

# Improved Synthesis of a Branched Poly(ethylene imine)-Modified Cellulose-Based Adsorbent for Removal and Recovery of Cu(II) from Aqueous Solution

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**ABSTRACT:** This study focuses on an improved synthesis of a branched poly (ethylene imine) (PEI)-modified cellulose-based adsorbent (Cell-*g*-PGMA-PEI). We aim to improve the adsorbent capacity by reducing side reaction of epoxide ring opening during graft copolymerization of glycidyl methacrylate (GMA) onto cellulose which increases the content of epoxy groups, anchors to immobilize branched PEI moieties. FTIR spectra provided the evidence of successful graft copolymerization of GMA onto cellulose initiated by benzoyl peroxide (BPO) and modification with PEI. The amount of epoxy groups of Cell-*g*-PGMA was 4.35 mmol g<sup>-1</sup> by epoxy titration. Subsequently, the adsorption behavior of Cu(II) on cell-*g*-PGMA-PEI in aqueous solution has been investigated. The data from the adsorption kinetic experiments agreed well with pseudo-second-order model. The adsorption isotherms can be interpreted by the Langmuir model with the maximum adsorption capacity of 102 mg g<sup>-1</sup> which was largely improved compared with the similar adsorbent reported. The dynamic adsorption capacity obtained from the column tests was 119 mg g<sup>-1</sup> and the adsorbent could be regenerated by HCl of 0.1 mol L<sup>-1</sup>. Results indicate that the novel pathway for the synthesis of Cell-*g*-PGMA-PEI exhibits significant potential to improve the performance of adsorbents in removal and recovery of Cu(II) from aqueous solution. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1799–1805, 2013

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## INTRODUCTION

Copper is an essential trace element for human beings, yet it would become a great threat to public health with excessive ingestion. Compared to pure copper, Cu(II) salts are more toxic because of their water soluble nature, with the main risks of gastrointestinal irritation, liver and kidney damage, and intravascular hemolysis. Their target organs are the gastrointestinal tract, cardiovascular and circulatory system, hematopoietic system, liver, kidneys, and nervous system.<sup>1</sup> However, industrial applications of heavy metals like metal processing, machine manufacturing, and organic synthesis which have introduced substantial amounts of Cu(II) into the aquatic and terrestrial environments are the causes of water quality deterioration and threaten the health of living organisms.<sup>2</sup> Among various sewage treatments, adsorption is an effective, efficient, and economic method for removal and recovery of heavy metals from wastewater for its wide variety of target pollutants, relatively high adsorption capacity, possible selectivity,<sup>3</sup> and repeatable utilization. Natural materials such as cellulose, chitosan, lignin, and zeolites could be physically and chemically modified to improve metal uptake ability. For instance, it is observed that the uptake of Cu(II) on chitosan-coated glass beads  $(1.26 \text{ mmol g}^{-1})^4$  and chitosan-coated perlite  $(3.09 \text{ mmol g}^{-1})^5$  is greater than chitosan spheres  $(1.02 \text{ mmol g}^{-1})$ .<sup>6</sup>

Our work focuses on an improved pathway to synthesize a branched poly (ethylene imine) (PEI)-modified cellulose-based adsorbent. We aim to improve the adsorbent capacity by increasing the content of epoxy groups which are the anchors to immobilize branched PEI molecules.

PEI is a typical water-soluble polyamine, which could be divided into two types: linear PEI (LPEI) and branched PEI (BPEI) according to their structures which are presented in Figure 1. BPEI is fully amorphous, unlike the linear form which is crystalline at room temperature. Furthermore, BPEI has a high concentration of polar groups containing nitrogen atoms with a molar ratio of primary to secondary to tertiary amine reported as 25 : 50 : 25.<sup>7,8</sup> Therefore, it possesses strong chelating ability for parts of heavy metal ions. However, because of the water soluble nature of BPEI, it has to be immobilized on matrix to ensure the maneuverability when used as adsorbent.<sup>9</sup> (The PEI below in this study refers to BPEI.)

