13rd International Electronic Conference on Synthetic Organic Chemistry (ECSOC-13), 1-30 November 2009.
http://www.mdpi.org/ecsoc-13/ & http://www.usc.es/congresos/ecsoc/13/

[f002]

Some Derivatives of Cellulose with Diethanolamine and Ethylendiamine

Nguyen Dinh Thanh,* Do Thanh Tuyen

Faculty of Chemistry, Hanoi University of Science, VNU, 19 Le Thanh Tong, Hanoi, Vietnam;
E-mail: ngdthanh@gmail.com; Tel.: +84 04 38261853; Fax: +84 04 8241140.

Abstract: Cellulose from cotton was modified through reaction of sodium carboxymethyl cellulose (NaCMC) with diethanolamine and an epichlorohydrin-ethylendiamine system in molar ratios of 1:1.5:1.5; 1:2:2; 1:3:3 and 1:4:4, respectively. The modification with epichlorohydrin-ethylendiamine was carried out in two steps: in the first step, NaCMC was reacted with epichlorohydrin, and in the second step, oxiran-2-ylmethyl carboxy-methylcellulose reacted with ethylendiamine gave cellulose-*g*-epichlorohydrin/ ethylendiamine. The surfaces of the obtained products have been investigated by SEM images. Their adsorption capability for Pb^{2+}, Cd^{2+} and Mn^{2+} ions (at concentrations of 10,000, 2,000, 1,000, 600, 400 and 100 ppm) have been investigated.

Keywords: Cellulose; Graft; Epichlorohydrin; Ethylendiamine.

Introduction

Ion exchange resins [1] are broadly employed for treatment of process water and wastewater. Commercially available synthetic resins provide a wide selection of ion selectivities and performance characteristics such that most applications can be addressed in a cost effective manner. Because of their relatively high cost and excellent durability, synthetic resins are regenerated repeatedly. However, the capital expenditure requirements and waste volumes associated with resin regeneration may be undesirable in some applications. In other instances, resin fouling or poisoning may be a problem.

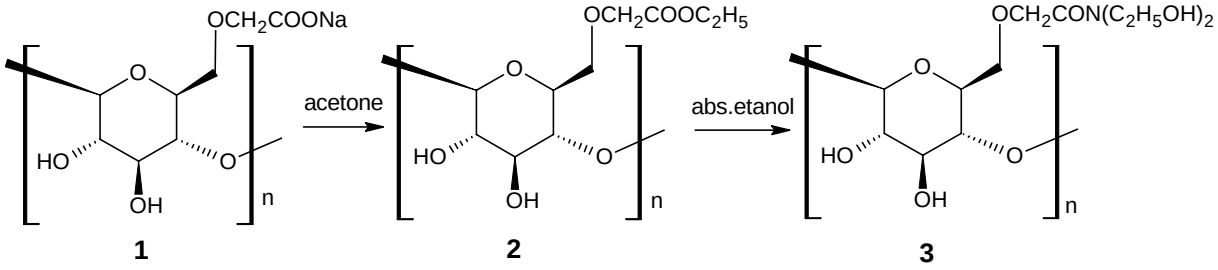
The constituent polymers most readily extracted are generally also the ones bearing most of the adsorption sites. Strategies developed to correct these problems include chemical modification, co-polymerization, and cross-linking [2-9]. Some reports describe the treatment of two widely available agricultural by-products, soybean hull

and sugar beet fiber, with epichlorohydrin to produce cation-exchange materials with increased capability and physical stability [4-5]. In this communication, we announce the synthesis of cellulose-*g*-epichlorohydrin/ethylendiamine from NaCMC and its absorption of Pb^{2+}, Cd^{2+} and Mn^{2+} ions.

Results and Discussion

Synthesis of O-[N,N-bis(2-hydroxyethyl)acetamido]cellulose

The derivative *O*-[*N*,*N*-bis(2-hydroxyethyl)acetamido]cellulose was synthesized by reacting the ethyl ester of carboxymethyl cellulose and diethanolamine in absolute ethanol for 8 hours (Scheme 1).



