Carbohydrate Polymers 75 (2009) 110–114

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Adsorption of Cu(II) and Pb(II) onto diethylenetriamine-bacterial cellulose

Wei Shen, Shiyan Chen, Shuaike Shi, Xin Li, Xiang Zhang, Weili Hu, Huaping Wang *

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 2999#, Rinmin North Road, Shanghai 201620, PR China

ARTICLE INFO

Article history:
Received 26 May 2008
Received in revised form 30 June 2008
Accepted 1 July 2008
Available online 9 July 2008

Keywords:
Adsorption
Regeneration
Cu(II)
Pb(II)
Diethylenetriamine-bacterial cellulose

ABSTRACT

Diethylenetriamine-bacterial cellulose (EABC) was synthesized by amination with diethylenetriamine on bacterial cellulose (BC). Its adsorption properties for Cu(II) and Pb(II) were investigated. The parameters affecting the metal ions adsorption, such as contact time, solution pH, and initial metal ions concentration have been investigated. The adsorption kinetics and adsorption isotherms were further studied. The results show that the adsorption rate could be well fitted by pseudo-second-order rate model, and adsorption isotherm could be described by the Langmuir model. The regeneration of EABC was also studied. This study provides the relatively comprehensive data for the EABC application to the removal of metal ion in the wastewater.

1. Introduction

It is very important to remove heavy metals from wastewater before it is drained because of the toxic effect to the health of human being and other living beings. Regarding removal of metal ions from wastewaters, different technologies and processes are currently used, such as: biological treatments, membrane process, advanced oxidation processes, chemical and electrochemical techniques, and adsorption procedures (Chauhan, Chauhan, Chauhan, Kumar, & Kumari, 2007; Vijayaraghavan, Palanivelu, & Velan, 2006). Among these treatments, adsorption is considered to be an effective and economic method which has attracted a considerable interest (Celis, Hermosin, & Cornejo, 2000; Chern & Chien, 2003; Oliveira, Franca, Oliveira, & Rocha, 2008). Lignocellulosic materials and wastes such as peanut skin, cotton, onion skin, rice hulls, maize stalks, barks, jute fibers, bagasse, rice straw, corncobs, and palm kernel husks have received much attention in heavy metal ion removal (Axtell, Sternberg, & Claussen, 2003; Conrad & Hansen, 2007). Various functional groups such as carboxylates, phenolic and aliphatic hydroxyls, and carbonyl groups in these materials have the ability to adsorb some metal ions. To increase the metal ion adsorption of cellulose, it was chemically modified by introducing different complexing groups such as aminoalkyl (Chauhan, Jaswal, & Verma, 2006), 2,2-diaminoethyl, and amidoxime (Saliba, Gauthier, Gauthier, & Petit-Ramel, 2000), or an ionic moiety such as phosphate (Oshima, Kondo, Ohto, Inoue, & Baba, 2008), thiolate (Navarro, Bierbrauer, Mijangos, Goiti, & Reinecke, 2008), carboxy (Li, Yang, Zhao, & Xu, 2007), and carboxymethyl (Pushpamalar, Langford, Ahmad, & Lim, 2006).

As biosynthesized cellulose, Bacterial cellulose (BC) is an extracellular cellulose produced by bacteria of genus Acetobacter (Klemm, Schumann, Udhardt, & Marsch, 2001). The primary structure of BC is similar to that of plant cellulose: an unbranched polymer of β-1, 4-linked glucopyranose residues. However, the fibrous structure of BC is different from that of plant cellulose. BC is composed of microfibrils, which have a ribbon-like structure, and the thickness (0.1×10^{-6} m) is two orders of magnitude smaller than that of plant cellulose (10×10^{-6} m). In addition, the microfibrils retain a fine network structure. Because of its characteristic microstructure, BC has various advantageous properties, such as high tensile strength, elasticity, large surface area, etc. Benefiting from its unique properties, BC has attracted an increased interest in commercial applications over the past few years. Important examples include raw materials for conductive carbon film, products for temporary skin and tissue replacement, separation membrane, calorie-free food such as Coco de Nata, and additives in the production of lattices and paper (Czaja, Young, Kawecki, & Brown, 2007; Iguchi, Yamanaka, & Budhiono, 2000; Klemm, Heublein, Fink, & Bohn, 2005; Pandey, Saxena, & Dubey, 2005; Shah & Brown, 2005; Yano et al., 2005).

