

Preparation of Amidoximated Bacterial Cellulose and Its Adsorption Mechanism for Cu^{2+} and Pb^{2+}

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ABSTRACT: Amidoximated bacterial cellulose (Am-BC) was prepared through successive polymer analogous reactions of bacterial cellulose with acrylonitrile in an alkaline medium followed by reaction with aqueous hydroxylamine. It was used as an adsorbent to remove Cu^{2+} and Pb^{2+} from aqueous solutions. The adsorption behaviors of Cu^{2+} and Pb^{2+} onto Am-BC were observed to be pH-dependent. The maximum adsorption capacity of 84 and 67 mg g^{-1} was observed, respectively, for Cu^{2+} and Pb^{2+} at pH 5. Scanning electronic microscopy (SEM) indicated that the microporous network structure of Am-BC was maintained even after the modification. The adsorption mechanisms for Cu^{2+} and Pb^{2+} onto Am-BC were investigated by Fourier transform infrared spectroscopy (FTIR), ζ potential measurement and X-ray photoelectron spectroscopy

(XPS). The results revealed that the mechanism for the adsorption of Cu^{2+} onto Am-BC could be mainly described as between metal ions and nitrogen atom in the amidoxime groups or oxygen atom in the hydroxyl groups. However, in the adsorption process for Pb^{2+} , precipitation played the important role along with electrostatic interactions, although chelation action also existed in the process accounted for the adsorption process. The regeneration of Am-BC was studied by treatment with a strong complexing agent, ethylenediaminetetraacetic acid (EDTA). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 8–15, 2010

Key words: Amidoximated bacterial cellulose; Cu^{2+} and Pb^{2+} ; adsorption; mechanism

INTRODUCTION

Most heavy metal ions are toxic or carcinogenic and hence present a threat to human health and the environment if they are discharged into various water resources without treatment. These heavy metal ions can be accumulated through the food chain even at low concentrations, leading to serious problems on aquatic life as well as to animal, plant life and human health. Among these heavy metal ions, copper, and lead ions are one of the most important pollutants. Copper ions can cause serious problems to human health such as stomach intestinal distress, kidney damage, anemia and even coma and eventual death.¹ In addition, copper may be found as a contaminant in food, especially shellfish, liver,

mushrooms, nuts, and chocolate.² Lead is widely used in many industrial applications such as storage manufacturing battery, printing, pigments, fuels, photographic materials, and explosive manufacturing.³ Lead is highly toxic as its presence in drinking water above the permissible limit (5 ng/mL) which can cause adverse health effects such as anemia, encephalopathy, hepatitis, and nephritic syndrome.⁴ Cost-effective treatment technologies, therefore, are needed to meet these requirements.

Up to now, many methods including precipitation, ion exchange, coagulation, flotation, adsorption, oxidation, and hyperfiltration have been developed to remove heavy metal ions from wastewater or aqueous solutions containing heavy metal ions.^{5,6} However, adsorption is one of the most attractive methods because the many low cost, efficient, and renewable materials those can be easily modified such as chitosan, dead microbial biomass, and agriculture waste materials are easily available as adsorbents.^{7–10} Adsorption of metal ions can be enhanced by the surface modification of the functional groups. In the adsorption process, metal ions from the aqueous solutions are transported through diffusion or convection to the surface of the adsorbent where those attach to the adsorbent surfaces due to physical and chemical interactions between the metal ions and the surface functional groups of the

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adsorbent. The mechanism of the removal of heavy metal ions involves processes such as complexation, adsorption on surface and pores, ion exchange, chelation or adsorption by physical or chemical forces.^{11–15} It has been reported that a complexing group (amidoxime, hydrazine, thioamide, and imidazoline groups) or an anionic moiety (carboxyl, sulfonic, and phosphonic groups) on the surface can favor metal ion adsorption through the ion exchange or chelation mechanism.^{8,16–20} Hence, there has been considerable interest to introduce useful functional groups on the surface of these adsorbents to enhance their adsorption capability to remove heavy metal ions. In particular, the amidoxime group on an adsorbent has been found to be one of the most effective chelating groups for adsorption or for the removal of heavy metal ions from the aqueous solutions.^{21–24}

Bacterial cellulose (BC) is extracellular cellulose produced by bacteria of genus *Acetobacter*.²⁵ Its molecular structure is identical to that of plant cellulose: an unbranched polymer of β -1,4-linked glucopyranose residues. However, BC has an ultrafine network composed of ribbon-like microfibrils whose thickness (0.1×10^{-6} m) is two orders of magnitude smaller than that of plant cellulose (10×10^{-6} m). The three-dimensional network endows BC unique properties including high tensile strength, high specific surface area. Therefore, it has been investigated in many field such as medical, food industry, separation membrane, and additives in the production of paper.^{26–28}

