Functionalized cotton via surface-initiated atom transfer radical polymerization for enhanced sorption of Cu(II) and Pb(II)

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ABSTRACT

The surface-initiated atom transfer radical polymerization (ATRP) was used to successfully prepare the aminated cotton and polyacrylic acid sodium (P(AA-Na))-grafted cotton for the efficient removal of Cu(II) and Pb(II) from aqueous solution in this study. The modified cotton surfaces were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). The grafted long polymers with high density of amine and carboxyl groups on the cotton surfaces were responsible for the enhanced adsorption of heavy metals. The sorption behaviors including sorption kinetics, isotherms and pH effect were investigated. The sorption equilibrium of Cu(II) and Pb(II) was achieved within 1 h on the P(AA-Na)-grafted cotton, much faster than 8 h on the aminated cotton. According to the Langmuir fitting, the maximum sorption capacities of Cu(II) and Pb(II) on the P(AA-Na)-grafted cotton were 2.45 and 2.44 mmol/g, respectively, higher than many adsorbents reported in the literature. The P(AA-Na)-grafted cotton had better adsorption behaviors for Cu(II) and Pb(II) than the aminated cotton.

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1. Introduction

Cotton, one of the abundant natural, biodegradable and renewable biomacromolecular materials, is a very promising raw material available for the preparation of various functional polymers. The surface property of cotton is of crucial significance to its widespread applications [1]. For environmental applications, pristine cotton has a very low heavy metal adsorption capacity, and surface modification has become a popular method for providing materials with desirable properties [2]. Chemical modification of cotton can be conducted to obtain efficient adsorption capacity as well as adequate structural durability [3]. The adsorption of metal ions from aqueous solution is usually controlled by the surface functional groups on the adsorbents [4]. It has been reported that the modified cotton containing amine, carboxyl, and sulfonic groups is effective for the removal of heavy metal ions [5].

Grafting of polymers onto the substrate surfaces is one of the widely used methods to functionalize materials [6]. Atom transfer radical polymerization (ATRP) is a recently developed controlled radical polymerization method [7]. Surface-initiated ATRP allows the preparation of well-defined polymer brushes on various types of substrates [8–10], such as silicate surfaces [11], zirconium phos-

phonate clay [12], polycaprolactone film surfaces [13] and cellulose nanocrystals [9]. It would be ideal if cotton surface can be functionalized with well-defined polymer brushes of controlled length and density for a new range of applications. By now, only one study has reported that the nanocrystals derived from cotton were modified by ATRP for absorption of 1,2,4-trichlorobenzene from water [9].

In this study, surface-initiated ATRP was employed to functionalize cotton for the efficient removal of Cu(II) and Pb(II) from aqueous solution. ATRP initiators were first immobilized on the cotton surfaces and then the well-defined functional polymer brushes of poly(glycidyl methacrylate) (P(GMA)) and poly(acrylic acid sodium) (P(AA-Na)), were prepared via surface-initiated ATRP. The aminated cotton was prepared through the ring-opening reaction of the P(GMA) grafted cotton with ethylenediamine (EDA) (Scheme 1). The modified cotton surfaces were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS), and the adsorption behaviors were also well studied.
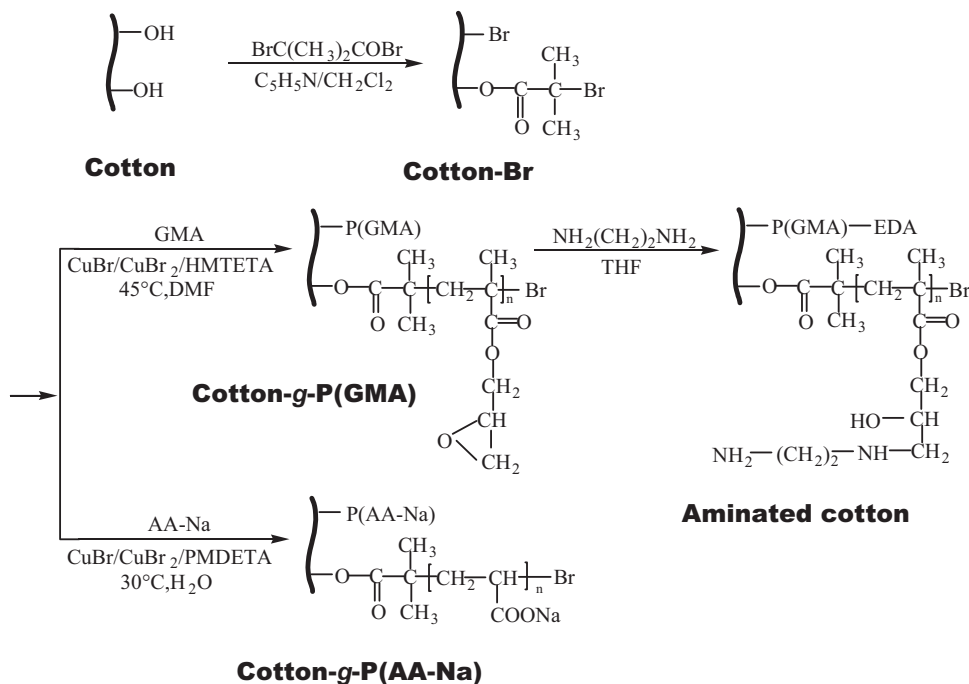
2. Materials and methods

2.1. Materials

Glycidyl methacrylate (GMA, >97%), 2-bromoisobutyrate bromide (BIBB, 98%), ethylenediamine, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), copper(I)

Scheme 1. Schematic diagram illustrating the reaction of hydroxyl groups on the cotton surface with BIBB to produce the cotton-Br surface, surface-initiated ATRP of GMA and AA-Na from the cotton-Br surface to produce the cotton-g-P(GMA) and cotton-g-P(AA-Na), and EDA immobilization on the cotton-g-P(GMA) to produce the aminated cotton.

bromide (CuBr, 99%), and copper(II) bromide(CuBr$_2$, >98%) were purchased from Aldrich Chemical Company. GMA was passed through a silica gel column to remove the inhibitor, and stored under an argon atmosphere at $-10\,°C$. Acrylic acid sodium (AA-Na, 99%) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%) were purchased from Sigma–Aldrich Corporation. The starting material (cotton) used in this study was medical degreased cotton, obtained from Beijing Kehu Medical Treatment Equipment Co., Ltd. Other chemicals are of reagent grade.