BC applied to adsorb metal ions has been reported in the previous literature (Evans, O'Neill, Malyvanh, Lee, & Woodward, 2003), but the adsorption capacity is relatively low from the previous reports (Chen et al., 2008; Oshima et al., 2008). Therefore, it is necessary to modify BC with a better mode in order to increase the adsorption capacity. In this paper, we focused on BC as a starting material to prepare a new adsorbent, diethylenetriamine-bacterial cellulose (EABC), and studied its adsorption properties of Cu(II) and

---

* Corresponding author. Tel.: +86 21 67792958; fax: +86 21 67792726.
E-mail address: wanghp@dhu.edu.cn (H. Wang).

0144-8617/$ - see front matter Crown Copyright © 2008 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.07.006

Pb(II) at different conditions. The effects of the parameters such as pH, and contact time on the adsorption properties were investigated. The adsorption kinetics of the first- and second-order kinetics and Langmuir and Freundlich isotherms were used to evaluate the adsorption process. The effect of regeneration of EABC using ethylenediaminetetraacetic acid (EDTA) on its adsorption capacity was also studied.

2. Experimental

2.1. Materials

BC was prepared in our laboratory according to the method reported by Klemm et al. (2001). Diethylenetriamine, epichlorohydrin, sodium hydroxide, nitric acid, EDTA and the salts of Cu(II) and Pb(II) ($CuSO_4.5H_2O$, $Pb(NO_3)_2$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used for the preparation of the standard solutions for the adsorption tests. The standards for analysis were prepared from stock solutions of 1000 ppm supplied by Shanghai Institute of Measurement and Testing Technology.

2.2. Preparation and characterization of EABC

The treatment of BC in 15% alkaline solution called mercerization was carried out for 1 h at a room temperature, followed by extensive washing with water. Then the mercerized BC (1 g) was put in a round-bottom flask equipped with a magnetic stirring bar. After this, a mixture of epichlorohydrin (3 mL) and 8% alkaline solution (100 mL) was added into the flask. The reaction was carried out at 20 °C for 10 h under stirring. After reaction, the product was washed with deionized water and anhydrous ethanol by turns until pH 7.0 was reached, and finally dried at 60 °C. The treated BC (1 g) was immersed in a mixture of diethylenetriamine (1 g) and deionized water (100 mL), and a desired amount of sodium bicarbonate as a catalyst (10 g/L) was added under continuous stirring at 50 °C for 2 h. After reaction, the product was washed with deionized water and anhydrous ethanol by turns until pH 7, and dried at 60 °C. Finally, white cellulosic ether powder was obtained.

2.3. Fourier transform-infrared (FT-IR) spectroscopy

The powder of BC, EABC, EABC with 43.19 mg/g Cu(II) adsorbed and EABC with 57.20 mg/g Pb(II) adsorbed were dried at 50 °C under vacuum. Subsequently, 1 mg of the samples were mixed with 100 mg of spectroscopy grade KBr, dried at 50 °C under vacuum, and pressed into a small tablet. FT-IR spectra were recorded on a NEXUS-670 Nicolet FT-IR instrument equipped with a MCT detector in the absorption mode with a resolution of 4 cm^{-1}, in the range of 4000–400 cm^{-1}.

2.4. Elemental analysis

The amount of diethylenetriamine grafted on BC was calculated based on the nitrogen content, determined by an elemental analyzer (Germany Elemental Analysensysteme GmbH, Vario EL III).

2.5. Adsorption experiments

EABC (0.01 g) was added to 10 mL of the different buffered metal ions solutions. The pH was adjusted using 0.1 N HNO_3 or 0.1 N NaOH. The mixture was stirred for different times (10–180 min) at room temperature (25 °C). The amount of remaining metal ions was determined by an atomic absorption spectrophotometer (ZEEnit 700, German). The amount of metal ions adsorbed on the adsorbent at adsorption equilibrium was calculated according to the following Eq. (1):

$$q_e = (C_0 - C_e)V/W \tag{1}$$

where C_0 and C_e are the initial and equilibrium metal ions concentrations (mg/L), respectively, V is the volume of the solution (L) and W is the weight of the EABC used (g).

