Preparation of a Novel Adsorbent and Heavy Metal Ion Adsorption

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ABSTRACT

The article focuses on the preparation of a novel adsorbent by grafting amino-terminated hyperbranched polymer to cotton fibers and the adsorption of heavy metal ions from aqueous solution. The prepared novel adsorbent was characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The experimental results show that the amino-terminated hyperbranched polymer was grafted to the oxidized cotton fibers, and the adsorbent with amino-terminated hyperbranched polymer was successfully obtained. The grooves on the surface of the grafted cotton fiber were filled with amino-terminated hyperbranched polymer. The adsorption experiments show that the adsorption amount of Cu^{2+} and Pb^{2+} was up to 16.1 mg/g and 13.4 mg/g with the metal ion concentration of 319.5 ppm and 315.9 ppm, respectively. When the dosage of adsorbent was 1.5 g in 100 mL metal ion solution, the adsorption rate of Cu^{2+} and Pb^{2+} reached 73.5 wt. % and 71.2 wt.%, respectively. The use of the adsorbent for the removal of metal ions is considered to be efficient and have great potential for practical applications.

Keywords: Adsorbent, Hyperbranched polymer, Adsorption, Heavy metals.

INTRODUCTION

With rapid economic development among many different industries, such as metal plating, smelting, mining, pigment, and metallurgical industries, more and more heavy metals are poured into rivers with wastewater [1,2,3]. The presence of elevated concentrations of heavy metals in the environment poses a serious threat to human health and other living beings due to their nondegradability and toxicity [4,5]. Even at low concentrations, heavy metals can also be toxic to organisms, including humans [6,7].

A number of studies have shown that cellulosic materials can adsorb metal ions, and by the introduction of functional groups into cellulosic substrates, the adsorptive amount for metal ions may be enhanced [8,9]. Ighodalo C. et al. [8] prepared Cell-PAN as a kind of adsorbent for metal ions. The study shows that the adsorption rate reached 44% and 56% for Zn^{2+} ion and Cr^{3+} ion, respectively. Claudinei F. Teixeira et al.[10] prepared COTALPy, a new adsorbent based on cotton fiber. The study shows that the maximum adsorption capacities of Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} and Fe^{2+} were 0.20 mmol/g, 0.18 mmol/g, 0.35 mmol/g, 0.22 mmol/g and 0.68 mmol/g, respectively. However, there were few studies focused on the modification of cellulose using hyperbranched polymers. Hyperbranched polymers have abundant functional groups that can be tailored, with respect to functionality and polarity, to adjust the properties for certain applications [11]. Cellulose is the most abundant compound in nature's biomass. Therefore, the adsorbent of heavy metal ions prepared from cellulosic materials have both good benefits in the economy and broad prospects in application.

In this paper, activated cotton fibers were obtained by the pretreatment of normal cotton fibers using a sodium hydroxide solution. The activated cotton fibers were, in turn, oxidized with sodium periodates solution to create oxidized cotton, which was later grafted by an amino-terminated hyperbranched polymer solution.

In this work, the influences of different heavy metal ions, contact time, and heavy metal ion concentration on the adsorption of the grafted cotton fibers were investigated. The influences of the different masses of adsorbent on adsorption rate were also studied, and the morphology, the chemical structure of the adsorbent was characterized by Fourier Transform Infrared Spectroscope (FT-IR), and Scanning Electronic Microscopy (SEM).

