



A novel starch-based adsorbent for removing toxic Hg(II) and Pb(II) ions from aqueous solution

Li Huang, Congming Xiao*, Bingxia Chen

College of Material Science and Engineering of Huaqiao University, Quanzhou 362021, China

ARTICLE INFO

Article history:

Received 7 February 2011

Received in revised form 28 May 2011

Accepted 30 May 2011

Available online 14 June 2011

Keywords:

Starch
Adsorbent
Synthesis
Toxic metal ions
Removal

ABSTRACT

A novel effective starch-based adsorbent was prepared through two common reactions, which included the esterification of starch with excess maleic anhydride in the presence of pyridine and the cross-linking reaction of the obtained macromonomer with acrylic acid by using potassium persulphate as initiator. The percentage of carboxylic groups of the macromonomer ranged from 14% to 33.4%. The cross-linking degree of the adsorbent was tailored with the amount of acrylic acid which varied from 10 wt% to 80 wt%. Both Fourier transform infrared spectra and thermogravimetric analysis results verified the structure of the adsorbent. The maximum gel fraction and swelling ratio of the adsorbent were about 72% and 6.25, respectively, and they were able to be adjusted with the amount of monomers. The weight loss percentage of the adsorbent could reach 96.9% after immersing in the buffer solution that contained α -amylase for 14 h. It was found that the adsorption capacities of the adsorbent for lead and mercury ions could be 123.2 and 131.2 mg/g, respectively. In addition, the adsorbent was able to remove ca. 51–90% Pb(II) and Hg(II) ions that existed in the decoctions of four medicinal herbs.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

As heavy-metal ions are non-biodegradable and tend to accumulate in living organisms, they are regarded as toxic [1]. It is well-known that the presence of heavy-metal ions such as mercury and lead ions in the environment is one of the serious threats for human health [2]. To solve this issue, various physical and chemical strategies have been developed [3]. Among them, adsorption is recognized as an effective and economic method [1,4]. Therefore, the choice of adsorbent is quite important. An effective and cheap one is certainly preferred.

Polysaccharides such as chitosan, starch, cellulose, alginate, and their derivatives are attractive alternatives as adsorbents due to their effective, low-cost and eco-friendly characteristic [1,5,6]. Starch is an annually renewable and biodegradable agriculturally derived biopolymer. It has been widely applied in various fields because of its inherent properties [7]. A variety of starch derivatives containing amide, amino, phosphate and other groups have been prepared and utilized to remove the metal ions from water for decades [8–12]. Starch-based sorbents can also be obtained by directly generating carboxylic groups at C-6 of anhydroglucose unit

[13]. It is anticipated that the attention on functionalizing starch for this purpose will be paid unceasingly.

Taking what mentioned above into consideration, it is significant to develop a new starch-based adsorbent. The novel adsorbent may be more effective or suitable for some special applications. In this article, starch was functionalized by the combination of esterification and cross-linking reactions. The formed starch-based adsorbent was subsequently applied as an adsorbent to investigate the metal ions' adsorption behavior. The starch-based adsorbent was further used to remove the toxic metal ions from the decoctions of four medicinal herbs. These experimental results are presented and discussed.

2. Experimental

2.1. Materials

Corn starch was dried before use. Maleic anhydride (m.p. 54–55 °C) and potassium persulphate were purified by recrystallizing from benzene and distilled water, respectively. Acrylic acid was purified by soaking with activated carbon. N,N-dimethylformamide, pyridine, xylene orange, 95% ethanol, lead nitrate, mercury nitrate, thiourea, sodium hydroxide, hydrochloric acid, boric acid, acetic acid, sodium dihydrogen phosphate and disodium phosphate were all analytical grade reagents and used as received. Four medicinal herbs including *I. indigotica*, *Angelica*

Abbreviations: SA, the starch-based adsorbents; SA–Pb, SA adsorbing lead ion; SA–Hg, SA adsorbing mercury ion.

* Corresponding author. Tel.: +86 0595 22691357.

E-mail addresses: xcm6305@yahoo.com.cn, congmingxiao@hqu.edu.cn (C. Xiao).

sinensis, honeysuckle and large-head *Atractylodes Rh* were used as received. All agents were purchased domestically.