2.2. Immobilization of ATRP initiators on cotton surfaces

As shown in Scheme 1, immobilization of ATRP initiators on cotton surfaces was accomplished via the reaction of hydroxyl groups with BIBB. Before experiments, the pristine cotton was washed by excess dichloromethane (DCM), acetone and water to remove the unattached components on the cotton fibers. About 0.3 g of cotton was transferred into a tube containing 15 mL of DCM. Then, 3 mL of BIBB and 1 mL of pyridine were slowly added into the tube. The reaction was left to proceed for 24 h at room temperature in an orbital shaker at 150 rpm. After the reaction, the cotton was washed thoroughly with DCM and acetone, and then with an excess amount of ultrapure water. Finally, the cotton-Br was dried at room temperature until constant weight.

2.3. Preparation of aminated cotton

For surface-initiated ATRP of GMA from the cotton-Br, the reaction was carried out as follows. Fifty milligrams of cotton-Br were first transferred into a round bottom flask, and then 1 mL of ultrapure water, 2 mL of DMF, 3 mL of GMA and 100 μL of HMTETA were added into the flask successively. The reaction solution was purged with nitrogen for about 10 min, and then 45 mg of CuBr and 9 mg of CuBr$_2$ were added into the flask. After about 2 min, the flask was sealed and kept in a 45 °C water bath for a predetermined time from 1 to 4 h. After the reaction, the cotton-g-P(GMA) was immersed subsequently in 50 mL of tetrahydrofuran (THF) for about 48 h, and the

solvent was stirred continuously and changed every 8 h to ensure the complete removal of the adhered and physically adsorbed reactants, prior to being dried under reduced pressure at 80 °C.

For the amination of cotton-g-P(GMA) with ethylenediamine (EDA), about 0.1 g of cotton-g-P(GMA) was added into a tube containing 2 mL of THF and 2 mL of EDA. The reaction mixture was shaken at 150 rpm and 25 °C for different hours. After the reaction, the aminated cotton was washed thoroughly with acetone and ultrapure water sequentially. Finally, 0.1 M HCl was used to remove the copper residue, and then 0.1 M NaOH solution was used to neutralize the excess acid. After being rinsed with ultrapure water till neutral, the aminated cotton was dried at room temperature until constant weight.

2.4. Preparation of P(AA-Na)-grafted cotton

The cotton-g-P(AA-Na) was synthesized as follows. The PMDETA ligand, CuBr and CuBr$_2$ were added in the mass ratio of [AA-Na]:[CuBr]:[CuBr$_2$]:[PMDETA] = 50:1:0.1:1.1. Two grams of AA-Na and 4 mL of ultrapure water were added to a Pyrex tube, and then 50 mg of cotton-Br was introduced into the reaction mixture. The mixture was stirred and degassed with nitrogen for 10 min. Then, 40 mg of CuBr and 4 mg of CuBr$_2$ were added into the tube. The reaction tube was sealed and shaken in an orbital shaker at 150 rpm and 30 °C for a predetermined time from 5 to 60 min. After the reaction, the obtained cotton-g-P(AA-Na) was immersed subsequently in 50 mL of deionized water for about 48 h, and the water was stirred continuously and changed every 8 h to ensure the complete removal of the adsorbed reactants, prior to being dried at 80 °C.

2.5. FTIR analysis

The samples of the pristine cotton, cotton-Br, cotton-g-P(GMA), cotton-g-P(AA-Na) and aminated cotton were dried at room temperature until constant weight. Their FTIR spectra were recorded on a Fourier transform infrared spectrometer (Perkin-Elmer 2000, USA) in the wavenumber range of 600–4000 cm^{-1} under ambient

conditions. An attenuated total reflection (ATR) accessory was employed for all IR spectral acquisitions.

2.6. SEM observation

The surface morphologies of the cotton before and after modification via surface-initiated ATRP and amination reaction were observed using an environmental scanning electron microscope (ESEM, FEI Quanta 200 FEG).

2.7. XPS study

XPS analysis of the pristine and modified cotton was carried out on an AEM PHI 5300X spectrometer with a monochromatized Al Kα X-ray source. The X-ray source was run at a reduced power of 150 W, and the pressure in the analysis chamber was maintained at less than 10^{-8} Torr during each measurement. All binding energies were referenced to the neutral C 1s peak at 284.6 eV to compensate for the surface charging effects. The software package XPS peak 4.1 was used to fit the spectra peaks, and the full width at half-maximum was maintained constant for all components in a particular spectrum.

2.8. Zeta potential measurement

A 10 mg aliquot of the pristine or modified cotton was cut into small pieces and put into 100 mL of deionized water, and then the solution pH was adjusted with NaOH or HCl solution to a desired value. After 1 h stabilization, the solution pH was recorded, and the supernatant with small particles was used to conduct zeta potential measurements with a zeta potential instrument (Delsa Nano C, Beckman Coulter, USA). All data were determined 10 times, and the average values were adopted.