Scheme 1. Synthesis of *O*-[*N*,*N*-bis(2-hydroxyethyl)acetamido]cellulose.

Some characteristic absorption banks appeared in IR spectra of this substance, for instance, the peaks at 1627 cm^{-1} ($\nu_{C=O\ amide}$), 1258 cm^{-1} (ν_{C-N}), 3422 cm^{-1} (ν_{OH}), 2929-2851 cm^{-1} ($\nu_{C-H\ sat.}$) and 1017 cm^{-1} ($\nu_{C-O-C\ ether}$). The surface of modified product displayed certain changes in comparison with cotton cellulose. This was indicated by comparing the SEM images of a cotton cellulose sample and those of *O*-[*N*,*N*-bis(2-hydroxyethyl)acetamido]cellulose (Figure 1); the surface of the latter was rough, and had several small hollows.

The absorption capability of *O*-[*N*,*N*-bis(2-hydroxyethyl)acetamido]cellulose towards heavy metal ions has been estimated from the absorption of Pb^{2+} ion at different concentrations (10,000; 2,000; 1,000; 600; 400 and 100 ppm) on this material (Table 1, column M_0).

Synthesis of cellulose-g-epichlorohydrin/ethylendiamine

Cellulose-*g*-epichlorohydrin/ethylendiamine (CMC-*g*-ECH/EDA) was synthesized in a two-step reaction. In the first step, the sodium of carboxymethyl cellulose was transformed into cellulose-*g*-epichlorohydrin by reaction between NaCMC and epichlorohydrin in acetone at a suitable temperature. Then, in a second step, cellulose-

g-epichlorohydrin reacted with ethylendiamine in ethanol under reflux conditions to give the desired product cellulose-*g*-epichlorohydrin/ethylendiamine (Scheme 2).

