

Synthesis and application of cotton-based chelate fibers grafted with poly(1-vinyl-1,2,4-triazole) side chains

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ABSTRACT: Cotton-based chelate fibers grafted with poly(1-vinyl-1,2,4-triazole) (PVTAZ) side chains were synthesized facilely by ozone-induced graft polymerization of 1-vinyl-1,2,4-triazole (VTAZ) monomer onto cotton fibers. The synthesis conditions were optimized to improve the yield and mechanical strength of the products. The obtained cotton-g-PVTAZ fibers were characterized and evaluated for batch adsorption of heavy metal ions from aqueous solutions. The maximum adsorption capacity of Ag(I), Pb(II), and Cu(II) on the fibers at pH 6.8 was 522, 330, and 184 mg/g, respectively. At 30% graft yield, the Young's modulus of cotton fiber increased about 26.5%, and its adsorption capacities of Ag(I), Pb(II), and Cu(II) increased about 2.6, 1.9, and 1.4 times, respectively. After washed with 0.1 mol/L HNO₃ solutions, the adsorbed metal ions were eluted, and the regenerated cotton-g-PVTAZ fibers could be used repeatedly for water treatment. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41617.

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INTRODUCTION

Rapid industrialization and urbanization in developing countries like China make environment pollution a serious problem today.¹ Of all the problems of environmental pollution, the pollution of the ecosystem by heavy metals is of special concern because metals cannot undergo biological degradation like organic pollutants and persist in the ecosystem having accumulated in different parts of the food chain.^{2,3} Although there are many methods for removal of heavy metals from wastewater, physical adsorption is revealed a highly effective and economic technique.⁴ A number of chelate adsorbents with coordination atoms such as N, O, and S have been researched extensively. The adsorbents are generally gelling spherical resins and have to be packed into a fluid-bed or column for use. As the adsorption rate of these adsorbents for metal-ions is not particularly large, the throughput for the separation is sometimes insufficient.

To overcome these disadvantages, chelate fibers immobilizing functional groups or polymeric side chains have been developed.^{5,6} Due to having a much smaller diameter and larger surface area than the spherical adsorbent resin, the chelate fiber possesses a high adsorption speed and capacity. Furthermore, the application of chelate fiber is very convenient, because it can be woven or knitted to various shapes.

Among the copolymerization methods to prepare chelate fibers, grafting functional polymer onto natural or synthetic fiber skel-

eton is revealed a highly effective and convenient technique.^{7–10} Free radical polymerization of functional monomers are often used in the grafting process, in which radicals are formed along the fibrous backbone by either chemical means^{11–14} or irradiation.^{15,16} Although a lot of fibers including poly(ethylene terephthalate), nylon-6, polypropylene, ramie, and wool have been used as raw materials for the grafting modification,^{17–21} cotton is always an attractive option for having several unique properties.^{15,22} For example, cotton fiber is hydrophilic due to having carboxylic acid groups and hydroxyl groups in the structure,²³ which can be used to generate peroxides under the treatment of surface ozonization.¹³ The generated peroxides are capable of initiating polymerization of vinyl monomers at decomposition temperature, resulting in polymer grafting onto the ozonated cotton fibers. A few grafted polymer side chains need to be further modified to make them more effective in coordination with heavy metal ions.²⁴

In this work, we report on the synthesis and application of cotton-based chelate fibers grafted with poly(1-vinyl-1,2,4-triazole) (PVTAZ) side chains. As the functional monomer, 1-vinyl-1,2,4-triazole (VTAZ) possesses an electron-rich aromatic ring with nitrogen atoms available for metal ion coordination.^{25,26} Surface ozonization method followed by a free radical polymerization of VTAZ aqueous solution was used to graft PVTAZ onto the cotton fibers. The graft process is simple and the graft