2.9. Sorption experiments

Sorption experiments were conducted to examine the sorption kinetics, sorption isotherm, as well as the effect of solution pH on the sorption of Cu(II) and Pb(II) on the modified cottons. All sorption experiments were carried out in 250 mL flasks, each of which contained 100 mL of solution prepared with $CuSO_4 \cdot 5H_2O$ or $Pb(NO_3)_2$. Fifty milligrams of aminated cotton or cotton-g-P(AA-Na) were added into each flask, and the flasks were shaken in a shaker at 25 °C and 150 rpm for 12 h for aminated cotton and 6 h for cotton-g-P(AA-Na). The preliminary study of kinetics showed that the sorption equilibrium of aminated cotton and cotton-g-P(AA-Na) was achieved within 12 h and 6 h, respectively.

In the kinetic experiments, the initial concentrations of Cu(II) and Pb(II) were 2 mmol/L, and the initial solution pH was adjusted to 5. After that, no pH adjustment was performed in the sorption process. In the investigation of sorption isotherm, the initial concentrations ranged from 0.4 to 2.0 mmol/L for Cu(II) and 0.2–1.6 mmol/L for Pb(II); solution pH values were kept within 5 ± 0.1 throughout the sorption experiments by adding HCl or NaOH solution at regular time intervals. In the pH effect experiments, the initial adsorbate concentration was 2 mmol/L. The initial solution pH values were in the range of 2–5.5 for Cu(II) and Pb(II) ions, and then the equilibrium pH was measured. After sorption, the adsorbents were separated from the solution by filtration through a 0.22 μm membrane. The residual Cu(II) and Pb(II) concentrations in the filtrate were analyzed with an inductively coupled plasma optical emission spectrometry (ICP-OES, IRIS Interpid II XSP).

3. Results and discussion

The processes of surface functionalization of cotton via surface-initiated ATRP are illustrated in Scheme 1: (i) the hydroxyl groups on the cotton surfaces reacted with BIBB to produce the cotton-Br, (ii) surface-initiated ATRPs of GMA and AA-Na from the cotton-Br surface were carried out to produce the cotton-g-P(GMA) and cotton-g-P(AA-Na) surfaces, respectively, and (iii) EDA was immobilized on the cotton-g-P(GMA) to obtain the aminated cotton. The preparation of the modified cottons was discussed below.

3.1. Preparation of aminated cotton

The physicochemical properties of cotton surface can be tuned by the choice of functional monomers. In this study, GMA with a reactive epoxide group was selected as the model monomer. To quickly establish an equilibrium between the dormant and active chains during surface-initiated ATRP, an excess amount of $CuBr_2$ was added, which allows thicker polymer brushes to be grown at a faster rate [13,14].

In this work, the grafting yield (GY) is defined as $GY = (W_b - W_a)/W_a$, where W_a and W_b are the weights of the dry cotton after and before graft copolymerization, respectively. The effects of ATRP reaction time on grafting yield and the sorption capacity of Cu(II) on the aminated cotton are shown in Fig. 1a. The grafting yield and sorption capacity increased at the initial stage with increasing ATRP time, and then leveled off after 3 h. With the increase of ATRP reaction time, the longer P(GMA) brushes were formed on the cotton surface to produce more reaction sites for amination. After the ATRP time of 3 h, the thickness increase rate of P(GMA) brushes decreased substantially. With increasing ATRP time, chain termination on the cotton surface, followed by bimolecular coupling or disproportionation reactions that consume the active chains, may become important to decrease the initially rapid rate of ATRP. Based on the maximum sorption capacity and grafting yield as shown in Fig. 1a, the ATRP reaction time was fixed at 3 h during the following experiments.

Fig. 1b illustrates the sorption capacity of Cu(II) on the aminated cotton prepared at different amination time. The sorption capacity increased quickly within 60 h, and the equilibrium was almost achieved at about 72 h. Since the amine groups of the aminated cotton were responsible for Cu(II) sorption, the amination reaction time between ethylenediamine and epoxy groups of the P(GMA) was fixed at 72 h to prepare the aminated cotton, which was used in the following sorption experiments.

3.2. Preparation of cotton-g-P(AA-Na)

In this work, acrylic acid sodium with carboxylate (–COONa) group was selected as another model monomer for the removal of Cu(II) and Pb(II) ions. The effects of ATRP reaction time on the grafting yield and sorption capacity of Cu(II) on the cotton-g-P(AA-Na) are shown in Fig. 1c. The grafting yield and sorption capacity of Cu(II) on the cotton-g-P(AA-Na) increased with increasing ATRP time, and then leveled off after 50 min. Such phenomenon was probably because the bimolecular coupling or disproportionation reactions consuming the active chains became predominant with increasing ATRP time. Therefore, the ATRP reaction time was fixed at 50 min in the following experiments.