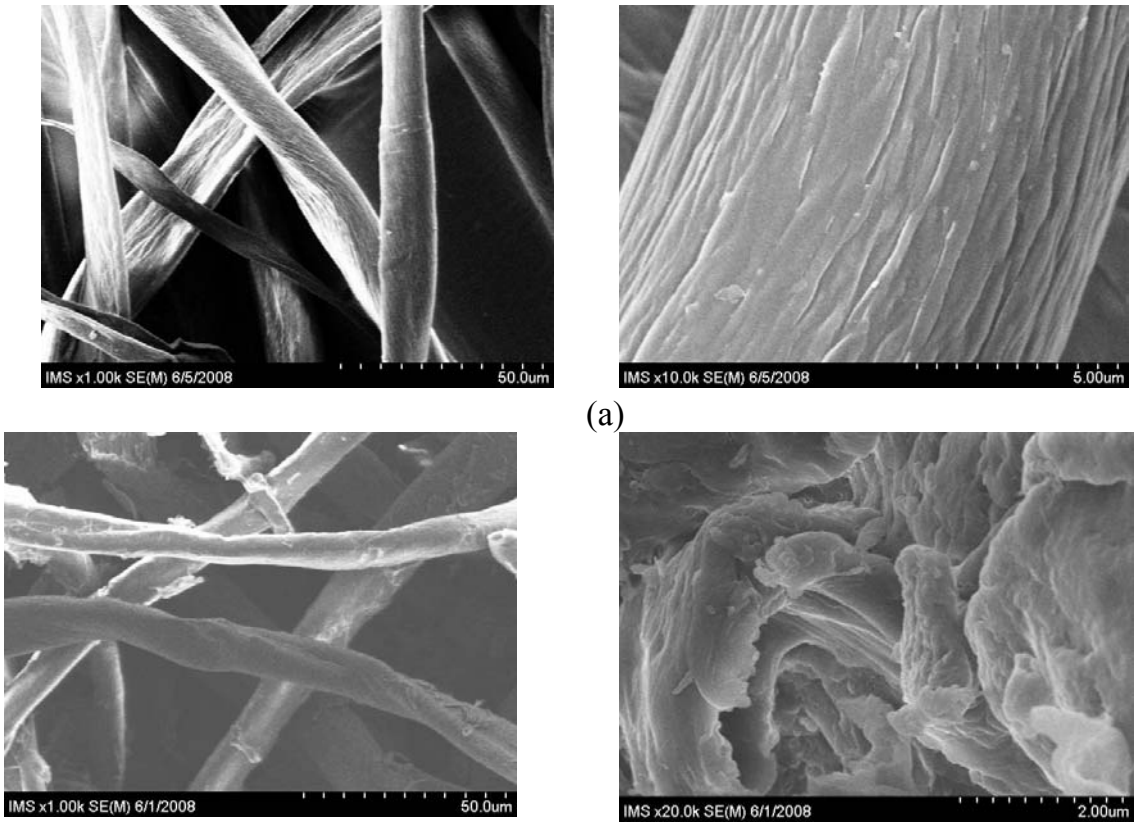
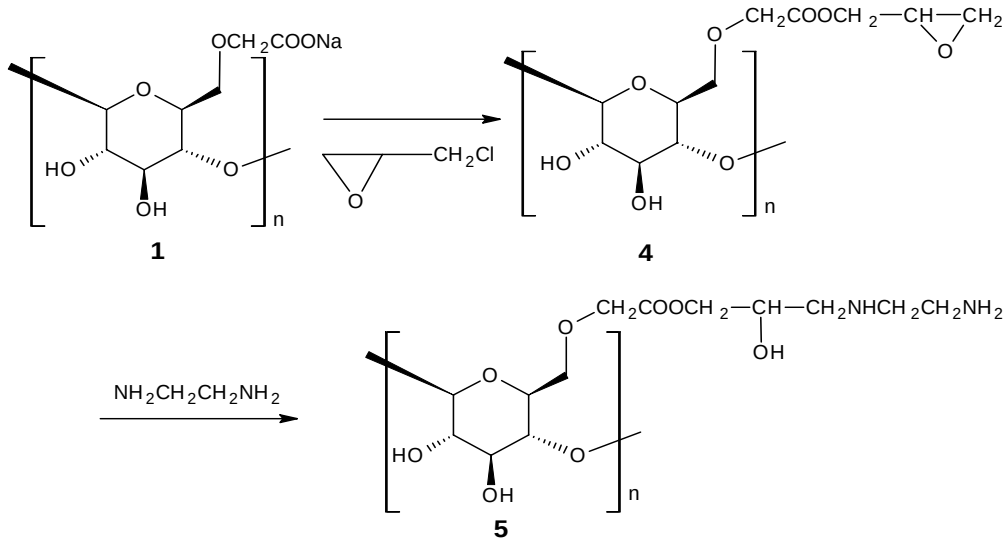


Figure 1. SEM surface image of (a) cotton cellulose; (b) carboxymethylcellulose modified with diethanolamine.



Scheme 2. Synthetic reaction cellulose-*g*-epichlorohydrin/ethylendiamine.

Molar ratios of reagents (NaCMC, epichlorohydrin and ethylendiamine) were varied as follows: 1:1.5:1.5; 1:2:2; 1:3:3 and 1:4:4. Some characteristic absorption bands appeared in the IR spectra of the synthesized material, for example, the peaks at 1258 cm^{-1} (ν_{C-N}), 3422 cm^{-1} (ν_{OH}), 3302 cm^{-1} (ν_{NH}), 2929-2851 cm^{-1} ($\nu_{C-H\ sat.}$), 1017 cm^{-1} ($\nu_{C-O-C\ ether}$).