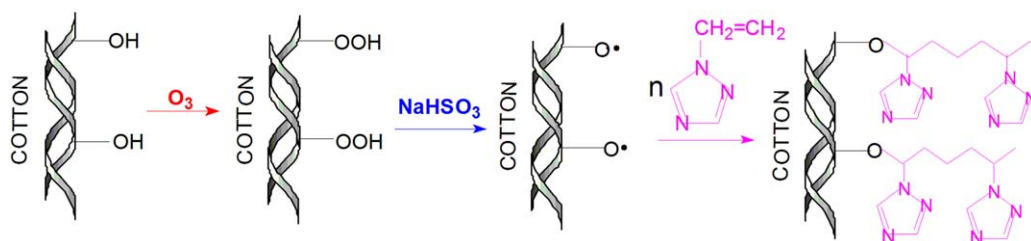


Figure 1. Schematic illustration of surface graft copolymerization of VTAZ on cotton fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

yield is facile to control. These points will become big merits in the industrial production of the adsorbent.⁵ The structure and properties of the obtained chelate fibers were characterized and discussed preliminarily.

EXPERIMENTAL

Materials

Cotton yarn fiber was obtained from the Jiamian Group (China). VTAZ was synthesized according to a procedure reported elsewhere.²⁶ 2,2'-Azobis(isobutyronitrile) (AIBN, 97%) was provided by Kanto Chemical and was recrystallized from methanol before use. Standard Cu(II), Pb(II), and Ag(I) solutions (1.0 mg/mL in 2% HNO₃) were purchased from Aldrich. Metal ion solutions in various pH conditions were prepared by directly diluting 1.0 mg/mL metal ion solution. Hydrochloric acid (37%), sodium hydroxide (96%), and sodium hydrogen sulfite (98%) were purchased from Sinopharm Chemical Reagent Company. Other chemicals were commercial products and used as received. Deionized water was used in all of the experiments.

Preparation of Cotton-g-PVTAZ Fiber

The process of surface activation, ozone treatment, and graft copolymerization of cotton fiber was shown schematically in Figure 1. Cotton yarn (5–10 mm in length, 1.0 g) was activated in 100 mL aqueous solution of NaOH (18%) for 24 h, and then neutralized with HCl aqueous solution (0.5 mol/L). The activation procedure was completed by filtration of the

fiber and drying at 80°C in vacuum for 24 h. The ozone treatment was carried out according to a method reported in earlier studies.^{27,28} A continuous stream of O₃/O₂ mixture was bubbled through 30 mL of the aqueous dispersion of cotton fiber at 30°C for 25–90 min. The O₂ flow rate was fixed at 200 mL/min to give an O₃ production rate of 1.4 g/h. After ozonization, the fiber was degassed under vacuum for 1 h, and then immersed immediately into an aqueous solution containing 2–10 wt % VTAZ. Under N₂ purge and protection, an aqueous solution of 2.8–4.0 × 10⁻⁴ mol/L NaHSO₃ which act as a redox initiator with peroxide was added to initiate graft polymerization at 40°C. After polymerization for 1–8 h, the grafted fibers were washed with a mixture of methanol and water (30/70 vol/vol) for several times, and then dried at 80°C in vacuum for 12 h. The graft yield was calculated by the weight change rate of the cotton fibers after the modification. Additionally, the graft yield could be manipulated by changing some parameters such as the ozonation period, grafting time, and monomer concentration.

Characterization of Cotton-g-PVTAZ Fiber

Fourier transform infrared spectroscopy (FTIR) spectra of the fibers were obtained by a Nicolet 870 spectrometer. Surface morphology and structure of the fibers were observed with the scanning electron microscopy (SEM, JEOL JSM-6309LV). Uniaxial tensile tests of the fibers were performed with an Instron 5574 tensile testing machine according to ASTM D2256 with a tensile speed of 10 mm/min. Each datum is the average of five parallel studies. The adsorption of heavy metal ions Ag(I), Pb(II), and Cu(II) from aqueous solutions was investigated in batch experiments. The suspensions were brought to desired pH by addition of sodium hydroxide (NaOH) and hydrochloric acid (HCl). The pH was maintained in the range