2.2. Synthesis of the starch-based adsorbent

Firstly, unsaturated starch-based macromonomer was prepared according to the literature [14] by the esterification of starch with maleic anhydride. Briefly, 6 g dry starch was pasted in 7 mL water at 70 °C and then dissolved in 15 mL N,N-dimethylformamide in a 250 mL flask. Meanwhile, 21.6 g maleic anhydride was dissolved in 44 mL N,N-dimethylformamide, and mixed with 22 mL pyridine. The solution of maleic anhydride was added into the flask in droplet under stirring at 30 °C. The mixture was allowed to react for 24 h with agitation at the same temperature. The crude product was precipitated from 95% ethanol and purified by washing with 95% ethanol for three times. The dried light yellow powder was pure macromonomer. The percentage of carboxylic groups of the macromonomer, which is determined by titration, ranged from 14% to 33.4%.

To prepare the starch-based adsorbents (SA) of different cross-linking degrees, 0.5 g macromonomer was dissolved in 5 mL distilled water at 70 °C, initiated with potassium persulphate and reacted with a predetermined amount of acrylic acid for 2 h. The formed solid was washed with water for three times, and dried SA sheets or membranes were obtained. The thickness of SA sheet was around 10 mm.

2.3. Characterizations of starch-based adsorbent

Powdered starch, the macromonomer and SA were mixed with dry KBr and compressed into disk, respectively. Then, Fourier transform infrared spectra of the samples were recorded using a Nexus 470 FTIR spectrometer. Thermogravimetric analysis of starch, the macromonomer and SA were performed with a TA V2.4F thermoanalyzer, which was conducted over the temperature range from 20 to 800 °C with a programmed temperature increment of 10 °C/min under N₂ atmosphere. The Au-coated surface of SA was examined with a Hitachi S-3500N scanning electron microscope.

To evaluate the gel fraction and swelling ratio of SA, dried SA pieces were weighed and placed in vials that contained 5 mL phosphate-buffer saline (0.1 M, pH 7.4) and maintained at 37 °C for 8 h. The samples were removed, blotted up the surface liquid with soft paper to obtain the wet mass W_1 , and then dried to obtain the dry weight W_2 . The gel fraction and swelling ratio of the samples were calculated according to the following formula: swelling ratio = W_1/W_0 , gel fraction = W_2/W_0 , respectively, where W_0 was the initial dry mass. An average of triplicate measurements was taken.

The degradability of SA was examined. The dried and weighed SA pieces were immersed in 5 mL buffer saline that contained 12.5 g/L α -amylase, and maintained at 37 °C for 14 h. At timed intervals, the samples were removed, dried and weighted. The weight loss percentages of the samples were calculated from the initial weight of samples (W_i) and the weight of dried samples (W_d): weight loss percentage (%) = $(W_i - W_d)/W_i \times 100$. An average of triplicate measurements was taken.

For evaluating the metal-ion chelating effect, fluorescence spectra of powdered SA, SA–Pb and SA–Hg (SA–Pb and SA–Hg represent SA adsorbing Pb or Hg ions respectively) were recorded at emission wavelength $\lambda_{em} = 380$ and 485 nm, respectively.

2.4. Adsorption of mercury and lead ions

Adsorption tests were carried out by placing 10 mg SA pieces in 20 mL solution of 100 mg/L Pb²⁺ or Hg²⁺ and kept at 25 °C or 37 °C. At predetermined intervals, 0.2 mL solution was sampled to analyze

the concentration of metal ions with UNICO UV-2800 UV-visible spectrophotometer at 576 and 578 nm, respectively. The adsorption capacities Q (mg/g) of the samples were calculated according to the formula $Q = (C_0 - C)V/W_0$, where C_0 and C ($\mu\text{g/mL}$) were the initial and equilibrium concentration of the metal ion in the solution, respectively, V was the volume (mL) of solution, and W_0 was the initial dry weight of SA (g).

The adsorption selectivity of SA for Pb²⁺ and Hg²⁺ in a binary mixture system was investigated at 37 °C. Firstly, pH of the solution was adjusted to 3.0–3.5 and xylenol orange was added as chelator to determine the total concentration of Pb²⁺ and Hg²⁺, by which the total adsorption capacity Q_t was calculated. In order to know the concentration of Pb²⁺ in the solution, thiourea was added to shield Hg²⁺ and pH was adjusted to 6. The concentration of Pb²⁺ was analyzed by UV spectrophotometry to obtain Q_{Pb} . Q_{Hg} was calculated as $Q_{Hg} = Q_t - Q_{Pb}$.