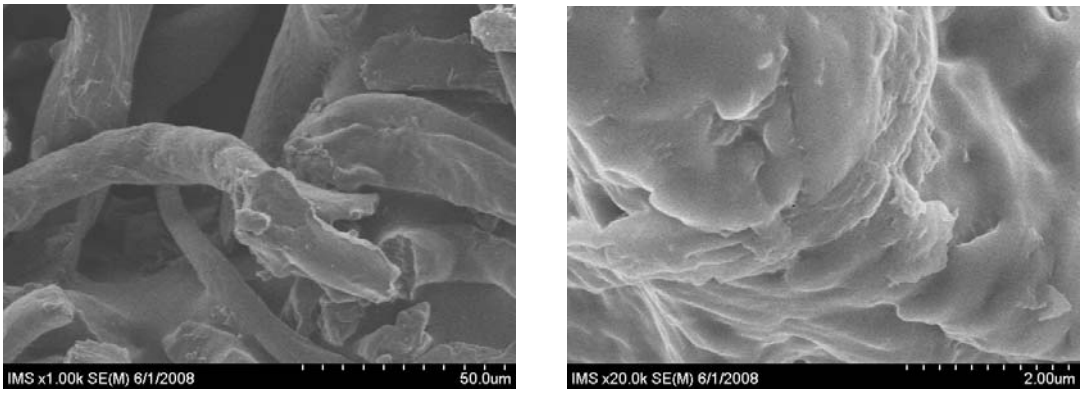


Figure 2. SEM surface image of cellulose-*g*-epichlohydrin/ethylendiamine (molar ratio 1:1.5:1.5).

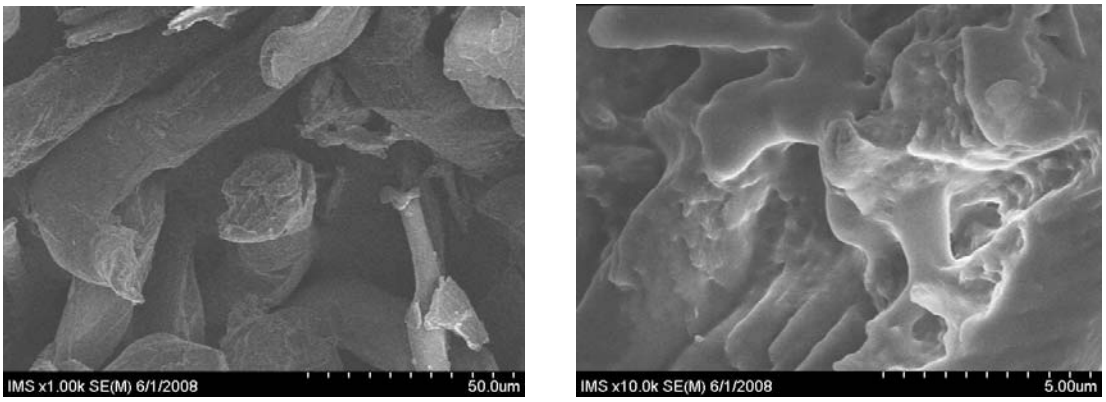


Figure 3. SEM surface image of cellulose-*g*-epichlohydrin/ethylendiamine (molar ratio 1:2:2).

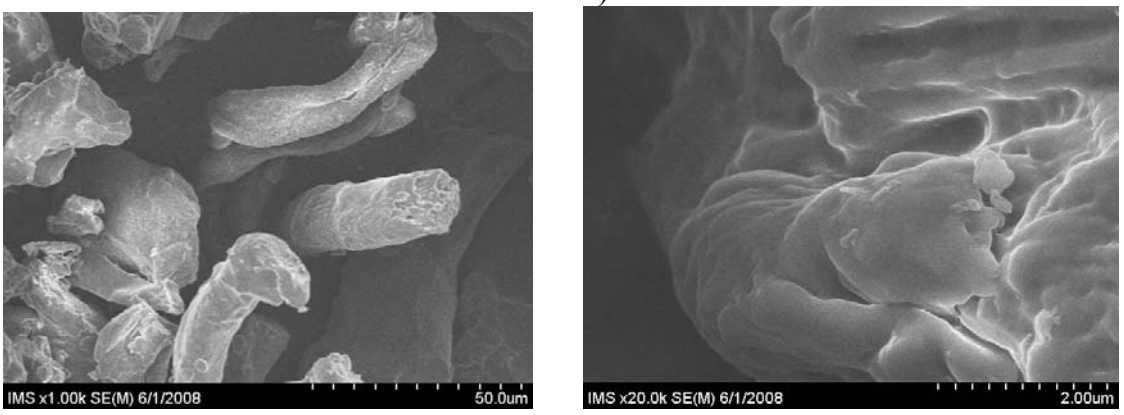


Figure 4. SEM surface image of cellulose-*g*-epichlohydrin/ethylendiamine (molar ratio 1:3:3).