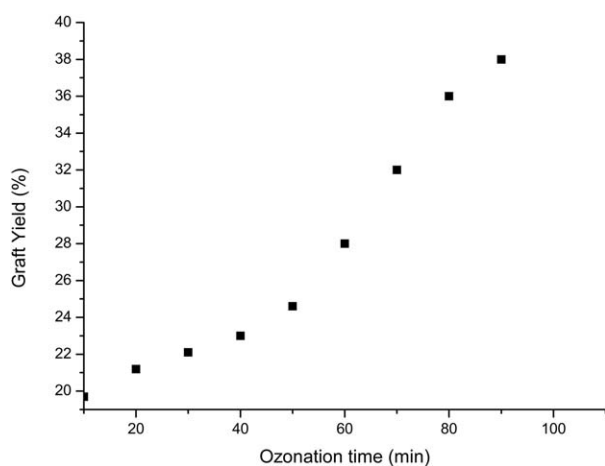


Figure 2. Effect of ozonation time on graft yield (graft copolymerization condition: 10% VTAZ concentration, graft time 6 h).

Table I. Mechanical Properties of Original Fiber and Oxidized Fiber

Sample	Young's modulus (cN/tex)	Stress at maximum load (cN/tex)	Elongation at break (%)
Untreated fiber	147 ± 12	11.2 ± 0.5	9.9 ± 0.7
Fiber oxidized for 30 min	130 ± 11	6.9 ± 0.7	7.8 ± 0.4
Fiber oxidized for 60 min	115 ± 10	5.3 ± 0.8	5.9 ± 0.5
Fiber oxidized for 90 min	83 ± 6	2.7 ± 0.7	2.6 ± 0.7

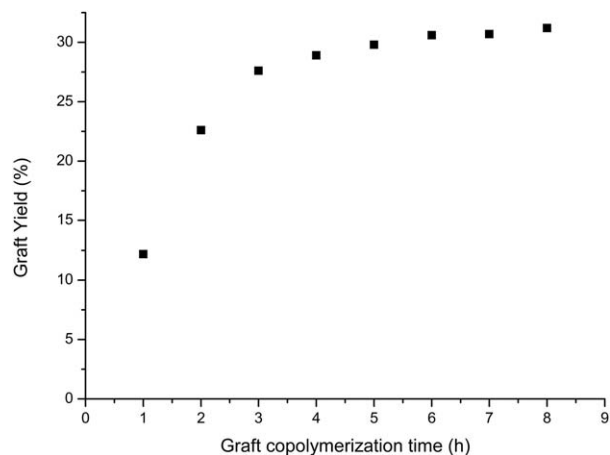


Figure 3. Effect of graft copolymerization time on graft yield (graft copolymerization condition: ozonation time 60 min, 10% VTAZ concentration).

of $0.1 \pm$ units until equilibrium was attained. A typical adsorption experiment was carried out by adding 10 mg of cotton-g-PVTAZ fiber to a 100 mL heavy metal ion solution at 25°C. The initial heavy metal ion concentrations (C_i , mg/L) varied from 25 to 250 mg/L, and the pH value varied from 2.0 to 8.2. After adsorption for 24 h, the cotton-g-PVTAZ fibers were filtered off. The heavy metal ion concentration on the filtrate was carefully analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OEM, Optima-8000 PE), which is identified as the equilibrium concentration of heavy metal ion (C_e , mg/L). Each datum is the average of five parallel studies. The amount of heavy metal ion adsorbed by the cotton-g-PVTAZ was taken as the difference between initial and equilibrium concentrations of solutions, and the adsorption capacity (Q_e , mg/g) of heavy metal ion adsorbed onto cotton-g-PVTAZ was obtained from the following equation [eq. (1)] and used for further adsorption isotherm analysis:

$$Q_e = (C_i - C_e)V/W \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of heavy metal (mg/L), respectively, V is the volume of heavy metal ion solution (L), and W is the weight of cotton-g-PVTAZ chelate fiber (g).