Reusability of SA was examined as follows. Twenty milliliters of 100 $\mu\text{g/mL}$ Pb²⁺ or Hg²⁺ solution was soaked with 100 mg SA for 3 h at 37 °C under stirring. After adsorption, the adsorbent was washed with distilled water for several times. Ions desorption was carried out by treating with 0.1 mol/L hydrochloric acid [3]. The adsorption–desorption procedure was repeated five times and the concentration of ions was measured by UV spectrophotometry every time.

2.5. Removal of toxic ions from the decoction of medicinal herb

Four decoctions of medicinal herbs were all prepared as follows. Five grams of dry medicinal herb was kept reflux with 100 mL distilled water for 6 h and filtered. The solid residue was kept reflux with 100 mL water for 4 h and filtered. The filtrates were merged and diluted with water until the volume of the solution was 250 mL. A brown clear liquid was obtained. The procedure was almost the same to the usual way to prepare decoction of medicinal herb for patients.

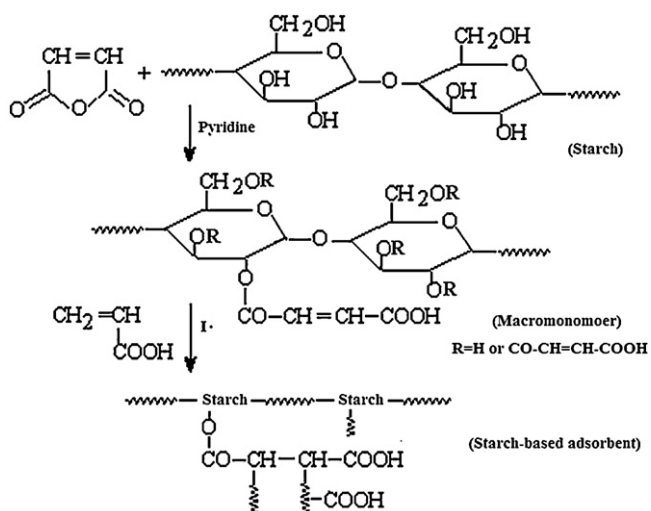
Twenty milliliters of decoction of medicinal herb was treated with 100 mg SA at 37 °C for 4 h. The lead and mercury ions in decoctions of medicinal herb were determined as described above.

3. Results and discussion

3.1. Preparation and characterization of the novel starch-based adsorbent

Scheme 1 presents a facile approach to prepare a novel starch-based adsorbent. The involved esterification and radical cross-linking are two kinds of ordinary reactions, and the chemicals we used are common agents. Moreover, the content of carboxylic groups and the cross-linking degree of the adsorbent are easily to be tailored by simply varying the feeding ratio of reagents. Especially, acrylic acid not only plays as a cross-linker, but also a carboxylic group contributor. In view of these, the synthesis route takes some advantages over the reported ones.

Compared with the Fourier transform infrared spectra of starch, one more characteristic adsorption peak appears at 1734 cm⁻¹ on those of the macromonomer due to the stretching vibration of carbonyl group (Fig. 1). Since the characteristic groups of SA are almost the same to those of the macromonomer, their spectra are similar to each other. As shown in Fig. 2, the remained fractions of starch, the macromonomer and SA at 650 °C are 33.7, 28.7 and 49.6%, respectively. This order is consistent with the microstructure of the samples. The crystallization ability of starch is higher than that of the macromonomer [15]. As a result, the thermal stability of starch is higher than that of the macromonomer. On the other hand, it is the cross-linked structure that greatly improves the ther-



Scheme 1. The preparation procedure of the starch-based adsorbent.