Recently, functionalized BC has been studied to adsorb some metal ions from the aqueous solutions.^{29–33} However, its adsorption efficiency was not satisfactory. In this study, amidoximated bacterial cellulose (Am-BC) was prepared through a simple two-step procedure and used as an adsorbent in a series of batch adsorption experiments as a function of the solution pH. In the present study, improvement in the adsorption efficiency was obviously improved as compared to the previous reports.^{31,32} The adsorption mechanisms and the regeneration of Am-BC using ethylenediaminetetraacetic acid (EDTA) were also studied.

EXPERIMENTAL

Materials

BC was prepared in our laboratory according to the method reported by Hestrin and Schramm.²⁵ Acrylonitrile (AN), hydroxylamine, EDTA, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ were purchased from Sinopharm Chemical Reagent. Deionized water was used for the preparation of the standard solutions for the adsorption tests. The standards for analysis were prepared from stock solutions of 1000 mg/L supplied by Shanghai

Institute of Measurement and Testing Technology. The prepared Am-BC used as adsorbent in the experiment was ground and sieved to less than 200 μm before used.

FTIR spectroscopy

Infrared spectra of BC, Am-BC, and the Am-BC with adsorbed metal ions were obtained by a NEXUS-670 FTIR Spectrometer. Pressed pellets were prepared by grinding the powder specimens with IR grade KBr in an agate mortar.

SEM observation

SEM was carried out on a scanning electron microscope (SEM, JSM-5600LV, JEOL, Japan). The BC and Am-BC were freeze-dried. The surface was coated with carbon and gold and photographed.

ζ potential measurement

A 0.1 g amount of dry powder of Am-BC was added into 100 mL of deionized water. The mixture was stirred for 12 h, and then the pH of the solution was adjusted with 0.1 M NaOH or 0.1 M HCl solution to a desired value. After 1 h stabilization, the supernatant with small fragments in it was used for ζ -potential measurements by a Zeta-Plus4 instrument (Brookhaven Instruments Corporation, Austin, TX).

XPS spectroscopy

XPS analysis before and after metal ions adsorption was performed using a model XSAM800 Instrument (KRATOS Product, Britain). An Mg $K\alpha$ target at 1253.6 eV and 16 mA \times 12.5 kV was used in the experiment. The sample was detected under 2×10^{-7} Pa. The binding energies (BE) were calibrated against the C 1s peak at 284.6 eV. The curve fitting was carried out with a mixed Lorentzian–Gaussian function.

Adsorption experiments

Batch adsorption experiments were conducted in 50 mL flasks. A 0.02 g amount of Am-BC was added into 10 mL solution with a known pH value (adjusted with 0.1 M NaOH or 0.1 M HNO_3). The mixture was shaken in a thermostatic water-bath shaker operated at 25°C and 200 rpm. Samples were taken out at the predetermined time intervals for the analysis of metal ion concentrations in the solution after the adsorption equilibrium was reached. The concentrations of Cu^{2+} and Pb^{2+} in the samples were analyzed with an atomic absorption spectrophotometer (ZEEnit 700, Germany). The initial

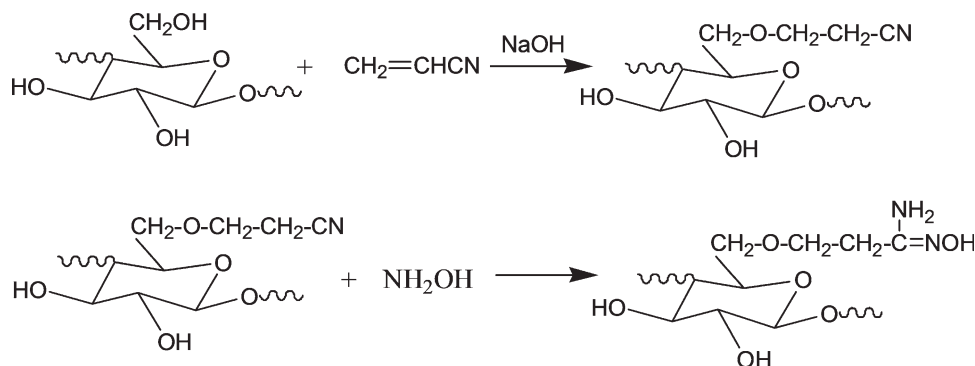


Figure 1 Synthetic route to Am-BC.

concentrations of metal ions in all of the test solutions were 200 mg L^{-1} , but the initial pH values of the solutions were different, ranging from two to about seven. After the experiment, the Am-BC was separated from the solution by filtration, rinsed with deionized water, and then prepared for other analyzes such as FTIR, SEM or XPS, and so forth. The amount of metal ions adsorbed on the adsorbent at adsorption equilibrium was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium metal ions concentrations (mg L^{-1}), respectively, V is the volume of the solution (L) and W is the weight (g) of the Am-BC used.

