R. E. Riman, W. L. Suchanek, K. Byrappa, C. W. Chen, P. Shuk and C. S. Oakes, *Solid State Ionics*., **2002**, 151, 393.
11. M. Stoy, U.S. Patent No. 4,110,529, **1978**.
12. M. T. Cooke, U.S. Patent No. 5,047,437, **1991**.
13. T. Godgevargova, A. Simeonova and A. Dimov, *J. Appl. Polym, Sci*., **2001**, 79, 283.
14. P. Lodeiro, R. Herrero and M. E. Sastre de Vicente, *J. Hazard. Mater*., **2006**, 177, 244.
15. W. W. Eckenfelder, Jr., “Industrial Water Pollution Control”, McGraw Hill, New York, 1989.
16. J. Goel, K. Kadirvelu, C. Rajagopal and V. K. Garg, *J. Hazard. Mater*., **2005**, 125, 211.
17. E. Malkoc, Y. Nuhoglu and M. Dundar, *J. Hazard. Mater*., **2006**, 138, 142.