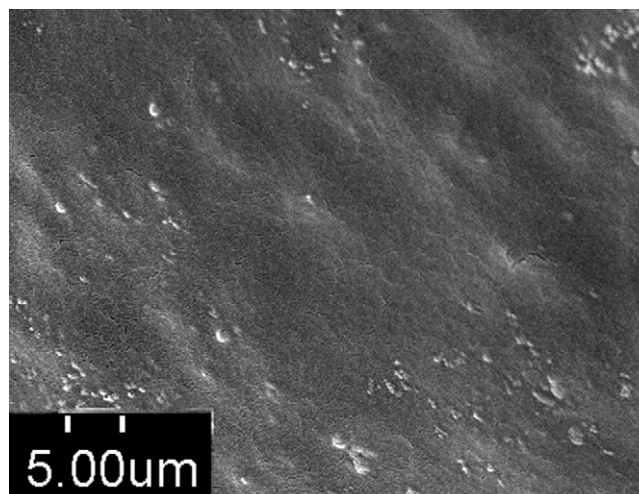


Fig. 3. The surface morphology of the starch-based adsorbent.

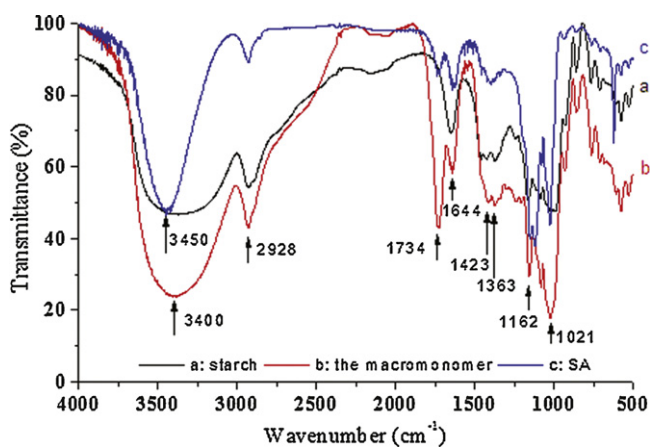


Fig. 1. Fourier transform infrared spectra of starch (a), the macromonomer (b) and the starch-based adsorbent (SA, c).

mal stability of SA. All analysis results indicate the reactions shown in **Scheme 1** are carried out as expected.

Considering the possible effect on the adsorption property, the outer and interior structures of SA sheet are measured. As

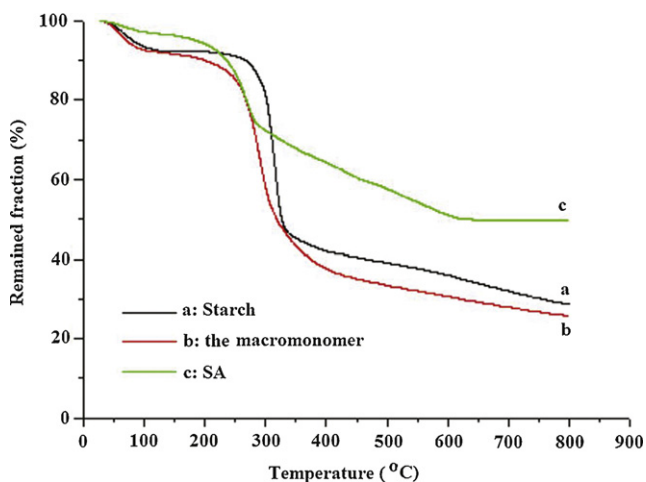


Fig. 2. Thermogravimetric analysis curves of starch (a), the macromonomer (b) and the starch-based adsorbent (SA, c).

observed with scanning electron microscope, there are only a few of cracks on the surface of SA sheet, and it is almost smooth (**Fig. 3**). On the other hand, the swelling ratio and gel fraction of SA reflect the cross-linked structure of SA. SA of higher cross-linking degree absorbs less water and contains fewer water-soluble components, which leads to lower swelling ratio and higher gel fraction. Since the cross-linking reaction is carried out among the unsaturated C=C bonds and the amount of cross-linkable C=C groups of the macromonomer is in direct ratio with its percentage of carboxylic groups, both the cross-linking degree and swelling ratio of SA depend on the percentage of carboxylic groups of the macromonomer and the feeding percentage of acrylic acid (**Figs. 4 and 5**).

As the backbone is biodegradable, the starch-based adsorbent is degradable as well, especially under the enzymatic catalytic action. In addition, maleic acid and acrylic acid fragments that probably formed during the enzymatic degradation are water-soluble, which may accelerate the degradation of SA. As expected, the weight loss percentage of SA ranges from 93.2 to 96.9% (**Fig. 6**). The degradability of SA implies it as an eco-friendly adsorbent.