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Figure 1. Chemical formulae of LPEI and BPEI.

As a matrix for adsorbent, cellulose itself is a unique polymeric product with multiple attributes such as good hydrophilicity yet poor solubility in common solvents, high thermal stability, relatively low cost of preparation.<sup>10</sup>. However, cellulose has some inherent drawbacks like relatively low degrees of accessibility, which restrict the application range. Surface modification seems to be a desirable solution. The study of Nikiforova and Kozlov<sup>11</sup> concluded that the modified cellulose-containing sorbent behaves as a weak acid cation exchanger with the sorption sites represented by carboxyl group in hydrogen ion or salt forms. Furthermore, Nikiforova et al.<sup>12</sup> found that modification of cotton cellulose, pinewood sawdust, and short flax fiber by Bright red CX5 dye fixed with water-soluble nitrogen-containing polymer leads to an increase in their sorption capacity for Cu(II) by 53%, 35%, and 32%, respectively. Anirudhan et al.<sup>13</sup> evaluated the performance of a carboxylate-functionalized graft copolymer of TiO2-densified cellulose (PGTDC-COOH) for Cu(II) removal from aqueous solutions and industrial effluents. The maximum binding capacity was found to be 75.82 mg  $L^{-1}$  (30°C, pH 5.0).

Among the various methods of modification, graft copolymerization offers an attractive and versatile means of imparting a variety of functional groups to cellulose.<sup>14</sup> Moreover, about 60% of all available polymers are obtained by radical polymerization<sup>15</sup> due to its attractive characteristics as follows<sup>16–18</sup>:

- 1. Applicable to a wide range of monomers.
- 2. Able to provide an unlimited number of copolymers.
- 3. Applicable to a variety of reaction conditions like solution, emulsion, and suspension under a wide range of temperature and mild reaction conditions.
- 4. Tolerable to water or other impurities compared with the great sensitivities of ionic polymerization and of coordination polymerization.
- 5. Relatively unsophisticated and inexpensive to implement compared with competitive technologies.

Among the various chemical initiation methods, the formation of free radicals on the cellulose molecules by direct oxidation with Ce(IV) ions has gained considerable attention, due to its ease of application and its high grafting efficiency compared with other known redox systems such as the Fe(II)-hydrogen peroxide system. In this technique, the presence of acid could ensure that the Ce(IV) ions produce free radicals on the cellulose backbone to initiate graft copolymerization effectively and efficiently.<sup>19–25</sup>

However, the epoxy groups of the monomer, glycidyl methacrylate (GMA), are unstable in acid environments. The presence of acid significantly affects the effect of the modification by PEI for the relatively lower amount of epoxy groups in the cellulose graft copolymer.

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Large quantities of previous work had been done in an attempt to reduce side reaction of epoxide ring opening while utilizing Ce(IV) ions as the initiator of the copolymerization with GMA. In the research of O'Connell et al.,<sup>26</sup> cerium (IV) ammonium nitrate (CAN) and 0.1*M* nitric acid were added and allowed to react with cellulose. The excess initiator solution was removed by suction and the cellulose fibers were rinsed with water. Although this two-step method restrained the ring-opening reaction to some degree by separating the polymerization procedures, it sacrificed the high grafting efficiency of Ce(IV) initiation. On the other hand, Navarro et al.<sup>27</sup> chose initiation by Ce(IV) ions without adding any acid. However, the graft percentage is also unsatisfying. Related details are listed in Table I.

Therefore, on the basis of previous work,<sup>26–28</sup> benzoyl peroxide (BPO) was chosen as the initiator specifically for GMA because of its tolerance of large scale of pH of reaction medium and chose the mixture of water and acetone as reaction medium<sup>28</sup> for better dispersion of reactants. Subsequently, the homopolymer would be extracted from the product by acetone. Afterward, the grafted copolymer Cell-*g*-PGMA would be modified by PEI. We anticipated a higher adsorption capacity of the improved adsorbent for Cu(II) than that previously reported.