Regeneration of Am-BC

Desorption of metal ions from Am-BC was examined in a 0.1 M EDTA solution at 25°C for 1 h. After the desorption test, the Am-BC was separated and washed with deionized water, and reused in the next cycle of adsorption experiment. The adsorption–desorption experiments were conducted for five cycles.

RESULT AND DISCUSSTION

Preparation of Am-BC

Am-BC was prepared under a simple two-step reaction as described previously shown in Figure 1.²¹ Firstly, BC was added into AN under alkaline conditions to prepare cyanoethyl bacterial cellulose (CE-BC). Secondly, CE-BC is treated either by an aqueous solution of hydroxylamine at a known concentration or by an aqueous solution of hydroxylamine hydrochloride, whose pH is adjusted to between 9 and 10 by adding sodium carbonate. After treatment at 80°C for 3 h, the modified bacterial cellulose is fil-

tered, washed with deionized water till neutral, dried under a vacuum, dried under a vacuum, and stored in a desiccator.

Elemental analysis of nitrogen content characterized is 7.99% in CE-BC, and 12.63% in Am-BC. According to the relations reported by Saliba et al.,²¹ the value of the degree of substitution in amidoxime groups obtained from the elemental nitrogen analysis was about 0.864, which is higher than that of plant cellulose (0.419). The results suggested that the amination can be influenced by the morphology of cellulose. As BC microfibrils are much thinner than fibers of plant cellulose, much more reactive hydroxyl groups on the surface of BC can be functionalized.

Scanning electron micrography (SEM)

BC is a three-dimensional network comprised of nanofibers. To make use of this specific structure for various applications, the microfibrinous structure of BC should be maintained during the subsequent procedure. Figure 2(a) shows the SEM image of the obtained Am-BC. Compared with that of original BC [shown in Fig. 2(b)], the ribbons of the Am-BC surface is around $0.1 \mu\text{m}$ and the microporous network structure is maintained through the amidoximation procedure.

Adsorption behavior

Figure 3 shows the experimental results for the Cu^{2+} and Pb^{2+} removal under various pH values at adsorption equilibriums. The pH values were varied between 2 ± 0.1 and 7 ± 0.1 . It shows that the adsorption capacity increased significantly with the increase of pH when pH was less than 5.0. When pH value was between 5.0 and 5.5, Cu^{2+} and Pb^{2+} adsorption onto Am-BC decreased with the increase of solution pH values. The maximum adsorption capacity of Cu^{2+} and Pb^{2+} were found to be 84 and 67 mg g^{-1} under the test condition, respectively, which is obviously higher than the animated BC we