EXPERIMENTAL

MATERIALS

The cotton fibers were obtained from Suzhou Yintong Cotton Industry Co., Ltd (Suzhou, China). Sodium hydroxide, sodium periodate, methyl acrylate, tetraethylenepentamine, methanol, salicylaldehyde, pyridine ， sodium methoxide, phenolphthalein, copper(II) chloride dehydrate, and lead (II) chloride were all analytical grade, and were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

METHODS

Treatment of Cotton Fiber

Cotton fibers were scoured by steeping them in sodium hydroxide solution (2 wt.%), with a bath ratio of 1:50, at 95℃, for 90 minutes [12], were washed with deionized water several times to remove the sodium hydroxide, and were dried in an oven at 90℃. After scouring, cotton fibers were then activated with sodium hydroxide solution (18 wt.%), with a bath ratio of 1:30, at 20±1℃, for two hours [13], were washed with deionized water several times to remove the sodium hydroxide, and were dried in an oven at 90℃ (activated cotton fiber). Purified cotton fibers were oxidized with sodium periodate solution (2 wt.%), with a bath ratio of 1:50, at 70℃, for three hours, were washed with deionized water several times to remove the oxidant, and dried in vacuum oven (oxidized cotton fiber).

Preparation of Amino-Terminated Hyperbranched Polymer

Amino-terminated hyperbranched polymer was synthesized, according to the method described by Feng Zhang et al. [14], by reacting tetraethylenepentamine (0.5mol) with methyl acrylate (0.5mol).

Preparation of Adsorbent

Cotton fibers oxidized with sodium periodate solution were grafted by amino-terminated hyperbranched polymer solution (2 wt.%), with a bath ratio of 1:50, at 60℃, for 2 hours. The grafted cotton fibers were washed with deionized water several times to remove unreacted amino-terminated hyperbranched polymer, and freeze-dried to constant weight.

Amino Content Test

Amino content of the adsorbent was tested by the salicylaldehyde method [15]. 10 mL salicylaldehyde pyridine standard solution (0.5 M) was added into a 250 mL iodine flask with 0.1 g adsorbent. After reacting for four hours at room temperature, 1 mL phenolphthalein pyridine standard solution (1 wt.%) was added. Then the above mixed solution was titrated with sodium methoxide pyridine standard solution (0.4233 M) until dark blue, the volume of sodium methoxide solution used was recorded. A blank experiment was done at the same time. The amino content (wt.%) of adsorbent was calculated by using the following equation:

$$-NH_2(\%)=\frac{(V_0-V_1)\times N\times M}{1000\times W}\times 100\% \quad (1)$$

Where V_0 is the volume of sodium methoxide pyridine standard solution (0.4233 M) consumed by 10 mL salicylaldehyde pyridine standard solution (0.5 M); V_1 is the volume of sodium methoxide pyridine standard solution (0.4233 M) consumed by 10 mL salicylaldehyde pyridine standard solution (0.5 M) reacted with 0.1 g adsorbent; N is the concentration of sodium methoxide pyridine standard solution (0.4233 M); M is the molecular weight of primary amine (g/mol); and W is the mass of the adsorbent (g).

Fourier Transform Infrared (Ft-Ir)

The activated cotton fibers, oxidized cotton fibers, and grafted cotton fibers were cut into micron-size powder, and then, samples were prepared in KBr pellets. FT-IR spectra were obtained with a Nicolet 5700.

Scanning Electron Microscopy (SEM)

The surface morphology of oxidized cotton fibers and grafted cotton fibers were observed by a HITACHI.S-570 scanning electron microscopy.

Sorption Of Heavy Metal

All solutions were prepared in deionised water. Around 300ppm Cu^{2+} and Pb^{2+} stock solution were prepared by dissolving $CuCl_2\cdot 2H_2O$ and $PbCl_2$,

respectively. In each case, 0.2 g adsorbent was added into 100 mL heavy metal ions solution, at room temperature, and continuously vibrated. After the schedule time, the aqueous phase was separated from the sample, by filtration. Concentrations of heavy metal ions of the initial and the remaining solutions were carried out by an inductively coupled plasma atomic emission spectrometer (ICP-OES).

The adsorption amounts (q_e) (mg/g) of adsorbent were calculated by using the following equation:

$$q_e = [(C_0 - C)V]/(1000m) \quad (2)$$

Where C_0 and C are the initial and the equilibrium concentration (ppm) of the metal ions, respectively; while V is the volume of the solution (mL); and m is the mass of adsorbents used (g).