#### **EXPERIMENTAL**

#### Materials

Reagent-grade cellulose microcrystalline (particle diameter 25  $\mu$ m), analytical grade glycidyl methacrylate (GMA), benzoyl peroxide (BPO), and poly (ethylene imine) (PEI) (MW 600, 99%) were obtained from Aladdin Reagent (China). The monomer, GMA, was distilled under reduced pressure before use. The Cu(II) standard solution was commercially available (National Analysis Center of Iron & Steel). Reagent-grade acetone, ethanol, *N,N*-dimethyl formamide (DMF), HCl, and NaOH were purchased from Tie Ta Regent, Chemical Regent Factory of Tianjin, Regent Chemical Limited Company, Beijing Chemical Works, and San He Chemical Regent Limited Company (Yan tai City, China), respectively.

## Synthesis of Adsorbent (Cell-g-PGMA-PEI)

The general procedures adopted for the synthesis of Cell-g-PGMA-PEI are depicted in Figure 2. Cellulose microcrystalline (1.0 g) was suspended in the mixture of 10 mL deionized water and 5 mL acetone in a flask. BPO (0.414 mmol) and monomer GMA (19.2 mmol) were added to above suspension with constant stirring. After bubbled with nitrogen for 15 min to remove oxygen in the system, all the contents were heated in a water bath at 70°C with continuous stirring under nitrogen protection for 2.5 h. The sensitive component for polymer grafting might be the hydroxyl methyl group in glucose unit, Cell-CH<sub>2</sub>OH. PGMA-grafted cellulose was collected after filtration and repeated washing with deionized water and acetone to remove unreacted monomer. And then the homopolymer was removed by Soxhlet extraction with acetone. Subsequently, the copolymer was vacuum dried at 50°C until constant weight of Cell-g-PGMA was obtained. It was converted into a chelating adsorbent by introducing PEI by the ring-opening reaction of the epoxy groups of the copolymer through a reaction with 99% PEI in DMF solution at 70°C for 8 h. The resulting product

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Table I. Comparison of Epoxy Groups Content Among Different Studies

	Cellulose (g)	Initiator (mol L <sup>-1</sup> )	Monomer (GMA) (mmol)	Epoxy groups (mmol g <sup>-1</sup> )
O'Connell et al. <sup>26</sup>	0.5	0.05 (CAN)	14	1.75
Navarro et al. <sup>27</sup>	5.0	0.027 (CAN)	189	0.82
This study	1.0	0.28 (BPO)	19.2	4.35

was washed with deionized water and ethanol and then vacuum dried at 50°C until the weight of Cell-*g*-PGMA-PEI became constant.

## Characterization

The FTIR spectra of cellulose, Cell-*g*-PGMA, and Cell-*g*-PGMA-PEI were recorded with a Bruker Vertex70 spectrophotometer between 4000 and 500 cm<sup>-1</sup> using the KBr pellet technique. Elemental analysis was performed with a Vario EI III Elemental Analyzer. A Sartorius PB-10 pH meter (model  $\mu$ -362) was used for pH measurements. The concentrations of Cu(II) in solution were determined by an analytikjena novAA300/400FL atomic absorption spectrophotometer (AAS) with the mean values of three replicates reported (RSD <3%). The amount of epoxy group within the Cell-*g*-PGMA was determined by the HCl/acetone chemical titration method.