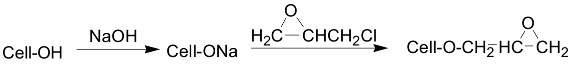
2.6. Regeneration of EABC

Desorption of metal ions from EABC was examined in a 0.1 M EDTA and HCl solution. The EABC was first equilibrated with metal ions in a solution with an initial concentration of 100 mg/L at pH 4.5 (1 g EABC was added into 50 mL metal ions solution). Then, the EABC with metal ions adsorbed was added into 50 mL of the desorption solution. The mixtures were stirred in a water bath shaker at 150 rpm and at 25 °C for 1 h, and samples were taken from the solution to monitor the amount of metal ions desorbed into the solution. After the desorption test, the EABC were separated and washed with deionized water, and reused in the next cycle of adsorption experiment. The adsorption–desorption experiments were conducted for five cycles.

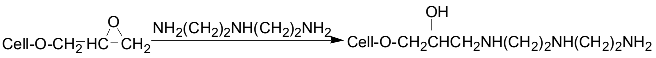
3. Results and discussion

3.1. Preparation and characterization of EABC

Hydroxyl groups of BC reacted with epichlorohydrin under alkaline condition to give an epoxy derivative [Eq. (2)]. EABC was synthesized by treatment of the epoxy derivative with diethylenetriamine [Eq. (3)].



$$\text{Cell-OH} \xrightarrow{\text{NaOH}} \text{Cell-ONa} \xrightarrow{\text{H}_2\overset{\text{O}}{\text{C}-\text{C}}\text{HCH}_2\text{Cl}} \text{Cell-O-CH}_2\text{-H}\overset{\text{O}}{\text{C}-\text{C}}\text{H}_2 \tag{2}$$



$$\text{Cell-O-CH}_2\text{-H}\overset{\text{O}}{\text{C}-\text{C}}\text{H}_2 \xrightarrow{\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2} \text{Cell-O-CH}_2\overset{\text{OH}}{\text{C}}\text{HCH}_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2 \tag{3}$$

Previous studies showed that the transformation of the epoxy group to the amine group increased with the increase of amine concentration and reaction temperature. Also, this transformation increased sharply with time, and then tended toward a steady value after 2 h (Gregorio, 2005). In this study, an optimum condition previously reported by Hassan, El-Wakil, and Sefain (2001) was used to synthesize EABC. Nitrogen content in it is 13.12% by elemental analysis. Under similar reaction condition, a nitrogen content of diethylenetriamine plant cellulose is only 4.12%. The results suggested that the amination (%) can be influenced by the morphology of cellulose. As BC microfibrils are much thinner than fibers of plant cellulose, much more reactive hydroxyl groups on the surface of BC can be functionalized.

3.2. FT-IR spectroscopy

Fig. 1 shows the FT-IR spectra of BC, EABC, EABC with Cu(II) adsorbed and EABC with Pb(II) adsorbed. The major peak located at around 3400 cm^{-1} in BC is attributed to –OH stretching vibration. But in EABC, the peak becomes broad because of the existence of –NH_2. The characteristic band at around 1060 cm^{-1} corresponding to C–O–C stretching is also observed in all the samples. Besides, compared with the spectrum of BC, the increase of broad peak around 1430 cm^{-1} is observed which confirms the existence of –NH in EABC, but it weakens after Cu(II) and Pb(II) adsorption, and the peak at around 3400 cm^{-1} becomes broad and shifts to around 3420 cm^{-1} after Cu(II) and Pb(II) adsorption. This suggests the formation of the complex between metal ions and N atoms (Nakano, Takeshita, & Tsutsumi, 2001).