3.3. Characterization

FTIR analysis was used to characterize the functionalized cottons. Fig. 2 shows the FTIR spectra of the (a) pristine cotton, (b) cotton-Br, (c) cotton-g-P(GMA), (d) aminated cotton, and (e) cotton-g-P(AA-Na). As shown in Fig. 2a, a broad band at 3325 cm^{-1}
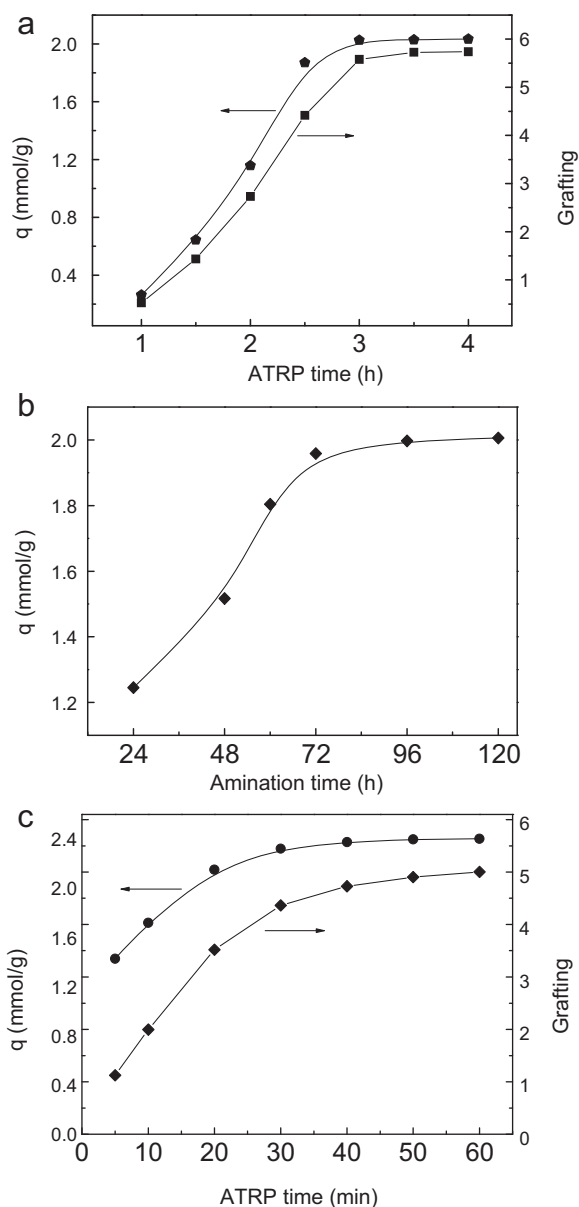
Fig. 1. Effects of (a) ATRP reaction time on grafting yield and the sorption capacity of Cu(II) on the aminated cotton, (b) amination time on the sorption capacity of Cu(II) on the aminated cotton, and (c) ATRP reaction time on the grafting yield and sorption capacity of Cu(II) on the cotton-*g*-P (AA-Na).


Fig. 2. FTIR spectra of the (a) pristine cotton, (b) cotton-Br, (c) cotton-*g*-P(GMA), (d) aminated cotton, and (e) cotton-*g*-P (AA-Na).

is assigned to hydroxyl groups of cotton. Other typical peaks are at $1161 \, cm^{-1}$, $1109 \, cm^{-1}$ and $895 \, cm^{-1}$, attributing to asymmetric bridge C–O–C stretching and C–H deformation, respectively [6]. The appearance of the stretching vibration of C=O at $1732 \, cm^{-1}$ for cotton-Br (Fig. 2b) indicated that BIBB had successfully been immobilized on the cotton surface. After the graft of P(GMA) and P(AA-Na) onto the cotton surface, the corresponding spectra changed substantially. As shown in Fig. 2c, the successful graft of P(GMA) was identified by the appearances of strong peak at $1723 \, cm^{-1}$ (C=O stretching vibration in GMA) and two other peaks at $1253 \, cm^{-1}$ and $1147 \, cm^{-1}$ (C–O symmetric and asymmetric vibrations in GMA) [15,16]. The peaks at $906 \, cm^{-1}$ and $842 \, cm^{-1}$ are the characteristic peaks of epoxy group, indicating that P(GMA) had successfully been grafted onto the cotton surface [16]. After the amination reaction of epoxy groups with EDA, the characteristic peaks of epoxy group disappeared (Fig. 2d). A broad band ranging from about 3100 to $3700 \, cm^{-1}$ corresponds to the combination of
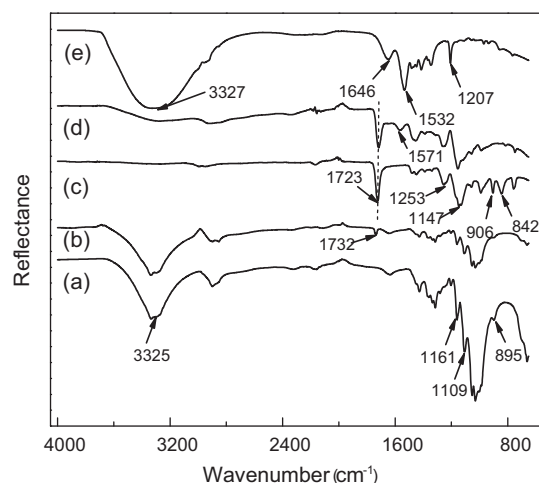
the stretching vibration of both OH and NH groups. In addition, the new peak at $1571 \, cm^{-1}$ in Fig. 2d could be assigned to the deformation vibration of NH group [17]. The above results indicated that the NH group was successfully introduced onto the surface of the aminated cotton. For cotton-*g*-P(AA-Na) (Fig. 2e), the broad peak at $3327 \, cm^{-1}$ was ascribed to the carboxylic OH group. The characteristic peaks at $1380 \, cm^{-1}$ and $1532 \, cm^{-1}$ were the symmetric and antisymmetric stretches of carboxylate group (COO$^-$), respectively [18,19], implying that the P(AA-Na) brushes were successful grafted onto the cotton surface. The band at $1646 \, cm^{-1}$ was attributed to the OH bending of water adsorbed on the cotton surface and molecular cellulose inside the cellulose polymer.