As known, an efficient adsorbent usually contains plenty of complexing or chelating sites for metal ions [16]. According to **Scheme 1**, lots of carboxylic groups have been incorporated onto starch chains by the strategy adopted to prepare the adsorbent. This is confirmed once more by comparing the fluorescence spectra of SA before and after adsorption. As shown in **Fig. 7**, the fluorescence intensities

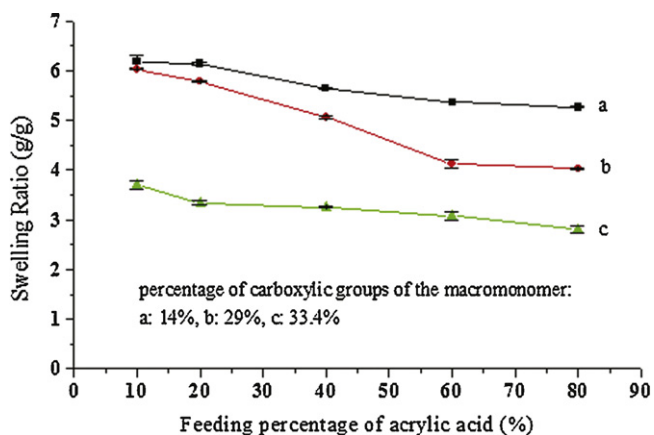


Fig. 4. Effect of feeding percentage of acrylic acid on swelling ratio of the starch-based adsorbents.

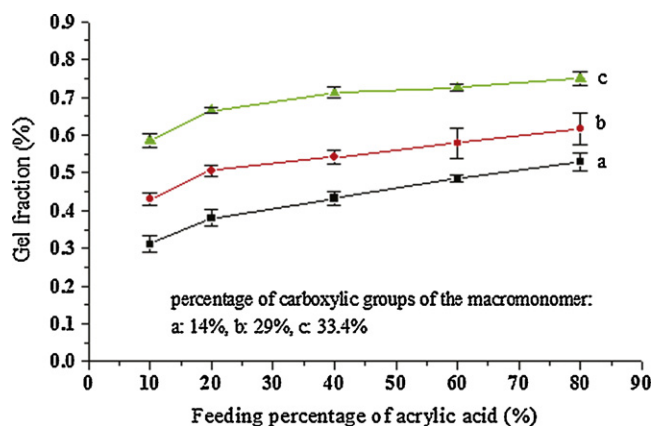


Fig. 5. Effect of the carboxylic group content of the macromonomer and feeding percentage of acrylic acid on the gel fraction of the starch-based adsorbent.

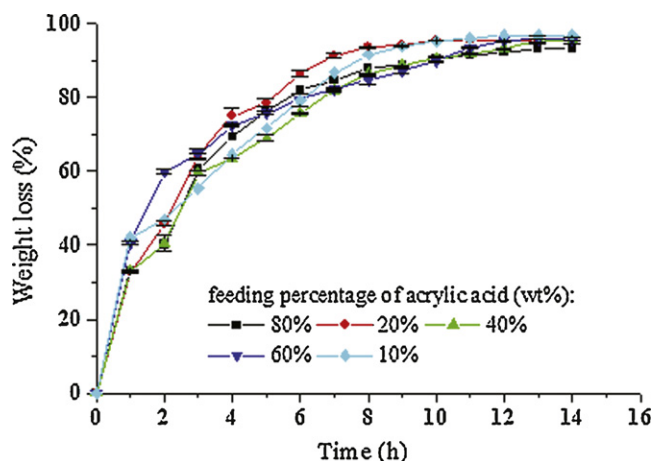


Fig. 6. Degradation of the starch-based adsorbent in phosphate-buffer saline (0.1 M, pH 7.4) containing α -amylase (12.5 g/L) at 37 °C.

of SA-Pb or SA-Hg show gradual enhancement as increasing the amount of chelating metal-ions.