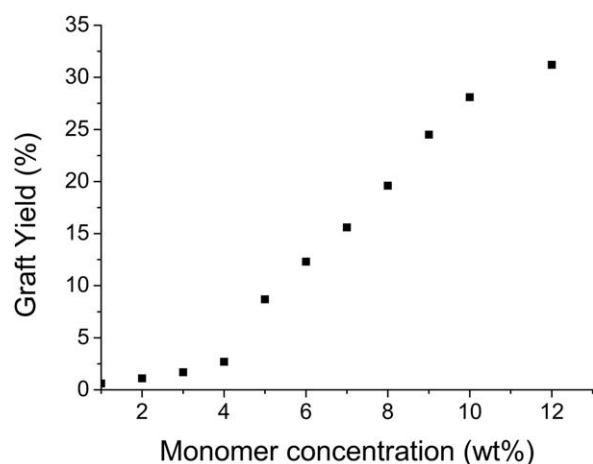


Figure 4. Effect of monomer concentration on graft yield (graft copolymerization condition: ozonation time 60 min, graft time 6 h).

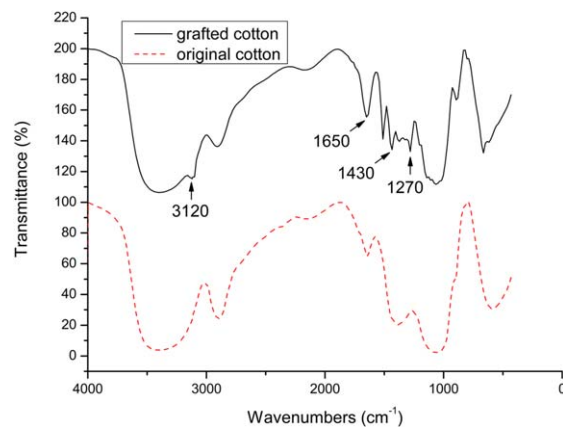


Figure 5. FTIR spectra of original fiber and 30% grafted fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

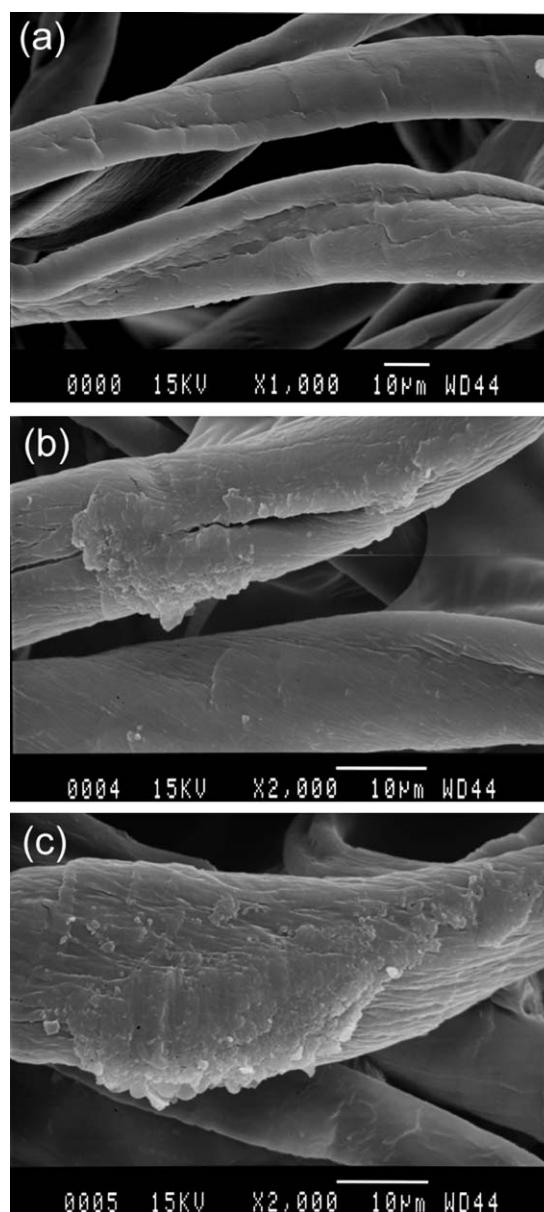


Figure 6. SEM images of original fiber (a), 20% (b), and 30% (c) grafted fiber.