The chemical compositions of the cottons before and after modification were determined by XPS. The respective XPS widescan and C 1s core-level spectra of the (a and b) pristine cotton, (c and d) cotton-Br, (e and f) cotton-*g*-P(GMA), (g and h) aminated cotton, and (i and j) cotton-*g*-P(AA-Na) are shown in Fig. 3. The C 1s core-level spectrum of the pristine cotton can be curve fitted into three peak components with binding energies (BEs) of 284.6, 286.2 and 287.7 eV attributable to the C–C/C–H, C–O/C–Br and O–C–O species, respectively [14]. The large amount of C–C linkage, not inherent to pure cellulose, means that there is a lot of non-cellulose on the fibre surface (most likely lignin and lignin fragments) [20]. A comparison of the wide-scan spectra of the pristine cotton (Fig. 3a) and cotton-Br (Fig. 3c) surfaces indicates that the Br 3d (at BE of about 69 eV) and Br 3p (at BE of about 182 eV) signals, characteristic peaks of covalently bonded bromine, have appeared on the cotton-Br surface [14]. The corresponding Br 3d core-level spectrum is presented in Fig. 3d′. The C 1s spectrum of the cotton-Br (Fig. 3d) surface can be curve fitted into four peak components with BEs of 284.6, 286.2, 287.7, and 288.7 eV, attributable to the C–C/C–H, C–O/C–Br, O–C–O and O=C–O species, respectively [14]. The C 1s spectrum of cotton-*g*-P(GMA) (Fig. 3f) can be divided into four peaks at 284.6, 286.2, 287.7, and 288.7 eV, corresponding to the C–C/C–H, C–O, O–C–O and O=C–O species, respectively [14]. After the amination reaction, the strong N 1s peak at about 399 eV is observed in Fig. 3g, and the corresponding N 1s core-level spectrum is shown in Fig. 3h′, suggesting that the amine group was introduced on the cotton surface. The corresponding C 1s spectrum (Fig. 3h) can be divided into five peak components with BEs of 284.6, 286.2, 285.3, 287.7, and 288.7 eV, attributed to the C–C/C–H, C–O, C–N, O–C–O and O=C–O species, respectively [14]. For the cotton-*g*-P(AA-Na) (Fig. 3i), the strong Na 1s peak at BE of about 1077 eV appeared in the wide-scan spectrum and the corresponding Na 1s core-level spectrum is shown in Fig. 3j′, indicating that the –COONa
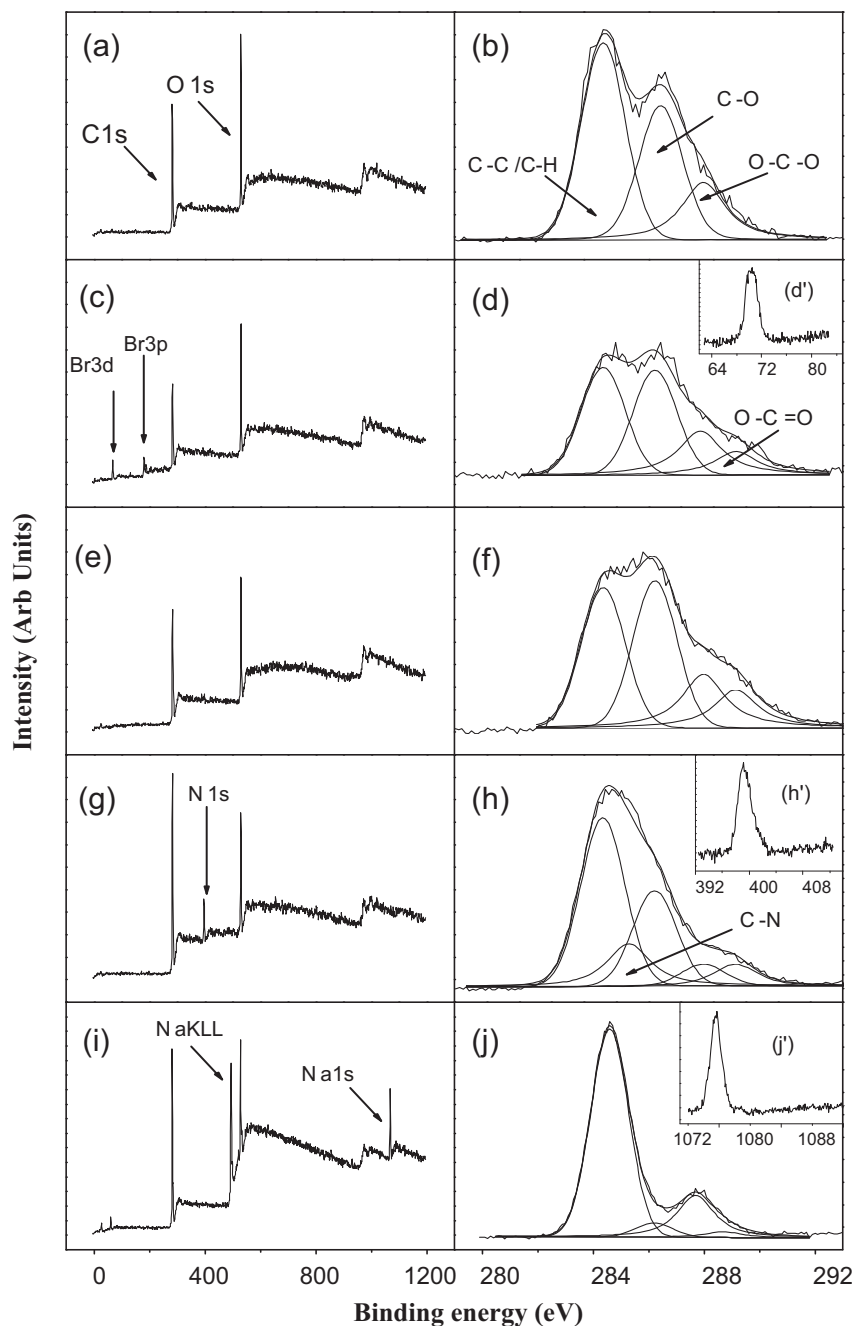
Fig. 3. XPS wide scan and C 1s core-level spectra of (a and b) pristine cotton, (c and d) cotton-Br, (e and f) cotton-*g*-P(GMA), (g and h) aminated cotton and (i and j) cotton-*g*-P(AA-Na), Br 3d core-level spectrum of (d′) cotton-Br, N 1s core-level spectrum of (h′) of aminated cotton and Na 1s core-level spectrum of (j′) of cotton-*g*-P (AA-Na).

group was introduced on the cotton surface. The C 1s spectrum of cotton-*g*-P(AA-Na) (Fig. 3j) can be curve fitted with four peak components with BEs of 284.6, 286.2, 287.7, and 288.7 eV, attributable to the C–C/C–H, C–O, O–C–O and O=C–O species, respectively [14]. It should be pointed out that the above peak deconvolutions of C 1s almost agree with the O, N and C contents from the respective wide-scan spectra.