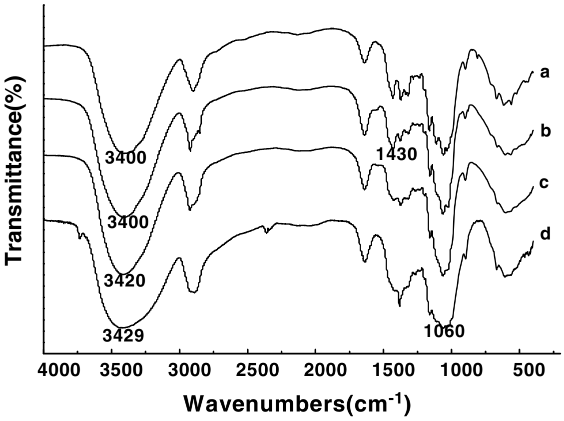


Fig. 1. IR spectra of (a) untreated BC, (b) EABC, (c) EABC with Cu(II) adsorbed, (d) EABC with Pb(II) adsorbed.

3.3. Effect of pH on Cu(II) and Pb(II) adsorption

The most important parameter for the adsorption experiments, effect of pH, was examined. The pH values were varied between 2 ± 0.1 and 5 ± 0.1, keeping the other parameters constant. Fig. 2 shows the influence of pH on the adsorption of Cu(II) and Pb(II) on EABC. The amount of adsorption increases with increasing pH to a maximum value (pH 4.5 ± 0.1). This may be ascribed to the protonation of the amino groups at the acidic conditions (Saliba et al., 2000). But when the pH value is above 4.5, the adsorption capacity declined. The reason may be explained that the very unstable complex between metal ions and the N atom when pH > 4.5 (Shukla, Zhang, Dubey, Margrave, & Shukla, 2002). So in the later experiments, the solution pH on the adsorption test was adjusted to about 4.5.

3.4. Effect of contact time

Fig. 3 shows the effect of contact time on the amount of metal ions adsorbed per gram of EABC at pH 4.5. As shown, the adsorption of the metal ions sharply increases during the first 60 min (92 and 98% of the total amount adsorbed for Cu(II) and Pb(II), respectively). The equilibrium is reached after 2 h of immersion. It is a relatively fast adsorption process (Saliba et al., 2000).

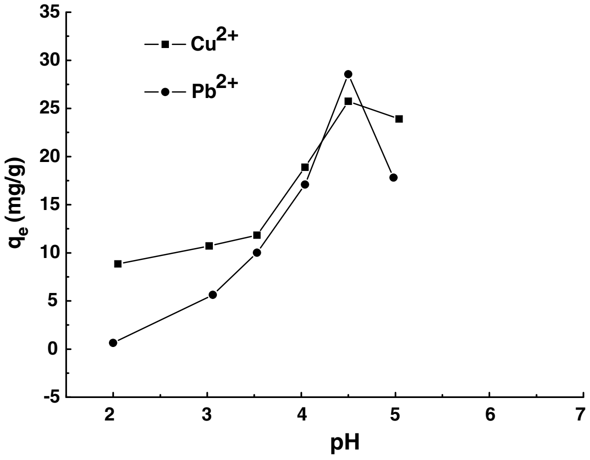


Fig. 2. The effect of pH on the amount of Cu(II), Pb(II) adsorbed onto EABC. Initial metal ion concentration 100 mg/L, pH 2 ± 0.1–5 ± 0.1, amount of EABC 0.01 g.

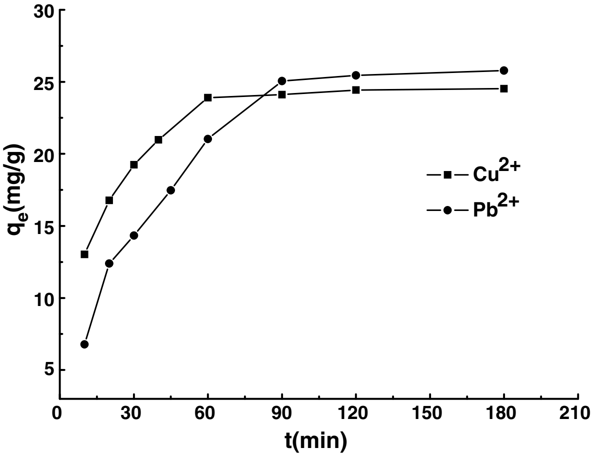


Fig. 3. The effect of contact time on the amount of Cu(II), Pb(II) adsorbed onto EABC. Initial metal ion concentration 100 mg/L, pH 4.5 ± 0.1, amount of EABC 0.01 g.