Table II. Mechanical Properties of Original Fiber and Graft Fiber

Sample	Young's modulus (cN/tex)	Stress at maximum load (cN/tex)	Elongation at break (%)
Untreated fiber	147 ± 12	11.2 ± 0.5	9.9 ± 0.7
20% grafted fiber	143 ± 14	6.7 ± 0.6	5.7 ± 0.6
28% grafted fiber	175 ± 18	7.8 ± 0.7	5.9 ± 0.8
30% grafted fiber	186 ± 14	9.1 ± 0.8	6.3 ± 1.1

The surface element components of filtered cotton-g-PVTAZ fibers were identified with energy-dispersive spectroscopy (EDS, JEOL JSM-5600LV). Desorption property of the cotton-g-PVTAZ fibers were carried out in 25 mL of HNO₃ aqueous solution (0.1 mol/L) at 25°C for 1 h. The final metal ion concentration in the aqueous elution medium was determined via the ICP-OEM method. To determine the reusability of the chelate fibers, consecutive chelation–elution cycles were repeated 10 times with the same chelate fibers.

RESULTS AND DISCUSSION

Effect of Ozonation Time on Graft Yield

The effect of ozonation time on the graft yield of VTAZ is investigated and the results are shown in Figure 2. The graft yield increases with increasing ozonation time, because more

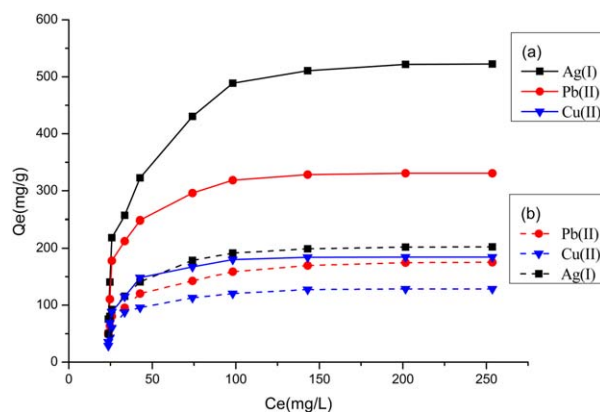


Figure 7. Adsorption capacity of 30% grafted fiber (a) and cotton fiber (b) (test condition: initial metal ion concentration $C_i = 25$ –250 mg/L, pH 6.8). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydroperoxide initiator points are generated on the cotton surface in the long time ozone treatment.^{16,28} However, the so called ozone deterioration occurs after long time oxidation with ozone, and the mechanical properties of the fibers deteriorate with increasing ozonation time (Table I). Therefore, after considering the effect of ozone deterioration, an optimized ozonation time of 60 min is selected in our experiments.