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-OES)

Heavy metal concentration of the initial and adsorbed solutions was measured by a Vista MPX inductively coupled plasma atomic emission spectrometer (ICP-OES).

RESULTS AND DISCUSSION

Preparation and Characterization of the Adsorbent

The preparation of the adsorbent is summarized in *Figure 1* (N refers to the multi-amino chemical chain extension). The cotton fibers were first oxidized by sodium periodate to cleave the 2, 3-vicinal diol of the cellulose glucose units to achieve the oxidized cotton fibers [16]. After that, the oxidized cotton fibers were grafted by the amino-terminated hyperbranched polymer solution, and aldehyde groups of the oxidized cotton fibers reacted with the amino groups of the amino-terminated hyperbranched polymer to obtain the adsorbent [17]. Amino content of the adsorbent was 8.13%.

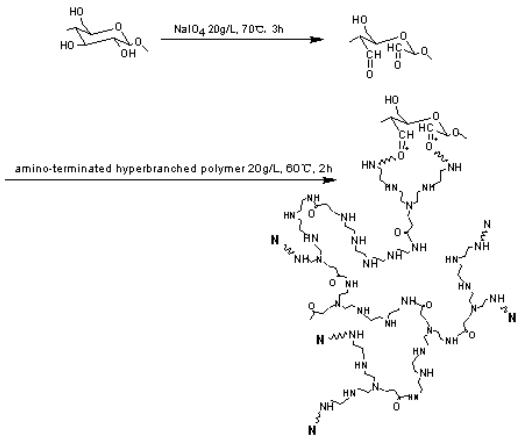

FIGURE 1. Preparation route used to obtain adsorbent.

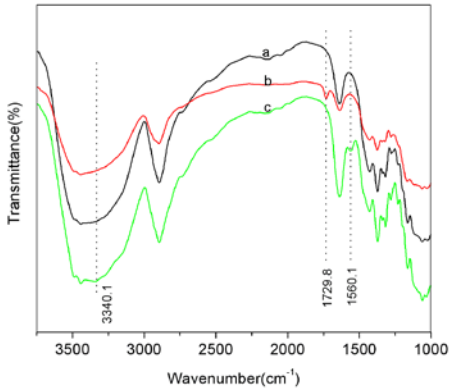

FIGURE 2. FT-IR spectrums of fibers: a- activated cotton fibers; b- oxidized cotton fibers; c- grafted cotton fibers.

The reaction was verified by the Fourier transform infrared spectrum. *Figure 2* shows the infrared spectrograms of the activated cotton fibers, oxidized cotton fibers, and grafted cotton fibers. In the infrared spectrum of the oxidized cotton fibers, the absorbance band at 1729.8 cm^{-1}, assigned to the stretching vibration of the $\sigma_{C=O}$ double band of the aldehyde group, which indicates the hydroxyls on the cellulose were oxidized into aldehyde groups. The absorbance bands at 1560.1 cm^{-1} and 3340.1 cm^{-1} of the grafted cotton fibers correspond to the δ_{N-H} and γ_{N-H} of the primary amine of the amino-terminated hyperbranched polymer, which indicates amino-terminated hyperbranched polymer was grafted to the oxidized cotton fibers, and the adsorbent with amino-terminated hyperbranched polymer was successfully obtained.