3.5. Effect of the initial metal ion concentration

Fig. 4 shows the effect of metal ion concentration on the adsorption of the different metal ions at pH 4.5. The figure shows that the amount of metal ions adsorbed increases with an increasing concentration and then tends to level off. The maximum milligrams per gram of metal ions adsorbed is 43.19 and 57.20 mg/g for Cu(II) and Pb(II), respectively. Generally, the adsorption of the metal ions by EABC is in the order: Pb(II) > Cu(II). This order may be because of the different stability of complexes between the different metal ions and the amine groups (Hassan & El-Wakil, 2003). At the present time no data is available about the stability constants of complexes formed between the metal ions studied and the amine derivatives.

3.6. Adsorption kinetics

To examine the underlying mechanism of the adsorption process, several kinetic models are used to test experimental data. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form (Lazaridis & Asouhidou, 2003):

$$dq_t/dt = k_1(q_e - q_t) \tag{4}$$

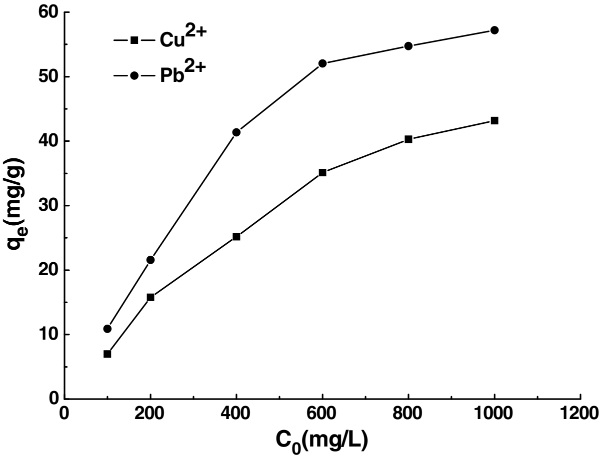


Fig. 4. The effect of metal ion concentration on EABC adsorption. pH 4.5 ± 0.1, amount of EABC 0.01 g, contact time 2 h.

where k_1 is the rate constant of pseudo-first-order adsorption and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (4) becomes

$$-\ln(1 - q_t/q_e) = k_1 t \tag{5}$$

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form

$$\mathrm{d}q_t/\mathrm{d}t = k_2(q_e - q_t)^2 \tag{6}$$

where k_2 is the rate constant of pseudo-second-order adsorption.

Integrating Eq. (6) and applying the initial conditions, we have

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{7}$$

The values of q_e, k_1, and k_2 can be calculated from the slopes and the intercepts of the straight lines and the data are given in Table 1. As shown in the data, the correlation coefficients for the first-order kinetic model are lower than those of the second-order kinetic model. Therefore, the Cu(II) and Pb(II) adsorption onto the EABC belong to the second-order kinetic model and the adsorption is a chemical process.

3.7. Adsorption isotherms

The adsorption data have been subjected to different adsorption isotherms, namely the Freundlich and Langmuir.

3.7.1. Freundlich isotherm

The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of Cu(II) and Pb(II) adsorbed onto EABC at equilibrium, q_e, is related to the concentration of Cu(II) and Pb(II) in the solution, C_e, following (Deng, Bai, & Chen, 2003; Karagoz, Tay, Ucar, & Erdem, 2008):

$$q_e = K_\mathrm{F} C_e^{1/n} \tag{8}$$

This expression can be linearized to give

$$\ln q_e = \ln K_\mathrm{F} + (1/n)\ln C_e \tag{9}$$

where K_F and n are the Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. A plot of $\ln q_\mathrm{e}$ versus $\ln C_e$ would result in a straight line with a slope of $(1/n)$ and intercept of $\ln K_\mathrm{F}$ and the constants are given in Table 2.