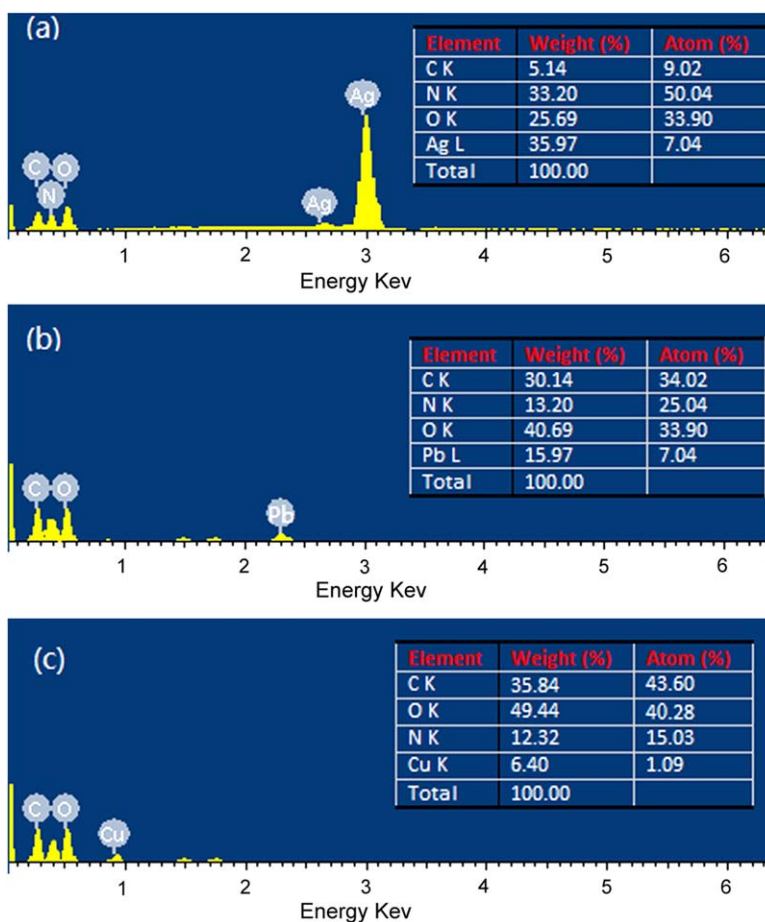


Figure 8. EDS spectra of 30% grafted fibers adsorbed fully with Ag(I) (a), Pb(II) (b), and Cu(II) (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

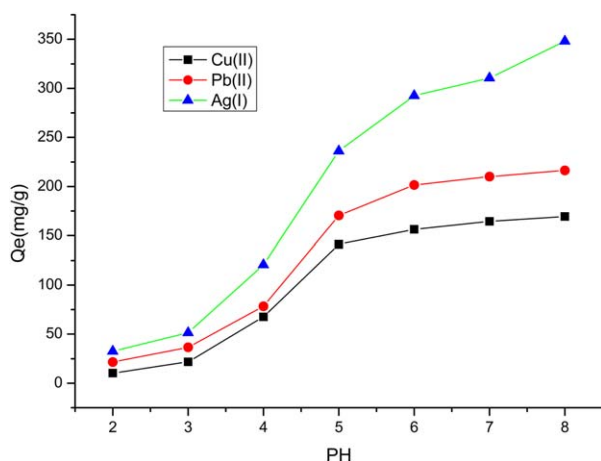


Figure 9. Effect of pH values on the metal ion adsorption capacities of 30% grafted fibers (test condition: initial metal ion concentration $C_i = 100$ mg/L). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Polymerization Time on Graft Yield

As shown in Figure 3, the graft yield increases rapidly at the first 3 h, and then it increases slowly for another 3 h. Finally, the graft yield is hard to increase after reaction for 6 h, because most of the active sites on the backbone are occupied by the polymeric chains, and the formation of homopolymers dominates the graft copolymerization. Thereby, an optimized polymerization time of 6 h is selected in our experiments.

Effect of Monomer Concentration on Graft Yield

As shown in Figure 4, graft yield increases with increased VTAZ concentration, especially when it exceeds 4% in the reaction medium. An optimized VTAZ concentration of 10 wt % is selected in our experiments to minimize the waste of unreacted monomer. Although the efficiency of the graft process was similar to previous reports,^{11,16,28} the VTAZ exhibit higher graft yield than the other monomer under the same conditions. Although the reason for this phenomenon is still under investigation, it has been reported that using reductive agent would enhance graft yield of cotton fibers significantly,²⁹ which suggests that the monomer VTAZ itself may act as reductive tertiary amine to improve the graft yield.

FTIR Spectra

The infrared spectra of the untreated cotton fibers and the cotton-g-PVTAZ fibers are shown in Figure 5. The effect of graft on the absorption bands of cotton fibers can be summarized as follows: the triazole rings of the cotton-g-PVTAZ give rise to several medium or strong peaks, e.g., the characteristic peaks in the 1430–1650 cm^{-1} range are due to ring stretching (C–C/

C–N) vibrations, the characteristic peak at 1270 cm^{-1} is due to the ring stretching (N–N) vibrations, and the characteristic peak at 3120 cm^{-1} is due to the ring stretching (C=C–H/N=C–H) vibrations.^{30,31} The appearance of these characteristic peaks indicated that triazole-based groups were successfully grafted onto the cotton fibers.

Surface Morphology

Figure 6 shows the SEM images of untreated cotton fibers and cotton-g-PVTAZ fibers. The untreated cotton fibers have a smooth surface [Figure 6(a)], while the cotton-g-PVTAZ fibers have a rough surface with leaf-like polymer aggregates [Figure 6(b,c)]. On comparing Figure 6(c) with Figure 6(b), we can see that there are more leaf-like polymer aggregates with higher graft yield.