The surface of the modified product showed remarkable changes in the comparison of its SEM images (Figures 2-4) with those of cotton cellulose and of *O*-[*N*,*N*-bis(2-hydroxyethyl)acetamido]cellulose (Figure 1) – the surface became rough, sometimes, there are also hollows, therefore, its surface area increased significantly, making absorption of metallic ions more easy.

Absorption capability of Pb^{2+}, Cd^{2+} and Mn^{2+} on cellulose-g-epichlorohydrin/ethylendiamine

Table 1. Absorption capability of modified cellulose types (diethanolamine and epichlorohydrin/ethylendiamine).

Pb^{2+} concentration (ppm)	**Absorption (mg/g)**				
	M_0 [a)]	**M_1 [b)]**	**M_2 [b)]**	**M_3 [b)]**	**M_4 [b)]**
10,000	414	517.5	724.5	828	931.5
2,000	310.5	351.9	414	434.7	455.4
1,000	227.7	248.4	269.1	289.8	310.5
600	168.3	207	227.7	279.45	289.8
400	132.2	141.4	159.1	172.6	187.3
100	38.5	40.1	42.3	45.6	48.8

[a)] M_0 was the amide of diethanolamine with CMC; [b)] M_1, M_2, M_3 and M_4 were cellulose-*g*-epichlorohydrin/ethylendiamine (with molar ratios 1:1.5:1.5; 1:2:2; 1:3:3 and 1:4:4, respectively).

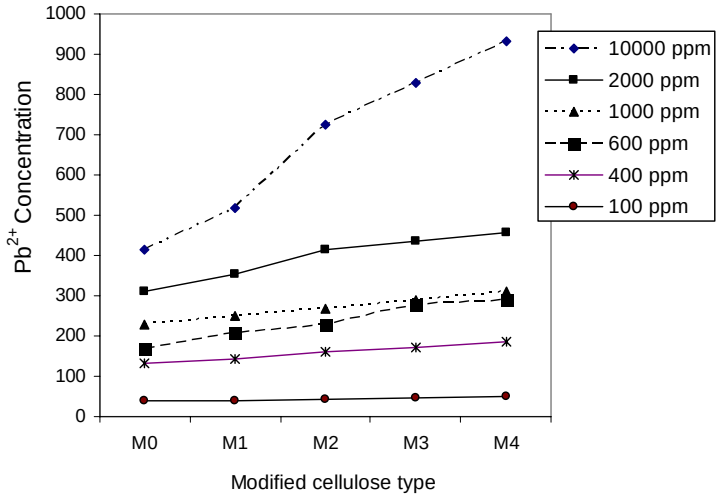


Figure 5. Relationships between Pb^{2+} concentration in solutions and absorption capability of modified cellulose types.

The absorption capability of heavy metal ions ON cellulose-*g*-epichlorohydrin/ethylendiamine *O*-[*N*,*N*-bis(2-hydroxyethyl)acetamido]cellulose has

been estimated by measuring the absorptions of Pb^{2+} ion at different concentrations (10,000; 2,000; 1,000; 600; 400 and 100 ppm) on this material. The experiments showed that the absorption capability of cellulose-*g*-epichlorohydrin/ethylendiamine for Pb^{2+} ion was more than the that of *O*-[*N*,*N*-bis(2-hydroxyethyl)acetamido]cellulose and that it increased when the reaction molar ratios were increased (see Tables 1 and 2).