3.7.2. Langmuir isotherm

According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once a sorbate occupies a site, no further adsorption can take place at this site. Thus, the Langmuir model is given by the equation (Ho, Chiu, & Wang, 2005):

$$C_e/q_e = C_e/q_m + 1/bq_m \tag{10}$$

where q_m and b, the Langmuir constants, are the saturated monolayer adsorption capacity and the adsorption equilibrium constant, respectively. A plot of C_e/q_e versus C_e would result in a straight line with a slope of $(1/q_\mathrm{m})$ and intercept of $1/bq_\mathrm{m}$ and the calculated data are listed in Table 2. It is found that the maximum adsorption capacity of Cu(II) and Pb(II) are 63.09 and 87.41 mg/g, respectively. The bond energy (b) of Cu(II) and Pb(II) are 0.002 and 0.003 L/mg, respectively. It can be concluded that EABC presents greater adsorption capacity and larger bond energy for Pb(II) than that for Cu(II).

Table 1
Pseudo-first and pseudo-second-order constants and values of R^2 for the adsorption of Cu(II) and Pb(II) onto EABC

Metal ion	Pseudo-first-order model			Pseudo-second-order model		
	C_0 (mg/L)	k_1 (min^{-1})	R_1^2	k_2 (g/mg min)	q_e (mg/g)	R_2^2
Cu(II)	100	0.0765	0.9517	0.0041	26.11	0.9994
Pb(II)	100	0.0284	0.9859	0.0010	31.41	0.9956

Table 2
Isotherm constants and values of R^2 for the adsorption of Cu(II) and Pb(II) onto EABC

Metal ion	Langmuir parameter			Freundlich parameter		
	b (L/mg)	q_m (mg/g)	R^2	K_F (L/g)	n	R^2
Cu(II)	0.002	63.09	0.9962	0.8028	1.68	0.9871
Pb(II)	0.003	87.41	0.9926	0.9952	1.61	0.9824

The Langmuir parameters given in Table 2 can be used to predict the affinity between the sorbate and adsorbent using the dimensionless separation factor R_L (Bhatnagar & Jain, 2005):

$$R_\mathrm{L} = 1/(1 + bC_0) \tag{11}$$

The values of R_L for adsorption of Cu(II) and Pb(II) onto EABC are shown in Fig. 5. They indicate that adsorption of Cu(II) and Pb(II) is more favorable at higher initial metal ion concentrations than at lower ones. Based on the coefficient obtained, it can be concluded that the Langmuir equation gives a better fit to the experimental data than the Freundlich equation.

3.8. Regeneration of EABC

For potential practical application, it is important to examine the possibility of desorbing the metal ions adsorbed on EABC and reusing them (Liu & Bai, 2006). Both EDTA and HCl solutions were examined in the study for EABC. The effect of five adsorption–desorption consecutive cycles on the efficiency of the individual adsorption of Cu(II) and Pb(II) on EABC was studied. Table 3 shows the corresponding desorption efficiencies obtained at EDTA and HCl solutions. For desorption conducted with EDTA solution, it was found that the Cu(II) and Pb(II) adsorbed on EABC were easily desorbed. The desorption efficiency reached about 99% after the first cycle. The desorbed EABC was highly effective for the readsorption of Cu(II) and Pb(II), and the adsorption ability of EABC was kept constant after several repetitions of the adsorption–desorption cycles. For desorption conducted with the HCl solution, the desorption efficiency reached about 90% after the first cycle which is lower than the EDTA solution. And the adsorption capacity reduced significantly after the third cycle. This may be attrib-

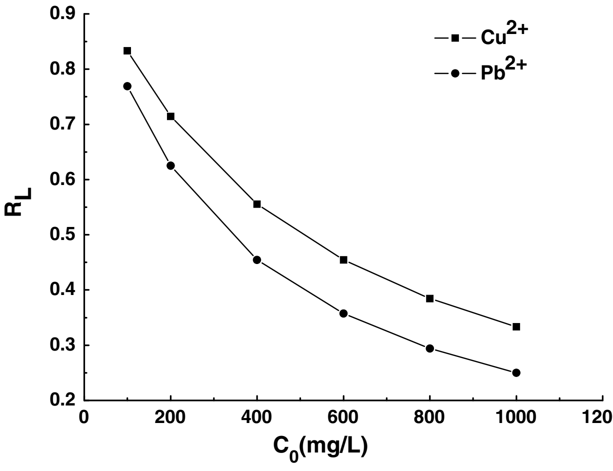


Fig. 5. Separation factor R_L for the adsorption of Cu(II) and Pb(II) onto EABC.