Mechanical Analysis

Uniaxial tensile properties of untreated cotton fiber and cotton-g-PVTAZ fiber are shown in Table II. The values of the tensile properties are normalized with respect to yarn linear density.^{32,33} Increasing the graft yield, progressive improvements in the tensile properties of the cotton-g-PVTAZ fibers is observed, which might be due to the stronger entanglement of side chains at higher graft yield. At 30% graft yield, the Young's modulus of cotton fiber increases about 26.5%, which indicates that the graft copolymerization can be used to prepare reinforced chelate fibers.

Adsorption Property

Figure 7 shows the Ag(I), Pb(II), and Cu(II) adsorption curves of the original cotton fibers and cotton-g-PVTAZ fibers at different initial metal ion concentrations. The amount of metal ions adsorbed by the fiber increases first with the initial metal ion concentration, and then levels off, which represents the saturation of the active chelate sites. The adsorption capacities of the cotton-g-PVTAZ chelate fiber are 128 mg/g for Cu (II), 330 mg/g for Pb (II), and 522 mg/g for Ag (I), which are improved 1.4, 1.9, and 2.6 times, respectively, compared with original cotton fiber. Compared with bead-like adsorbents of poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole), the adsorption capacities of the cotton-g-PVTAZ chelate fiber for Pb(II) improved from 135 mg/g to 330 mg/g.³⁰ As shown in Figure 8, EDS is used to analyze the surface element contents on the chelate fibers adsorbed fully with Ag(I), Pb(II), and Cu(II), respectively. Although it is difficult to accurately estimate the surface ratio of each metal ion, the higher EDS counting ratio of Ag (I) to carbon implies a high adsorption capacity of Ag (I), which accords with the results in Figure 7 very well.

Figure 9 shows the effect of pH values on the adsorption capacity of cotton-g-PVTAZ fibers. The adsorption capacity of chelate fiber increases with the increasing pH value of metal ion solution. The adsorption is very weak at a pH value less than 3, while the adsorption of metal ions jumps up with the increasing

Table III. Desorption Efficiency (DE) of Graft Fiber at Different Recycle Times

Recycle times	1	2	3	4	5	6	7	8	9	10	Average
DE of Ag(I) (%)	95.4	94.7	94.4	93.7	93.5	93.0	92.8	92.6	91.8	91.4	93.3
DE of Pb(II) (%)	99.5	98.8	98.5	98.1	97.7	97.4	97.2	96.5	96.1	95.3	97.5
DE of Cu(II) (%)	99.8	99.4	99.1	98.6	98.3	98.0	97.6	97.2	96.8	96.5	98.1

pH values from 3 to 8.2. The effects of pH values on the cotton-g-PVTAZ fibers are surface charge, degree of ionization, and speciation. At low pH values, surface charges of the fibers tend to neutralize, which leads to a decrease in adsorption and coordination of cations.

Desorption Property

An ideal chelate fiber should not only possess higher adsorption capability, but also show better desorption property, which will significantly reduce the overall cost for the adsorbents. To determine desorption property and reusability of the 30% grafted fibers, consecutive chelation–elution cycles are repeated 10 times with the same chelate fibers. After the experiment, the average desorption efficiency for Ag(I), Pb(II), and Cu(II) is calculated to be 93.3%, 97.5%, and 98.1%, respectively (Table III). This indicates that the cotton-g-PVTAZ chelate fibers have very good desorption property and reusability.

CONCLUSIONS

Cotton-based chelate fibers grafted with PVTAZ side chains were synthesized successfully by ozone-induced graft polymerization of VTAAZ monomer onto cotton fibers. The graft process is simple and the graft yield is facile to control. The optimized ozonation and graft copolymerization time is 60 min and 6 h, respectively. The optimized monomer concentration is 10 wt % in aqueous solution. After the copolymerization, the Young's modulus of cotton fiber increases about 26.5% at 30% graft yield. The maximum adsorption capacity of Ag(I), Pb(II), and Cu(II) on the fibers at pH 6.8 was 522, 330, and 184 mg/g, respectively. After washed with 0.1 mol/L HNO₃ solutions, the adsorbed metal ions were eluted, and the regenerated cotton-g-PVTAZ fibers could be used repeatedly for removal of heavy metals in water.

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