#### **Adsorption Procedure**

Batch tests were conducted in closed 100-mL Erlenmeyer flasks. For each experiment, 50 mg of the adsorbent was shaken with 30 mL of  $Cu(NO_3)_2$  solution of a specified metal ion concentra-



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Figure 2. Scheme for preparation of Cell-g-PGMA-PEI.

tion inside a thermostat shaker (rotating speed 150 rpm) at 28°C. The solution pH was adjusted to a defined value with 0.1 mol  $L^{-1}$  HNO<sub>3</sub> and 0.1 mol  $L^{-1}$  NaOH.

Continuous adsorption experiments were performed using a glass chromatographic column (inner diameter: 7.5 mm) filled with adsorbent Cell-PGMA-PEI 0.2 g. The Cu(NO<sub>3</sub>)<sub>2</sub> solution with the concentration of about 10 mmol L<sup>-1</sup> were fed to the columns at the rate of 90 mL h<sup>-1</sup> using a peristaltic pump. The concentration of Cu(II) of the eluant was monitored until the concentration was equal to 10 mmol L<sup>-1</sup>. Subsequently, 0.1 mol L<sup>-1</sup> HCl solution was used as eluant with a constant flow rate of 90 mL h<sup>-1</sup>. The concentration of Cu(II) in the eluant was monitored until Cu(II) could not be detected.

## **RESULTS AND DISCUSSION**

#### Adsorbent Characterization

The graft percentage  $(G_P)$  and the graft efficiency  $(G_E)$  were calculated by eqs. (1) and (2) below

$$G_p = \frac{(w_2 - w_1)}{w_1} \times 100\%$$
(1)

$$G_E = \frac{(w_2 - w_1)}{w_2} \times 100\%$$
 (2)

where  $w_1$ ,  $w_2$ , and  $w_3$  are the weights of the pure cellulose microcrystalline, graft copolymer, and the monomer charged, respectively. It is determined that the  $G_P$  is 170% and the  $G_E$  is 60%. The amount of epoxy groups of Cell-g-PGMA measured by HCl/acetone chemical titration method is 4.35 mmol g<sup>-1</sup>. Compared with previous work cited in Table I, copolymerization carried out in our research yielded significant increase in epoxy group content with lower charged amount of monomer, which rendered Cell-g-PGMA better dispersion in DMF, a solvent for PEI modification.

The FTIR spectra of pure cellulose microcrystalline, Cell-g-PGMA, and Cell-g-PGMA-PEI are presented in Figure 3.



**Figure 3.** FTIR spectra of (A) Cell-g-PGMA-PEI, (B) Cell-g-PGMA, and (C) pure cellulose microcrystalline.

Table II. Elemental Analysis of Cell-g-PGMA and Cell-g-PGMA-PEI

Sample	Carbon content (%)	Hydrogen content (%)	Nitrogen content (%)
Cell-g-PGMA	47.04	6.81	0.0
Cell-g-PGMA-PEI	49.20	8.28	10.88

Characteristic absorption peaks for Cell-g-PGMA are the carbonyl stretching at 1730 cm<sup>-1</sup> and epoxy vibrations absorption at 904 and 842 cm<sup>-1</sup>, which provide the evidence of graft copolymerization with GMA on the surface of the cellulose microcrystalline.<sup>26</sup> The disappearance of the epoxy vibration peaks and the N[sbond]H vibration absorption at 1560 cm<sup>-1</sup> in the FTIR spectra (A) confirm the successful modification with PEI.<sup>29</sup>

To clarify and assess the grafting of poly-GMA and PEI, elemental analysis for Cell-*g*-PGMA and Cell-*g*-PGMA-PEI was performed (Table II). The presence of nitrogen in Cell-*g*-PGMA-PEI provided further evidence of the functionalization with PEI. Moreover, according to the nitrogen content of Cell-*g*-PGMA, the amount of PEI grafted onto Cell-*g*-PGMA was found to be ~0.56 mmol g<sup>-1</sup> (nitrogen 7.77 mmol g<sup>-1</sup>).