Table 3
Desorption efficiencies of Cu(II) and Pb(II) on EABC from five adsorption–desorption cycles

Cycle number	EDTA solution		HCl solution	
	Desorption percentage (%)		Desorption percentage (%)	
	Cu(II)	Pb(II)	Cu(II)	Pb(II)
1	98.9	99.3	94.2	93.8
2	98.3	97.8	89.3	91.1
3	98.5	97.2	83.6	86.2
4	96.4	96.5	75.6	79.7
5	95.1	95.9	70.1	72.4

uted to the different mechanisms of the two reagents. EDTA can form steady complex with metal ions. However, the desorption took place in the HCl solution mainly due to the ion exchange. It can be conclude that EDTA is a better desorption solution than the HCl solution.

4. Conclusion

In conclusion, EABC was synthesized and characterized by FT-IR and element analysis. The capacity of EABC in adsorption Cu(II) and Pb(II) was investigated. The experimental data showed that the best adsorption performance of EABC for Cu(II) and Pb(II) ions was obtained in solution at pH 4.5 ± 0.1. The adsorption process reached the adsorption equilibrium at about 2 h. The adsorption kinetics closely followed the pseudo-second-order kinetic model, indicating the importance of chemical adsorption in the process. The experimental adsorption isotherm data were well fitted with Langmuir model and the maximum adsorption capacity of Cu(II) and Pb(II) were found to be 63.09, 87.41 mg/g, respectively, in the solution of pH 4.5 ± 0.1. The dimensionless separation factor R_L had shown that EABC could be used for removal of Cu(II) and Pb(II) from aqueous solutions. The prepared EABC could be regenerated successfully without significantly affecting its adsorption efficiency. This study provides the relatively comprehensive data for the EABC application to the removal of metal ion in the wastewater.

Acknowledgements

This work was financially supported by School Fund, New Century Excellent Talents in University (NCET-05-0420) and Shanghai Leading Academic Discipline Project (B603).

References

Axtell, N. R., Sternberg, S. P. K., & Claussen, K. (2003). Lead and nickel removal using Microspora and Lemna minor. *Bioresource Technology, 89*, 41–48.

Bhatnagar, A., & Jain, A. K. (2005). A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water. *Journal of Colloid and Interface Science, 281*, 49–55.

Celis, R., Hermosin, M. C., & Cornejo, J. (2000). Heavy metal adsorption by functionalized clays. *Environmental Science and Technology, 34*, 4593–4599.

Chauhan, G. S., Chauhan, K., Chauhan, S., Kumar, S., & Kumari, A. (2007). Functionalization of pine needles by carboxymethylation and network formation for use as supports in the adsorption of Cr^{6+}. *Carbohydrate Polymers, 70*, 415–421.

Chauhan, G. S., Jaswal, S. C., & Verma, M. (2006). Post functionalization of carboxymethylated starch and acrylonitrile based networks through amidoximation for use as ion sorbents. *Carbohydrate Polymers, 66*, 435–443.

Chen, S. Y., Zou, Y., Yan, Z. Y., Shen, W., Shi, S. K., & Zhang, X., et al. (2008). Carboxymethylated-bacterial cellulose for copper and lead ion removal. *Journal of Hazardous Materials*. doi:10.1016/j.jhazmat.2008.04.09.

Chern, J. M., & Chien, Y. W. (2003). Competitive adsorption of benzoic acid and *p*-nitrophenol onto activated carbon: Isotherm and breakthrough curves. *Water Research, 37*, 2347–2356.

Conrad, K., & Hansen, H. C. B. (2007). Sorption of zinc and lead on coir. *Bioresource Technology, 98*, 89–97.

Czaja, W. K., Young, D. J., Kawecki, M., & Brown, R. M. (2007). The future prospects of microbial cellulose in biomedical applications. *Biomacromolecules, 8*, 1–12.

Deng, S. B., Bai, R. B., & Chen, J. P. (2003). Aminated polyacrylonitrile fibers for lead and copper removal. *Langmuir, 19*, 5058–5064.

Evans, B. R., O'Neill, H. M., Malyvanh, V. P., Lee, I., & Woodward, J. (2003). Palladium-bacterial cellulose membranes for fuel cells. *Biosensors and Bioelectronics, 18*, 917–923.