3.2. Adsorption properties of the novel starch-based adsorbent

The driving forces for attaching metal ions to adsorbent include physical and chemical interactions between the ions and the func-

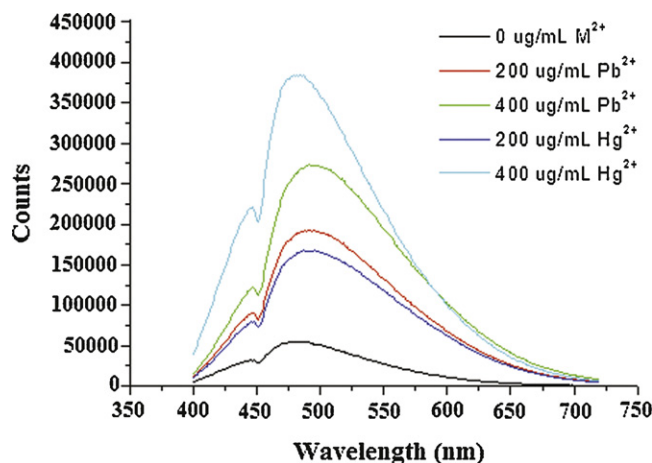


Fig. 7. Fluorescence spectra of the starch-based adsorbents chelating the mercury or lead ions.

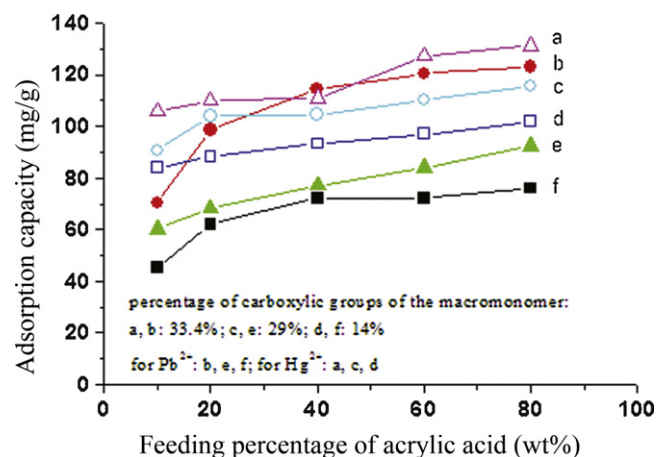


Fig. 8. Effect of the carboxylic group content of the macromonomer and feeding percentage of acrylic acid on the mercury and lead ions' adsorption capacities of the starch-based adsorbent.

tional groups of adsorbent [17]. As mentioned above, SA possesses the ability of binding Pb^{2+} and Hg^{2+} ions. Therefore, it is expectable that SA is a good candidate as adsorbent for these two ions. The adsorption of ions on SA is examined under different conditions. It is found that the adsorption of Pb^{2+} or Hg^{2+} ions on different SA samples can reach equilibrium within 40 min. It is also found that the influence of pH and temperature on the adsorption is neglectable when $pH < 7$ and the examined temperatures is 25 or 37 °C (i.e. ambient and human body temperatures, respectively). In addition, SA that obtained from the macromonomer of higher percentage of carboxylic groups or higher feeding percentage of acrylic acid exhibits higher capacities for Pb^{2+} or Hg^{2+} ions (Fig. 8). The last phenomenon is mainly attributed to more binding sites for ions have been incorporated onto SA. Typically, the adsorption capacities of SA-80, which is prepared by cross-linking the macromonomer that contains 33.4% carboxylic groups with acrylic acid in the ratio of 80:20 (wt%), for Pb^{2+} and Hg^{2+} ions are 123.2 and 131.2 mg/g, respectively.

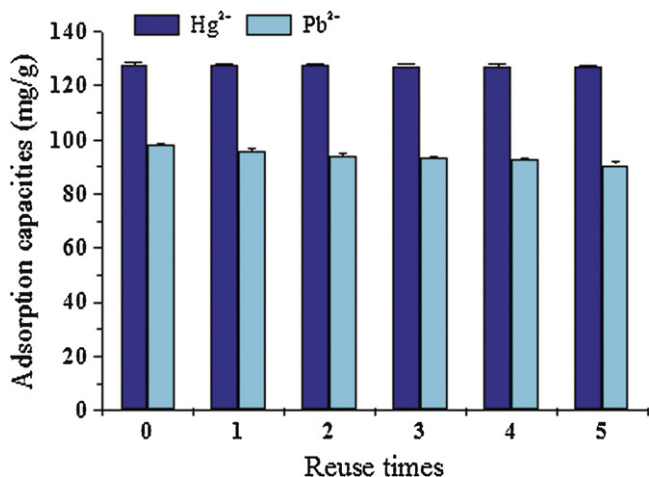
The adsorption capacities of SA-80 for Pb^{2+} and Hg^{2+} in a binary mixture are 100.65 and 57.85 mg/g, respectively, which suggest that there is competitive adsorption between Pb^{2+} and Hg^{2+} ions. The selectivity coefficient $K_{Pb(II)/Hg(II)}$ equals to 1.74, which means that SA adsorbs Pb^{2+} prior to Hg^{2+} from a binary mixture.