## Adsorption Characterization

**Initial pH.** The solution pH can affect the surface charge of the adsorbent, the degree of ionization, and the speciation of pollutants,<sup>30</sup> which may eventually influence the removal efficiency of the adsorbent. The adsorption of Cu(II) was examined over the pH range of ~2.0–7.0. The relationship between initial pH and removal efficiency is shown in Figure 4. Results indicated that adsorption capacity of Cu(II) increased with the increase of initial pH and the removal efficiency rose from 54.22% (pH 2.3) to the maximum of 99.98% (pH 6.8) simultaneously.

At low pH values, highly protonated adsorbent does not perform well due to high concentration of hydrogen ion which



**Figure 4.** Effect of initial pH values on Cu(II) removal efficiency (%) (adsorbent: 50 mg, temperature:  $28^{\circ}$ C, time: 24 h, initial concentration of Cu(II): 35 mg L<sup>-1</sup>).

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competes the binding points on the adsorbents with Cu(II). The cationic degree of PEI is strongly affected by pH value. As the pH increases, the protonation ratio decreased. The electrical repulsion force and competition from hydrogen ion become weaker, thus the removal efficiency increases rapidly. Of course, as for solution with high pH, the removal of Cu(II) may slightly attribute to precipitation of Cu(II) under alkaline condition.<sup>31</sup> Results suggested that the adsorbent cell-*g*-PGMA-PEI exhibits a relatively broad scale of pH (3.5–7.0) to achieve satisfactory removal efficiency (above 94%).

Adsorption Kinetics. Experimental data generated from Cu(II) adsorption of  $q_e$ -t tests by Cell-g-PGMA-PEI was evaluated by kinetic models to understand the mechanisms and kinetics of the adsorption process.

Figure 5 shows that within the first 1 h, 87% of  $q_e$  was achieved, in the subsequent long period of time;  $q_t$  of the adsorption grew relatively slow. Characteristic curves were used to describe the adsorption kinetics and to facilitate a more accurate inference in adsorbent selection for engineering practice.<sup>32</sup> The pseudo-first-order kinetic model [eq. (3)]<sup>33</sup> and the pseudo-second-order kinetic model [eq. (4)]<sup>34</sup> were applied to fit the experimental data where  $q_t$  is the amount of Cu(II) adsorbed by Cell-g-PGMA-PEI at any time (t),  $q_e$  is the amount of Cu(II) adsorbed by Cell-g-PGMA-PEI at equilibrium,  $k_1$  is the rate constant of the pseudo-first-order kinetic model, and  $k_2$  is the rate constant of the pseudo-second-order kinetic model.

$$q_t = q_e (1 - e^{-k_1 t}) \tag{3}$$

$$q_t = \frac{t}{\frac{1}{k_2 j_B^2} + \frac{t}{q_B}}$$
(4)

As Table III shows, the correlation coefficient  $(R^2)$  for the nonlinear plots of  $q_t$  against time from the pseudo-second-order equation is greater than that of the pseudo-first-order equation,



**Figure 5.** Effect of contact time on Cu(II) adsorption by adsorbent Cell*g*-PGMA-PEI (adsorbent: 50 mg, temperature:  $28^{\circ}$ C, initial concentration of Cu(II): 500 mg L<sup>-1</sup>, initial pH: 4.7).

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Table III. The Parameters of Pseudo-First-Order Kinetic Model and Pseudo-Second-Order Kinetic Models for Cu(II) Adsorption

Model	$R^2$	$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$V_0$ (mg g <sup>-1</sup> min <sup>-1</sup> )
The pseudo-first-order kinetic model	0.9753	68.85	0.17		
The pseudo-second-order kinetic model	0.9979	72.14		0.004	20.74

which suggests that the sorption system of Cu(II) by Cell-*g*-PGMA-PEI is not a pseudo-first-order reaction but agrees with the pseudo-second-order model, based on the assumption that the rate-limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate and provides the best correlation of the data. Furthermore, according to the pseudo-second-order kinetic model, when time is infinitely close to zero, the initial chemical reaction rate  $V_0$  [eq. (5)] is obtained.<sup>34</sup>

$$V_0 = k_2 q_B^2 \tag{5}$$

Adsorption Isotherm. Adsorption isotherms describe the relationship between the amount of Cu(II) adsorbed and the concentration of Cu(II) in the liquid at equilibrium. Langmuir model and Freundlich model are the most common mathematical models for describing adsorption isotherms in aqueous solution.