Gregorio, C. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science, 30*, 38–70.

Hassan, M. L., & El-Wakil, N. A. (2003). Heavy metal ion removal by amidoximated bagasse. *Journal of Applied Polymer Science, 87*, 666–670.

Hassan, M. L., El-Wakil, N. A., & Sefain, M. Z. (2001). Thermoplasticization of bagasse by cyanoethylation. *Journal of Applied Polymer Science, 79*, 1965–1978.

Ho, Y. S., Chiu, W. T., & Wang, C. C. (2005). Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresource Technology, 96*, 1285–1291.

Iguchi, M., Yamanaka, S., & Budhiono, A. (2000). Bacterial cellulose – A masterpiece of nature's arts. *Journal of Materials Science, 35*, 261–270.

Karagoz, S., Tay, T., Ucar, S., & Erdem, M. (2008). Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. *Bioresource Technology, 99*, 6214–6222.

Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition, 44*, 3358–3393.

Klemm, D., Schumann, D., Udhardt, U., & Marsch, S. (2001). Bacterial synthesized cellulose – Artificial blood vessels for microsurgery. *Progress in Polymer Science, 26*, 1561–1603.

Lazaridis, N. K., & Asouhidou, D. D. (2003). Kinetics of sorptive removal of chromium(VI) from aqueous solutions by calcined Mg-Al-CO_3 hydrotalcite. *Water Research, 37*, 2875–2882.

Li, F. T., Yang, H., Zhao, Y., & Xu, R. (2007). Novel modified pectin for heavy metal adsorption. *Chinese Chemical Letters, 18*, 325–328.

Liu, C. X., & Bai, R. B. (2006). Adsorptive removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes. *Journal of Membrane Science, 284*, 313–322.

Nakano, Y., Takeshita, K., & Tsutsumi, T. (2001). Adsorption mechanism of hexavalent chromium by redox with condensed-tannin gel. *Water Research, 35*, 496–500.

Navarro, R., Bierbrauer, K., Mijangos, C., Goiti, E., & Reinecke, H. (2008). Modification of poly(vinyl chloride) with new aromatic thiol compounds. Synthesis and characterization. *Polymer Degradation and Stability, 93*, 585–591.

Oliveira, W. E., Franca, A. S., Oliveira, L. S., & Rocha, S. D. (2008). Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions. *Journal of Hazardous Materials, 152*, 1073–1081.

Oshima, T., Kondo, K., Ohto, K., Inoue, K., & Baba, Y. (2008). Preparation of phosphorylated bacterial cellulose as an adsorbent for metal ions. *Reactive and Functional Polymers, 68*, 376–383.

Pandey, L. K., Saxena, C., & Dubey, V. (2005). Studies on pervaporative characteristics of bacterial cellulose membrane. *Separation and Purification Technology, 42*, 213–218.

Pushpamalar, V., Langford, S. J., Ahmad, M., & Lim, Y. Y. (2006). Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. *Carbohydrate Polymers, 64*, 312–318.

Saliba, R., Gauthier, H., Gauthier, R., & Petit-Ramel, M. (2000). Adsorption of copper(II) and chromium(III) Ions onto amidoximated cellulose. *Journal of Applied Polymer Science, 75*, 1624–1631.

Shah, J., & Brown, R. M. (2005). Towards electronic paper displays made from microbial cellulose. *Applied Microbiology and Biotechnology, 66*, 352–355.

Shukla, A., Zhang, Y. H., Dubey, P., Margrave, J. L., & Shukla, S. S. (2002). The role of sawdust in the removal of unwanted materials from water. *Journal of Hazardous Materials, 95*, 137–152.

Vijayaraghavan, K., Palanivelu, K., & Velan, M. (2006). Biosorption of copper (II) and cobalt (II) from aqueous solutions by crab shell particles.. *Bioresource Technology, 97*, 1411–1419.

Yano, H., Sugiyama, J., Nakagaito, A. N., Nogi, M., Matsuura, T., & Hikita, M., et al. (2005). Optically transparent composites reinforced with networks of bacterial nanofibers. *Advanced Materials, 17*, 153–155.