The surface morphologies of the functionalized cottons at various stages were characterized by SEM. The images of the (a′) pristine cotton, (a) cotton-Br, (b) cotton-*g*-P(GMA), (c) aminated cotton and (d) cotton-*g*-P(AA-Na) are illustrated in Fig. 4. The surfaces of the pristine cotton and cotton-Br were relatively smooth. After functionalization, the surfaces of cotton-*g*-P(GMA), aminated cotton and cotton-*g*-P(AA-Na) became much rougher. The introduction of long polymer brushes with high densities of amine and

–COONa groups onto the cotton surface can therefore be expected to change the surface properties and enhance the sorption of heavy metals.

The aminated cotton and cotton-*g*-P(AA-Na) obtained in this study were used to remove Cu(II) and Pb(II) from aqueous solution, and the sorption behaviors including sorption kinetics, isotherm and effect of solution pH were investigated.
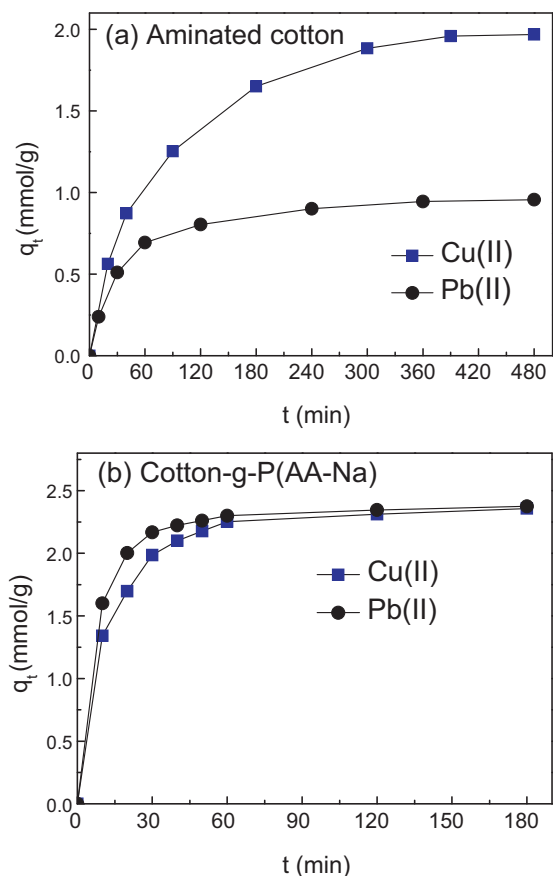
3.4. Sorption kinetics

The sorption kinetics of Cu(II) and Pb(II) on the aminated cotton and cotton-*g*-P(AA-Na) is shown in Fig. 5. With the increase of the sorption time, the sorption of Cu(II) and Pb(II) on the two adsorbents was rapid at the initial stage and then increased slowly
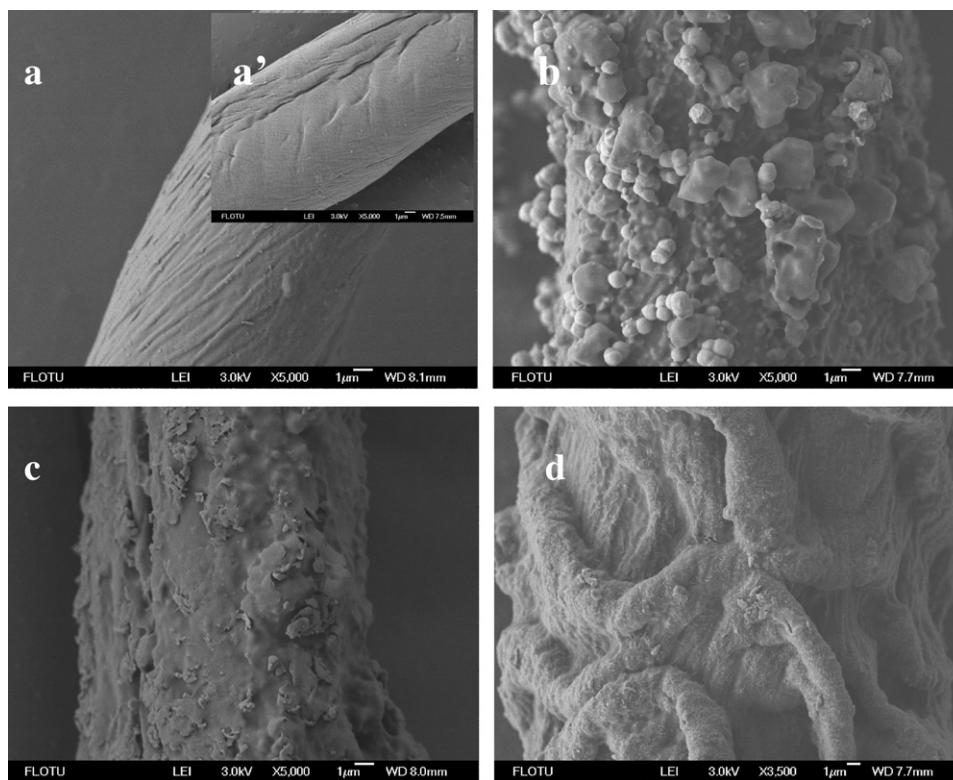
Fig. 4. SEM micrographs of the cotton before and after modification: (a′) pristine cotton (5000×), (a) cotton-Br (5000×), (b) cotton-g-P(GMA) (5000×), (c) aminated cotton (5000×), and (d) cotton-g-P(AA-Na) (3500×).