The Langmuir adsorption isotherm is often applicable for modeling the adsorption on homogeneous surface sites, which is based on the assumption that the adsorption occurs on monolayer and all sites are identical and equivalent with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites.<sup>35,36</sup> The Langmuir adsorption isotherm model can be represented as eq. (6) and the Langmuir constants can be estimated from the linear plot of  $C_e/q_e$  versus  $C_e$  [eq. (7)]<sup>36</sup> where  $K_L$  is the Langmuir constant,  $q_m$  is the Langmuir constant related to the maximum adsorption capacity,  $q_e$  is the amount of Cu(II) adsorbed by Cell-g-PGMA-PEI at



**Figure 6.** Langmuir adsorption isotherm for Cu(II) on Cell-*g*-PGMA-PEI (temperature: 28°C, adsorbent dose: 50 mg, solution volume: 30 mL, pH: 5.0).

equilibrium, and  $C_e$  is the equilibrium concentration in solution.

The Freundlich adsorption isotherm is applicable for multilayer adsorption on the heterogeneous surface.<sup>37</sup>  $K_F$  and n are related to adsorption capacity and energy of adsorption, respectively.<sup>38</sup> The Freundlich isotherm model can be represented as eq. (8). The value of  $K_F$  and n can be obtained from the slope and intercept of a linear plot of log  $q_e$  versus log  $C_e$  [eq. (9)].<sup>39</sup>

$$q_B = \frac{q_m K_L C_B}{1 + K_L C_B} \tag{6}$$

$$\frac{C_B}{q_B} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_B \tag{7}$$

$$q_B = K_F C_B^{1n} \tag{8}$$

$$\lg q_B = \frac{1}{n} lcgC_B + lcgK_F \tag{9}$$

The linear Langmuir adsorption isotherm and linear Freundlich adsorption isotherm for Cu(II) on Cell-*g*-PGMA-PEI are presented in Figures 6 and 7 with the characteristic constants of the two isotherm models listed in Table IV.

From Table IV, it could be easily deduced that the Langmuir isotherm model fits the experimental data better in terms of the values of correlation coefficients  $R^2$  and the theoretical value of maximum adsorption capacity from the Langmuir isotherm (102 mg g<sup>-1</sup>) is close to the experimental data (98 mg g<sup>-1</sup>). Hereby, a dimensionless constant, commonly known as separation factor ( $R_L$ ), defined by Webi and Chakravort<sup>40</sup> can be



**Figure 7.** Freundlich adsorption isotherm for Cu(II) on Cell-g-PGMA-PEI (temperature: 28°C, adsorbent dose: 50 mg, solution volume: 30 mL, pH: 5.0).

Table IV. Langmuir and Freundlich Adsorption Isotherm Constants

	K <sub>F</sub>	n	<i>q</i> <sub>m</sub>	KL	$R^2$
Freundlich model	25.8321	3.8808			0.9757
Langmuir model			102.2495	0.0806	0.9946

Temperature, 28 °C; adsorbent dose, 50 mg; solution volume, 30 mL; pH, 5.0.

represented as eq. (10) where  $K_L$  (L mg<sup>-1</sup>) refers to the Langmuir constant and  $C_0$  is initial concentration of Cu(II) (mg L<sup>-1</sup>).

$$R_L = \frac{1}{1 + K_L C_0}$$
(10)

In this context, lower  $R_L$  value reflects that adsorption is more favorable. In a deeper explanation,  $R_L$  value indicates the adsorption nature to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). Consequently, the  $R_L$  values of Cell-g-PGMA-PEI ranging from 0.01873 to 0.002635 indicate a favorable adsorption of Cu(II) onto Cell-g-PGMA-PEI.