Table 2. Absorption capability of Pb^{2+}, Cd^{2+} and Mn^{2+} onto CMC-*g*-ECH/EDA with ions at different concentrations

C_o (ppm)	Pb^{2+}			Cd^{2+}			Mn^{2+}		
	h_{pic} (mm)	*C* (ppm)	*q* (mg/g)	h_{pic} (mm)	*C* (ppm)	*q* (mg/g)	h_{pic} (mm)	*C* (ppm)	*q* (mg/g)
500	1.2	172	164	5.1	294	103	1.8	303	99
1,000	1.7	355	323	9.4	599	201	3.6	625	187
1,500	2.5	647	427	14.3	946	277	5.6	984	258
2,000	3.3	940	530	21.0	1,420	290	8.1	1,432	284
2,500	4.3	1,306	596	27.5	1,881	310	10.8	1,916	292
3,000	5.5	1,745	627	34.4	2,369	315	13.4	2,382	309

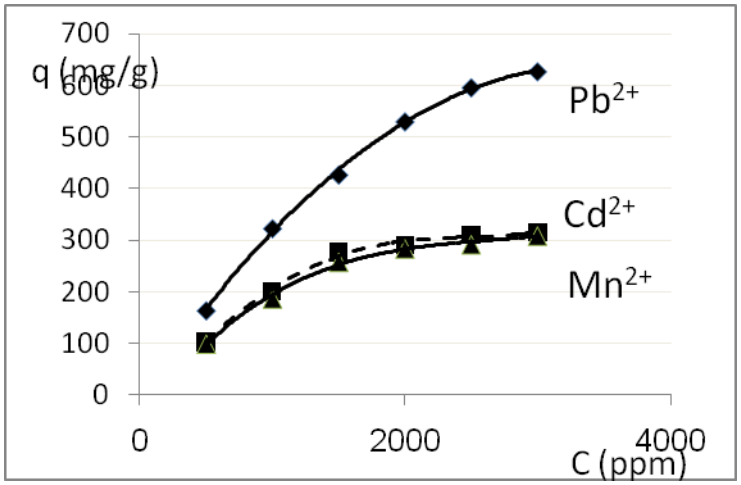


Figure 6. Influence of ion concentration in solutions to absorption capability of CMC-*g*-ECH/EDA.

CMC-*g*-ECH/EDA samples that were synthesized under optimal reaction conditions (reaction time, molar ratio of reagents) have been treated with Pb^{2+}, Cd^{2+} and Mn^{2+} solutions at different concentrations. The absorption results indicated that the CMC-*g*-ECH/EDA samples have remarkable absorption capabilities for the investigated heavy metal ions. It was also shown that absorption capacity *q* of CMC-*g*-ECH/EDA increased when the solution concentrations increased. At first, *q* increases rapidly, then the absorption rate slows down and reaches maximum values. Actually, the absorption curve lines are Langmuir isothermal absorption lines (see Figure 6). From Table 2, it is seen that CMC-*g*-ECH/EDA adsorbed Pb^{2+}, Cd^{2+} and

Mn^{2+} ions well and the absorption capabilities varied in the order: $Pb^{2+} > Cd^{2+} > Mn^{2+}$.

Experimental Part

General method

IR spectra (4000-400 cm^{-1}), were recorded at room temperature as KBr pellets on a Bruker FT-IR spectrophotometer (Bruker, Germany). Sample surfaces were scanned on a Hitachi S4800 instrument (Japan). Metallic contents were measured using the Fire Atomic Absorption Spectral method (F/AAS) on a PYE UNICAM instrument (Philips, United Kingdom). Solutions of Pb^{2+}, Cd^{2+} and Mn^{2+} ions were prepared in 1,000 per part milligram concentration from $Pb(NO_3)_2$, $CdSO_4$ and $MnCl_2 \cdot 4H_2O$ salts (Merck).

Synthesis of O-[N,N-bis(2-hydroxyethyl)acetamido]cellulose

A mixture of the ethyl ester of carboxymethylcellulose (0.78 g.) and diethanolamine (1.2 mL.) in 95% ethanol (30 mL.) was refluxed on a steam bath in a 100-mL. round-bottomed flask for 8 hours and then cooled. The solid which separates was collected by filtration with suction on a Büchner funnel, washed with three portions of 95% ethanol (50 mL. each) and dried at 50–60°C to give 1 g. of white product.