As mentioned above, SA is a thin sheet and its surface is basically smooth and dense. Thus, the chelation of carboxylic groups is the primary contribution to the adsorption ability of SA. The ion-exchanging capability of SA is verified with its reusability analysis. It is found that the adsorption capacities of SA after five reuse cycles only decline 7.7 and 0.89 mg/g for Pb^{2+} and Hg^{2+} , respectively (Fig. 9). The change of the adsorption capacity is small, which indicates that the reusability of SA is well enough.

Being inspired with the effective removal of toxic Hg(II) and Pb(II) ions from water, we attempt to apply the adsorbent in the field concerning Chinese medicine. The most important form of traditional Chinese medicine is decoction of medicinal herbal. However, industrial activities have generated significant quantities of contaminants and the contaminants have been introduced into the earth's surface environment including soil and the surface water recently [18]. As a result, excess heavy metal ions exist in a lot of medicinal herbs. It is imaginable that the decoction of medicinal herbal may contain too much lead and mercury ions, and cause potential adverse effects to human health after repeated administration. To deal with this issue, we think it is better to remove the toxic ions from decoction of medicinal herbal before clinical usage.

Table 1The content of mercury and lead ions in the decoctions of four medicinal herbs before and after adsorbing with the starch-based adsorbent.^a

Medicinal herbs	C _{Pb(II)} (mg/kg) ^b			C _{Hg(II)} (mg/kg) ^b		
	Initial	Remained	Removed (%) ^c	Initial	Remained	Removed (%) ^c
<i>Angelica sinensis</i>	20.5	10.025	51.1	20.32	7.05	65.3
Honeysuckle	59.99	14.975	75.0	60.97	6.425	89.5
<i>I. indigotica</i>	40.37	31.85	21.1	56.36	6.975	87.6
Large-head atractylodes Rh	39.66	9.3	76.6	29.1	9.775	66.4

^a 20 mL decoction is treated with 100 mg SA.^b C_{Pb} and C_{Hg} are the content of mercury and lead ions, respectively.^c Removed (%) is calculated as (initial concentration – remained concentration)/initial concentration × 100.**Fig. 9.** Effect of reuse times on the mercury and lead ions' adsorption capacities of the starch-based adsorbent.

Accordingly, four randomly chosen decoctions of medicinal herbals are treated with SA. The content of Pb²⁺ and Hg²⁺ ions in the decoctions of four medicinal herbals before and after disposing are listed in Table 1. As seen, lead or mercury ion contents in four decoctions of medicinal herbals are over the upper limits, 5.0 and 0.2 mg/kg for Pb²⁺ and Hg²⁺ ions, respectively [19]. About 51.5–89.5% Pb²⁺ and Hg²⁺ ions are removed by the current disposal, except 21.1% Pb²⁺ is removed from indigotia. It is anticipated that the toxic ions-content of decoction of medicinal herbal can be lower than the limit by increasing the amount of SA or the disposing times. Thus, SA is an effective adsorbent for purifying decoction of medicinal herbal.

4. Conclusions

A novel starch-based cross-linked adsorbent is synthesized from renewable natural starch and some common chemical reagents via two common reactions. The structure of the adsorbent can be tailored by changing the feeding ratio of reagents. As a result, the adsorption ability of the adsorbent is easily modulated. Owing to the incorporation of plenty of carboxylic groups, such an adsorbent is able to remove lead and mercury ions efficiently. In addition, the adsorbent is successfully utilized to remove most of toxic Pb²⁺ and Hg²⁺ ions from decoctions of four medicinal herbals. The degradable, effective and cheap characters make this starch-based adsorbent a promising candidate for decontaminating aqueous solutions such as drinking water, decoction of herbal medicine and the others.