Fig. 5. Sorption kinetics of Cu(II) and Pb(II) on the (a) aminated cotton and (b) cotton-g-P(AA-Na) at initial pH 5 (final pH values in the range of 5.3–5.4).

due to less active sorption sites available. The differences in the sorption kinetics between Cu(II) and Pb(II) on the two adsorbents are not obvious. The cotton-g-P(AA-Na) had fast sorption kinetics, and the sorption equilibrium of Cu(II) and Pb(II) was achieved within 1 h, much faster than 8 h for the aminated cotton. Sorption kinetics is dependent on the functional groups on the adsorbents and adsorbent porosities, and the nonporous adsorbents normally have high sorption velocity for some pollutants since the sorption occurs on the adsorbent surface. The sorption of cationic heavy metals on the amine groups of the adsorbents via chelation interaction is relatively slow [21,22], while the adsorbent with carboxyl groups has fast sorption for Cu(II) via cationic exchange [23]. The cotton-g-P(AA-Na) in this study had satisfactory sorption velocity for both Cu(II) and Pb(II). It is notable that the aminated cotton had much higher sorption capacity for Cu(II) (1.97 mmol/g) than Pb(II) (0.96 mmol/g) at 8 h, while the cotton-g-P(AA-Na) had almost the same sorption cpacities for Cu(II) (2.25 mmol/g) and Pb(II) (2.30 mmol/g) at 1 h.

3.5. Sorption isotherm

Maximum sorption capacity is also one of important properties to evaluate some adsorbents, and it can be obtained from sorption isotherms. Fig. 6 illustrates the sorption isotherms of Cu(II) and Pb(II) on the aminated cotton and cotton-g-P(AA-Na). The sorption capacities on the aminated cotton increased gradually with increasing equilibrium concentrations of Cu(II) and Pb(II), and the sorption capacities gradually approached the maximum values after the equilibrium concentration of 0.8 mmol/L. The higher sorption capacity of Cu(II) than Pb(II) on the aminated cotton may be attributed to the stronger affinity to amine groups and higher hydration energy of Cu(II) [24], which was consistent with other reports on their sorption on the aminated adsorbents [21,22]. By contrast, the sorption capacities of Cu(II) and Pb(II)
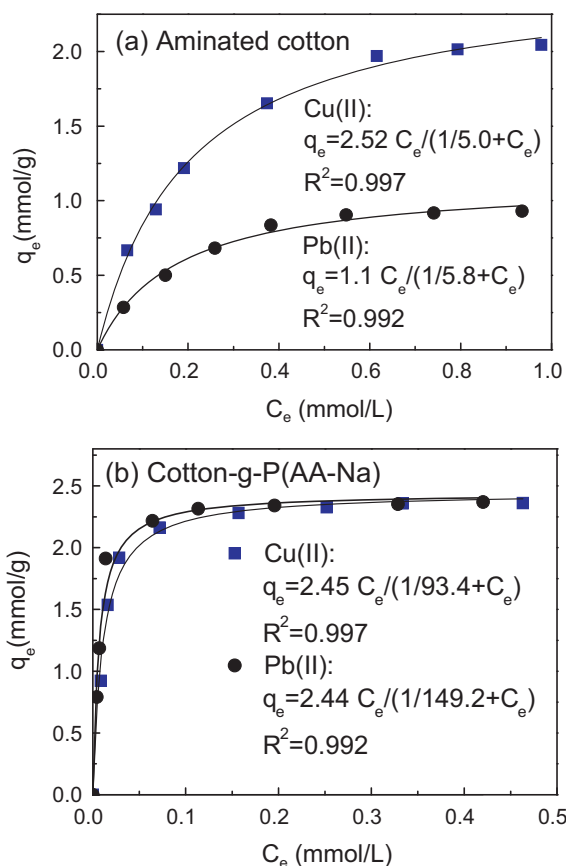
Fig. 6. Sorption isotherms of Cu(II) and Pb(II) on the (a) aminated cotton and (b) cotton-*g*-P (AA-Na).

Fig. 7. Effect of solution pH on the sorption of Cu(II) and Pb(II) on the (a) aminated cotton and (b) cotton-*g*-P(AA-Na) as well as (c) zeta potentials on the pristine and modified cottons.