Synthesis of cellulose-g-epichlorohydrin/ethylendiamine

A mixture of sodium carboxymethyl cellulose (2.0 g.) and epichlorohydrin (0.5 mL.) in acetone (30 mL.) was stirred at room temperature in a 100-mL. round-bottomed flask for 6 hours. Then ethylendiamine (0.8 mL.) and epichlorohydrin (0.4 mL) were added to the stirred reaction mixture. The reaction mixture was refluxed on a water bath at 55–65^{o}C for 8 hours and then cooled. The solids which separated were filtered with suction on a Büchner funnel, washed with three portions of 95% ethanol (50 mL. each) and dried in air to give 3 g. of pale yellow cellulose-*g*-epichlorohydrin/ ethylendiamine product.

Determination of absorption of Pb^{2+}, Cd^{2+} and Mn^{2+} ions

Weighed 0.1 g. of modified cellulose and added in 100-mL. conic flask. A volume of 50 mL. of 1000 ppm concentration of Pb^{2+} ion was added. The obtained mixture was stirred in 30 minutes and left in 24 hrs. and filtered. Took 2.5 mL. of obtained

filtrate and diluted into 100 mL solution. Ion contents were determined using F/AAS method and capacity of absorption (q) was calculated by expression:

$$q = \frac{Co - C}{a}.V$$

where q – amount of metallic ion absorbed on 1.0 gram of modified cellulose (mg./g.); C_o – initial concentration of metallic ion (mg./l. or ppm); C – concentration of metallic ion on absorption equilibrium (mg./l. or ppm); a – amount of modified cellulose (g.); V – volume of absorption solution (L.)

Acknowledgments

This publication is completed with financial support from the Grant QGTD.08.03, Vietnam National University, Hanoi.

References and Notes

1. *Ion Exchange and Solvent Extraction: A Series of Advances,* Volume 18; SenGupt, A.K.; Ed.; CRC Press: Boca Raton, FL, USA, **2007**.
2. Lee, S.-H; Park, S.-M; Kim, Y. Effect of the concentration of sodium acetate (SA) on cross linking of chitosan fiber by epichlorohydrin (ECH) in a wet spinning system. *Carbohydr. Polym.* **2007**, *70*, 53-60.
3. Obokata, T.; Isogai, A. The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin. *Colloids Surf. A Physicochem. Eng. Aspects* **2007**, *302*, 525-531.
4. Coelho, T.C.; Laus, R.; Mangrich, A.S.; Valfredo, T.F; Mauro, C.M.L. Effect of heparin coating on epichlorohydrin cross-linked chitosan microspheres on the adsorption of copper (II) ions. *Reactive Funct. Polym*. **2007**, *67*, 468-475.
5. Orlando, U.S.; Baes, A.U.; Nishijima, W.; Okada, M. Preparation of agricultural residue anion exchangers and its nitrate maximum adsorption capability. *Chemosphere* **2002**, *48*, 1041-1046.
6. Orlando, U.S.; Baes, A.U.; Nishijima, W.; Okada, M. A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. *Bioresour. Technol.* **2002**, *83*, 195-198.
7. Nikonovich, G.V.; Leont'ieva, S.A.; Shatkina, V.P. ; Usmanov, Kh.U.; Adylov, A.A.; Tashpulatov, Yu. T. Study of the supermolecular structure of cross-linked cellulose derivatives. Products of reaction of cellulose and epichlorohydrin. *Polym. Sci. USSR* **1965**, *7*, 2337-2346.
8. Šimkovic, I.; Laszlo, J.A.; Thompson, A.R. Preparation of a weakly basic ion exchanger by crosslinking starch with epichlorohydrin in the presence of NH_4OH. *Carbohydr. Polym.* **1996**, *30*, 25-30.
9. Kuzayev, A.I.; Ol'khova, O.M. Gel-permeation chromatography of epichlorohydrin oligomers. *Polym. Sci. USSR* **1982**, *24*, 2520-2529.