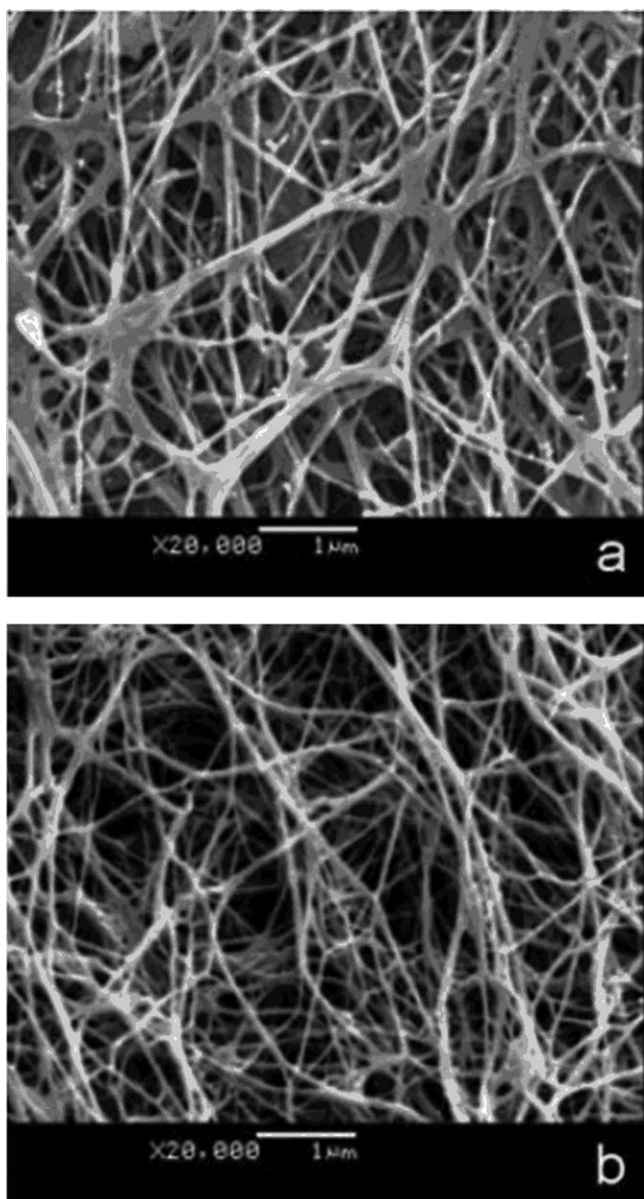


Figure 2 Scanning electron micrograph of Am-BC (a) and BC (b).

previously reported.³² From pH 5.5 to 7.0, the adsorption increased again with the increase of pH, which resulted from the precipitation of Cu^{2+} and Pb^{2+} at higher pH. From the results in Figure 3, we can conclude that pH plays an important role in the Cu^{2+} and Pb^{2+} adsorption onto Am-BC. The change of the adsorption extent of adsorption with the pH indicates that more than one mechanism operate in the adsorption of Cu^{2+} and Pb^{2+} on Am-BC.

FTIR spectra analysis

The FTIR spectra of BC, CE-BC, Am-BC, and metal ions-loaded Am-BC are shown in Figure 4. The

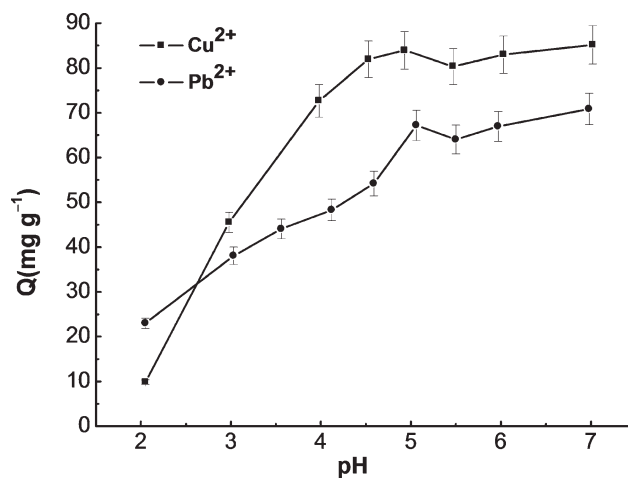


Figure 3 The effect of pH on the amount of Cu^{2+} and Pb^{2+} adsorbed onto Am-BC. Initial metal ion concentration 200 mg L^{-1} , pH 2 ± 0.1 to 7 ± 0.1 , contact time 3 h, amount of Am-BC 0.02 g.

peaks at 1063 and 2899 cm^{-1} corresponding to C—O—C and C—H stretching bands are observed in all the samples. The major peak located at around 3400 cm^{-1} in BC is attributed to —OH stretching vibration [Fig. 4(a)]. On grafting of cyano groups onto BC, a sharp peak at 2252 cm^{-1} is observed in CE-BC [Fig. 4(b)]. Then this peak disappeared and two new absorption peaks at 1658 and 912 cm^{-1} appeared in Am-BC [Fig. 4(c)]. These correspond to the stretching vibration of C=N and N—OH bonds, respectively. This conforms that cyano groups were converted to amidoxime groups by reacting with hydroxylamine. Moreover, the peak at around 3445 cm^{-1} becomes broader, compared with that of BC which might come from the combination of the stretching vibration bands of both —OH and —NH₂

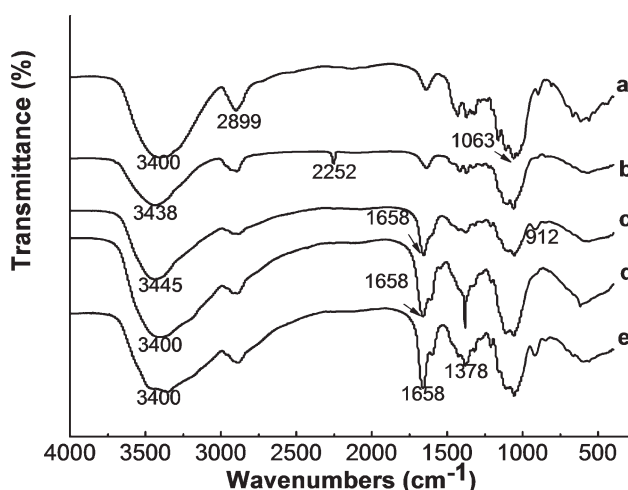


Figure 4 FTIR spectra of BC (a), CE-BC (b), Am-BC (c), Am-BC with Cu(II) adsorbed (d), Am-BC with Pb(II) adsorbed (e).