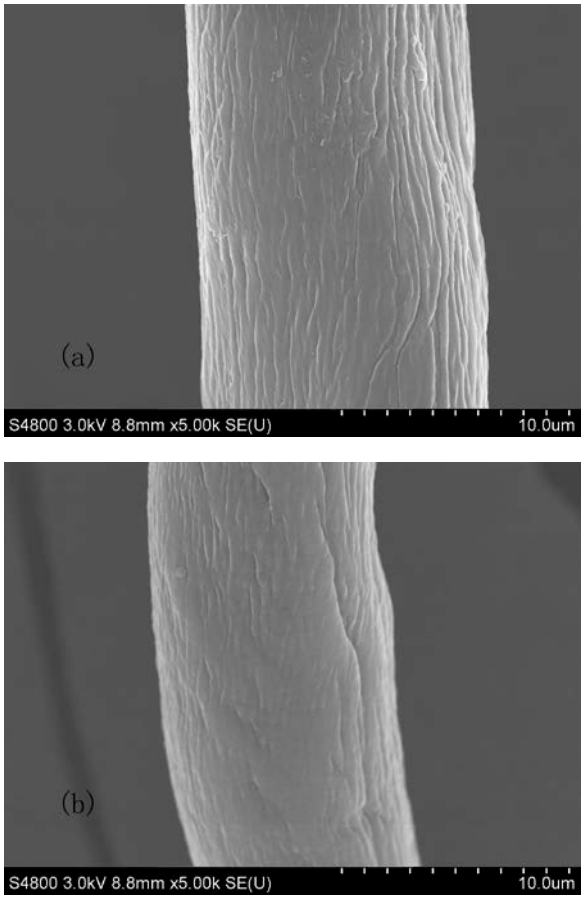

FIGURE 3. SEM image of oxidized cotton fiber (a) and grafted cotton fiber (b).

It can also be concluded that amino-terminated hyperbranched polymer was successfully grafted to the surface of the cotton fiber based on the SEM image (*Figure 3*). After grafting, the surface of the grafted cotton fiber did not resemble the surface of the oxidized cotton fiber. The surface of the oxidized cotton fiber had many grooves on it because of the oxidation and hydrolysis of the cellulose macromolecule chains, while the grooves on the surface of the grafted cotton fiber were filled up with amino-terminated hyperbranched polymer.

ADSORPTION OF HEAVY METAL IONS

Adsorption properties of adsorbent, which were prepared from oxidized cotton fibers modified by amino-terminated hyperbranched polymer, were studied by varying heavy metal ions, contact time, and heavy metal ion concentrations. Samples of 0.2g adsorbent were placed into Erlenmeyer flasks containing 100 mL of Cu^{2+} and Pb^{2+} metal ion solution of known concentration around 100ppm, 200ppm, 300ppm, respectively. Contact time was selected 30 min, 60 min, 90 min, 120 min, 180 min, 240 min, 360 min and 480 min, respectively.

In order to investigate the effect of contact time on the adsorption amount, the experiments were carried from 30 min to 480 min. *Figure 4* shows the changes of the amount of metal ion adsorption with the increasing of contact time. It can be observed that the amount of metal ion adsorption increased with the increasing of contact time, and reached the adsorption equilibrium at 240 min, to a maximum adsorption amount. After that, increasing the amount of contact time had no effect on the amount of metal ion adsorption.

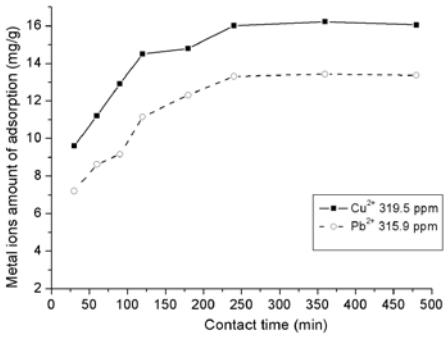

FIGURE 4. Metal ions amount of adsorption at different contact time.

Adsorption rates of adsorbent were studied by varying the mass of adsorbent by 0.25 g, 0.5 g, 0.75 g, 1 g, 1.25 g and 1.5 g, respectively, in 10.3 ppm 100 mL Cu^{2+} solutions and 9.8 ppm 100 mL Pb^{2+} solutions at room temperature for 240 min. *Figure 5* shows the changes of adsorption rate with the increasing of mass of the adsorbent. It can be observed that the adsorption rates increased with the increasing mass of adsorbent. When the dosage of adsorbent was 1.5 g, the adsorption rate of Cu^{2+} and Pb^{2+} reached 73.5 wt.% and 71.2 wt.%, respectively.