on the cotton-*g*-P(AA-Na) increased quickly at low equilibrium concentrations, and the sorption capacities almost reached the maximum values at the equilibrium concentration of 0.1 mmol/L. To obtain the maximum sorption capacities, the Langmuir equation was used to describe the sorption isotherms, which has been successfully applied to many sorption processes [2,21]. The Langmuir equation can be expressed as $q_e = q_m C_e(1/b + C_e)$, where q_m is the maximum sorption capacity (mmol/g), b is the sorption affinity constant (L/mmol), and C_e is the equilibrium concentration of Cu(II) and Pb(II) ions in solution (mmol/L). The modeling results and the corresponding parameters calculated from the plots are also shown in Fig. 6. It can be found that the sorption affinity constants (b) for the adsorption of Cu(II) and Pb(II) on the cotton-*g*-P(AA-Na) are much higher than those on the aminated cotton, which are consistent with their sorption kinetics shown in Fig. 5. The maximum sorption capacities of Cu(II) and Pb(II) on the aminated cotton are 2.52 and 1.1 mmol/g, respectivly, while their corresponding values on the cotton-*g*-P(AA-Na) are 2.45 and 2.44 mmol/g. In fact, the maximum value of 2.52 mmol/g obtained from the modeling is overestimated, higher than the experimetal value. The cotton-*g*-P(AA-Na) actually had higher sorption capacity for Cu(II) and Pb(II) than the aminated cotton. In the literature, many modified adsorbents have been used to adsorb Cu(II) and Pb(II), and some adsorbents with relatively high sorption capacities for Cu(II) and Pb(II) reported in past few years are listed in Supplementary data Table S1. It can be seen that the sorption capacities of Cu(II) and Pb(II) on most of the modified adsorbents are less than 2 mmol/g, and only the adsorbents including the thiourea-modified chitosan, charred xanthated sugarcane bagasse, polyazomethineamides powder, and succinic anhydride modified cellulose had high sorption capacities for Cu(II) or Pb(II) [25,26].
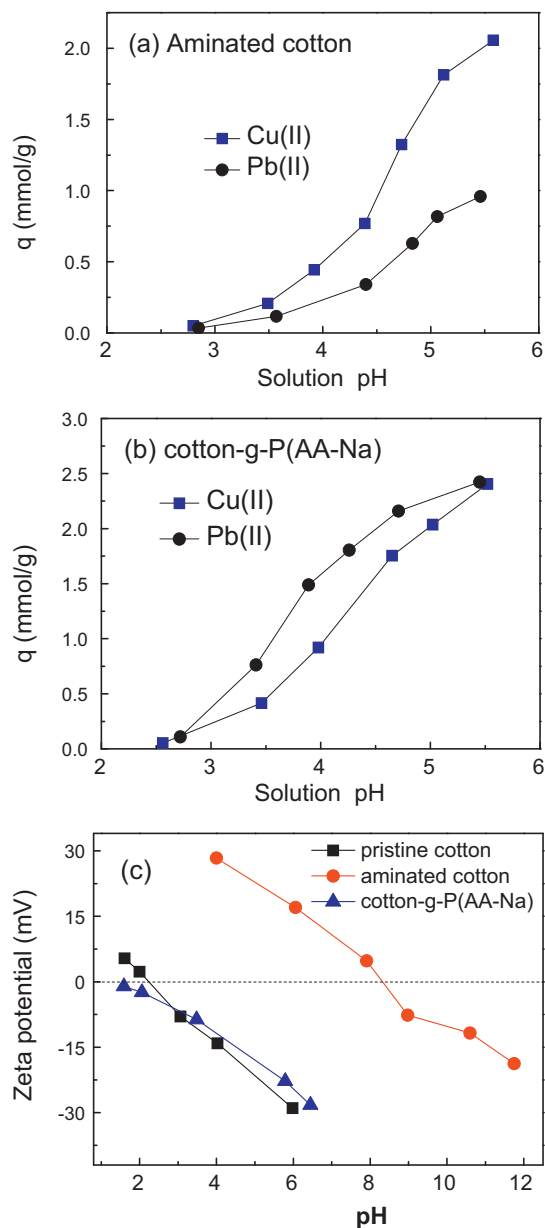
An aminated resin prepared by surface-initiated ATRP in our previous paper was efficient for some heavy metal removal, and the maximum sorption capacities of Cu(II) and Pb(II) were 2.6 and 0.97 mmol/g, respectively [27]. Evidently, the cotton-*g*-P(AA-Na) prepared by SI-ATRP in this study had satisfactory sorption capacities for Cu(II) and Pb(II).

3.6. Effect of solution pH

The effect of solution pH (equilibrium pH) on the sorption of Cu(II) and Pb(II) on the aminated cotton and cotton-*g*-P(AA-Na) is shown in Fig. 7a and b. The sorption was pH-dependent, and the sorption capacities of Cu(II) and Pb(II) on the aminated cotton and cotton-*g*-P(AA-Na) both increased with increasing solution pH. For the aminated cotton, almost no sorption took place at pH around 3 because the protonated amine groups prevented the cationic metals from approaching the sorption sites via electrostatic repulsion [22,28], which was verified by the zero point of

zeta potential at pH 8.3 (see Fig. 7c). With the increase of solution pH, some amine groups on the aminated cotton may chelate with Cu(II)/Pb(II). For the cotton-g-P(AA-Na), almost no sorption observed at pH below 2.5 since the carboxylate anions were converted to be the carboxylic acid, which hindered the sorption of metal ions on the cotton-g-P(AA-Na). At high pH values, more ionized carboxyl groups were available, and more cationic Cu(II)/Pb(II) were exchanged and adsorbed on the adsorbent. The similar result was also reported elsewhere [23]. The zeta potentials on the cotton-g-P(AA-Na) shown in Fig. 7c were consistent with the metal sorption.

It should be pointed out that currently it is expensive to prepare the adsorbents using the surface-initiated ATRP technology. With the development of industrialization, it is possible to prepare some efficient adsorbents via ATRP for the removal of some pollutants from water.

4. Conclusions

The aminated cotton and cotton-g-P(AA-Na) were successfully prepared via surface-initiated ATRP technique, which were verified by the FTIR and XPS analysis. The SEM observation illustrated that the modified cotton surfaces became much rougher due to the presence of long polymer brushes. The optimized adsorbents had high sorption capacity for heavy metals. The sorption of Cu(II) and Pb(II) on the cotton-g-P(AA-Na) was much faster than that on the aminated cotton. The maximum sorption capacities of Cu(II) and Pb(II) on the cotton-g-P(AA-Na) obtained by the Langmuir fitting were 2.45 and 2.44 mmol/g, respectively, higher than some natural adsorbents reported. Solution pH had significant effect on the sorption capacities, and the sorption of Cu(II) and Pb(II) increased with increasing solution pH in the range of 2–5.5. This study demonstrates that surface-initiated ATRP is a useful method to modify cotton with satisfactory sorption behaviors, and the modified cotton with P(AA-Na) brushes has the promising application in the removal of heavy metals from wastewater due to its high sorption capacity and fast sorption rate.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.06.054.

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