#### **Dynamic Adsorption**

Based on the batch tests of static adsorption, the maximum static adsorption capacity of Cell-*g*-PGMA-PEI obtained from the Langmuir adsorption isotherm is 102 mg g<sup>-1</sup>. However, static adsorption means that the initial concentration of Cu(II) is fixed, and during the adsorption process, the concentration of Cu(II) in solution would keep decreasing until the equilibrium is established.

Whereas, in industrial process, the dynamic adsorption capacity is more important; therefore, the column study for Cu(II) adsorption was performed. The Cu(II) solution (concentration: 300 mg L<sup>-1</sup>) was passed through the column (diameter: 7.5 mm, height: 20 cm) which was filled with 0.2 g adsorbent at a constant flow rate of 90 mL h<sup>-1</sup>. To evaluate the modification of cellulose on the improvement of Cu(II) adsorption, the adsorption capacity of cellulose microcrystalline and Cell-g-



Figure 8. Elution curve of the adsorbent Cell-g-PGMA-PEI after dynamic adsorption (adsorbent dose: 0.2 g, temperature: 28°C, initial pH: 5.0).

PGMA were also investigated. Samples were collected at intervals until the concentration of the effluent from the column is equal to the initial concentration. After that, 0.1 mol  $L^{-1}$  HCl was used as the eluant for desorption, the volume and concentration of the eluant passed through the column were monitored and then the dynamic adsorption capacity was calculated from the amount of the eluant. The desorption curve of column study is presented in Figure 8 where *C* is the Cu(II) concentration of the eluant.

The dynamic adsorption capacity of Cell-g-PGMA-PEI, Cell-g-PGMA, and cellulose microcrystalline were 119, 1.4, and 0.5 mg  $g^{-1}$  for the first cycle and 97.8% of the Cu(II) adsorbed on Cell-g-PGMA-PEI was eluted with 15 mL 0.1 mol L<sup>-1</sup> HCl. Apparently, PEI modification afforded more effective sorption sites<sup>41,42</sup> and hence greatly improved adsorption capacity.

After four adsorption–desorption cycles, the dynamic adsorption capacity remained as high as 97.45 mg g<sup>-1</sup>. High efficiency of adsorption and desorption of Cu(II) proved Cell-*g*-PGMA-PEI as an effective adsorbent for removal and recovery of Cu(II) from aqueous system.

## CONCLUSION

An improved synthesis of cellulose-based adsorbent (Cell-*g*-PGMA-PEI) has been developed employing BPO as initiator to raise the amount of the epoxy groups in the intermediate (Cell-*g*-PGMA) and enhance the subsequent modification with BPEI to achieve better performance in adsorption.

The adsorption of Cu(II) agreed well with Langmuir isotherm and pseudo-second-order kinetic models, and the adsorbent (Cell-g-PGMA-PEI) exhibits satisfactory removal efficiency (above 94%) in a relatively broad scale of pH (3.5–7.0). Based on Langmuir isotherm adsorption model, the monolayer adsorption capacity was determined to be 102 mg g<sup>-1</sup> (temperature: 28°C, initial pH: 5.0) which is largely improved to more than three times that reported in literature ( $q_m = 30 \text{ mg g}^{-1}$ , pH 6.0).<sup>43</sup> Furthermore, the adsorbent could be easily regenerated using 0.1 mol L<sup>-1</sup> HCl as eluant indicating that the novel pathway for the synthesis of Cell-g-PGMA-PEI exhibits significant potential to improve the performance of adsorbents in removal and recovery of Cu(II) from aqueous solution.

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