Acknowledgements

This work is supported by the Natural Science Foundation of Fujian Province of China (No. 2010J01291 or E1010026) and the Basic Research Item of Central Universities (JB-JD1001).

References

- [1] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.* 30 (2005) 38–70.
- [2] M. Özacar, İ.A. Sengil, H. Türkmenler, Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin, *Chem. Eng. J.* 143 (2008) 32–42.
- [3] L. Önnby, C. Giorgi, F.M. Plieva, B. Mattiasson, Removal of heavy metals from water effluents using supermacroporous metal chelating cryogels, *Biotechnol. Prog.* 26 (2010) 1295–1302.
- [4] A.R. Hajjipour, S. Habibi, A.E. Ruoho, Modification of polyacrylic acid using calix[4]arene derivative for the adsorption of toxic heavy metals, *J. Appl. Polym. Sci.* 118 (2010) 818–826.
- [5] K.R. Krishnapriya, M. Kandaswamy, A new chitosan biopolymer derivative as metal-complexing agent: synthesis, characterization, and metal(II) ion adsorption studies, *Carbohydr. Res.* 345 (2010) 2013–2022.
- [6] S.K. Papageorgiou, F.K. Katsaros, E.P. Kouvelos, N.K. Kanellopoulos, Prediction of binary adsorption isotherms of Cu²⁺, Cd²⁺, and Pb²⁺ on calcium alginate beads from single adsorption data, *J. Hazard. Mater.* 162 (2009) 1347–1354.
- [7] D.R. Lu, C.M. Xiao, S.J. Xu, Starch-based completely biodegradable polymer materials, *eXPRESS, Polym. Lett.* 6 (2009) 366–375.
- [8] M.I. Khalil, S. Farag, Utilization of some starch derivatives in heavy metal ions removal, *J. Appl. Polym. Sci.* 69 (1998) 45–50.
- [9] L. Guo, C.M. Sun, G.Y. Li, C.P. Liu, C.N. Ji, Thermodynamics and kinetics of Zn(II) adsorption on crosslinked starch phosphates, *J. Hazard. Mater.* 161 (2009) 510–515.
- [10] A. Dong, J. Xie, W. Wang, L. Yu, Q. Liu, Y. Yin, A novel method for amino starch preparation and its adsorption for Cu(II) and Cr(VI), *J. Hazard. Mater.* 181 (2010) 448–454.
- [11] G.X. Xing, S.F. Zhang, B.Z. Ju, J.Z. Yang, Study on adsorption behavior of crosslinked cationic starch maleate for chromium(VI), *Carbohydr. Polym.* 66 (2006) 246–251.
- [12] B.S. Kim, S.T. Lim, Removal of heavy metal ions from water by crosslinked carboxymethyl corn starch, *Carbohydr. Polym.* 39 (1999) 217–223.
- [13] K. Chauhan, G.S. Chauhan, J.H. Ahn, Novel polycarboxylated starch-based sorbents for Cu²⁺ ions, *Ind. Eng. Chem. Res.* 49 (2010) 2548–2566.
- [14] F.C. McIntire, J.R. Schenck, Polysaccharides acid esters as cation exchange media, *J. Am. Chem. Soc.* 70 (1948) 1193–1194.
- [15] C.M. Xiao, J. Ye, Preparation of the carboxylic derivatives of starch with maleic anhydride, *Chin. J. Appl. Chem.* 22 (2005) 643–646 (in Chinese).
- [16] D.K. Kweon, J.K. Choi, E.K. Kim, S.T. Lim, Adsorption of divalent metal ions by succinylated and oxidized corn starches, *Carbohydr. Polym.* 46 (2001) 171–177.
- [17] S.Y. Chen, W. Shen, F. Shen, F. Yu, W.L. Hu, H.P. Wang, Preparation of amidoximated bacterial cellulose and its adsorption mechanism for Cu²⁺ and Pb²⁺, *J. Appl. Polym. Sci.* 117 (2010) 8–15.
- [18] C.Y. Yin, Emerging usage of plant-based coagulants for water and wastewater treatment, *Process Biochem.* 45 (2010) 1437–1444.
- [19] The executive commission of the pharmacopoeia commission of China, in: *Chinese Pharmacopoeia (Volume I)*, People's Medical Publisher, Beijing, 2005.