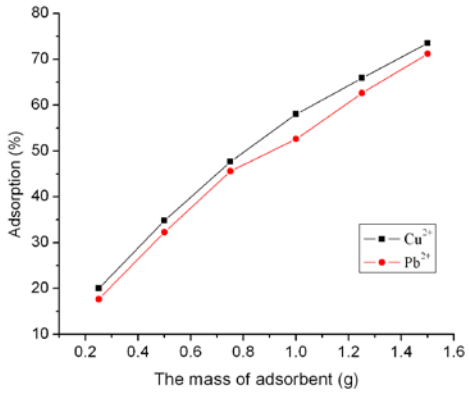

FIGURE 5. Adsorption rate at different mass of adsorbent.

The amino groups present on the adsorbent were responsible for the binding of heavy metal ions. Adsorbent with abundant amino groups could have chelated with heavy metal ions by releasing hydrogen ions, and free amino groups also could attract the positively charged heavy metal ions [18]. The mechanism of heavy metal ions adsorption is showed in *Figure 6*. A^+ refers to heavy metal ions, such as Cu^{2+} and Pb^{2+}.

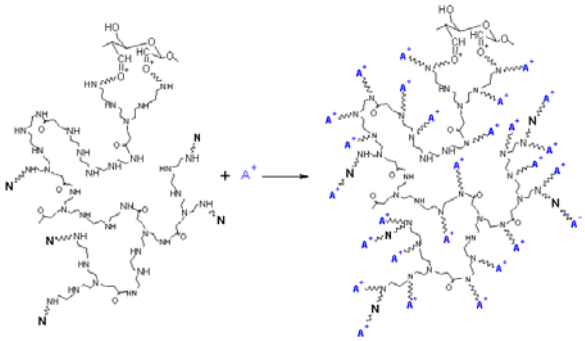

FIGURE 6. Mechanism of heavy metal ions react with adsorbent.

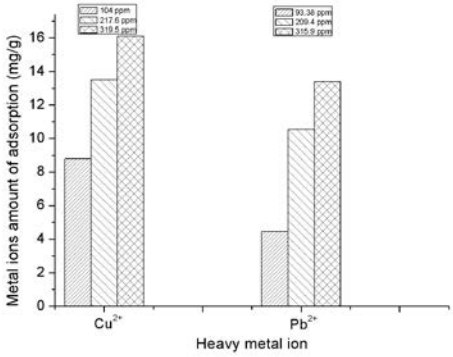

FIGURE 7. Adsorption amount of metal ions under different concentration by the adsorption of 240 min.

Figure 7 shows the adsorption amount of two different kinds of metal ions under different metal ion concentrations by the adsorption for 240 min. The results showed that the adsorption amount increased with the heavy metal ions concentration increasing. The adsorption amount of Cu^{2+} and Pb^{2+} was up to 16.1 mg/g and 13.4 mg/g with the metal ion concentration of 319.5 ppm and 315.9 ppm, respectively.

CONCLUSION

In this study, a novel adsorbent was successfully prepared by grafting amino-terminated hyperbranched polymer to the surface of the cotton fibers. The adsorbent was characterized by a Fourier transform infrared spectrum, scanning electron microscope, which indicated that the adsorbent was successfully obtained. The adsorption experiment shows that the adsorption amount of Cu^{2+} and Pb^{2+} was up to 16.1 mg/g and 13.4 mg/g with the metal ion concentration of 319.5 ppm and 315.9 ppm, respectively. When the dosage of adsorbent was 1.5 g in 100 mL metal ion solution, the adsorption rate of Cu^{2+} and Pb^{2+} reached 73.5 wt.% and 71.2 wt.%, respectively. The use of the adsorbent for the removal of metal ions is considered to be efficient and have great potential for practical applications.

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