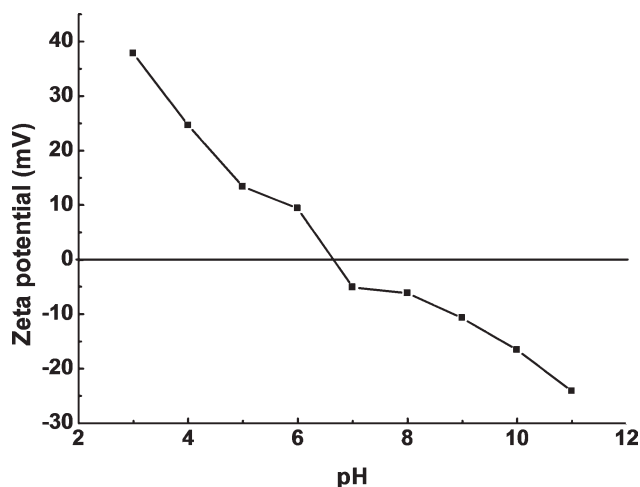


Figure 5 The ζ potentials of Am-BC.

groups. Besides, the increase of intensity around 1378 cm^{-1} related to the N—H bending band is observed, which also confirms the existence of —NH_2 in Am-BC. When Am-BC was loaded with metal ions, the variation of the peak can be explained by the formation of the complex between metal ion and amidoxime groups [Fig. 4(d,e)].³³

ζ potential analysis

The ζ -potentials of Am-BC under different solution pH values are shown in Figure 5. Am-BC has positive ζ -potentials in an acidic condition and negative ζ -potentials in a basic condition, with a point of zero ζ -potential at about pH 6.6, which is close to the pKa values of 6.3–6.6 for the amino group in chitosan reported by others.^{34–36} The positive ζ -potentials at greater pH values for the Am-BC can be attrib-

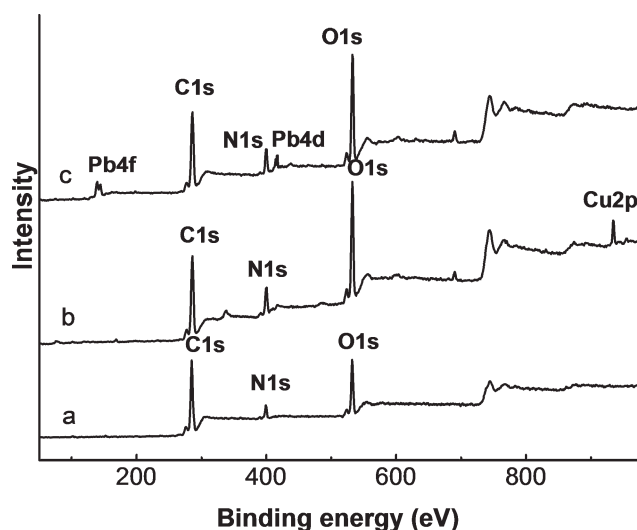


Figure 6 XPS spectra of Am-BC (a), Am-BC with Cu(II) adsorbed (b), Am-BC with Pb(II) adsorbed (c).

uted to the protonation behavior of the nitrogen atoms in the —NH_2 group introduced on the surface of the Am-BC. Similarly, the negative ζ -potentials of the Am-BC at pH greater than 6.6 may be attributed mainly to the —OH groups of the Am-BC.

Copper and lead as the prevalent contaminants in many industrial effluents are known to exist in different forms in aqueous solution at different pH values. At pH below 6.6, Cu^{2+} and Pb^{2+} are the major species which transport and attach to Am-BC may be affected, due to the positive ζ -potentials possessed by Am-BC. With the increase in pH, the protonation behavior of the nitrogen atoms can become weaker. Am-BC can adsorb them through chelation. With the increase of pH from 6 to 7, CuOH^+ and PbOH^+ dominates.³⁷ Hence, from an electrostatic interaction point of view, the adsorption of copper and lead on Am-BC can be enhanced at $\text{pH} > 6.6$, due to the negative ζ -potentials of Am-BC.

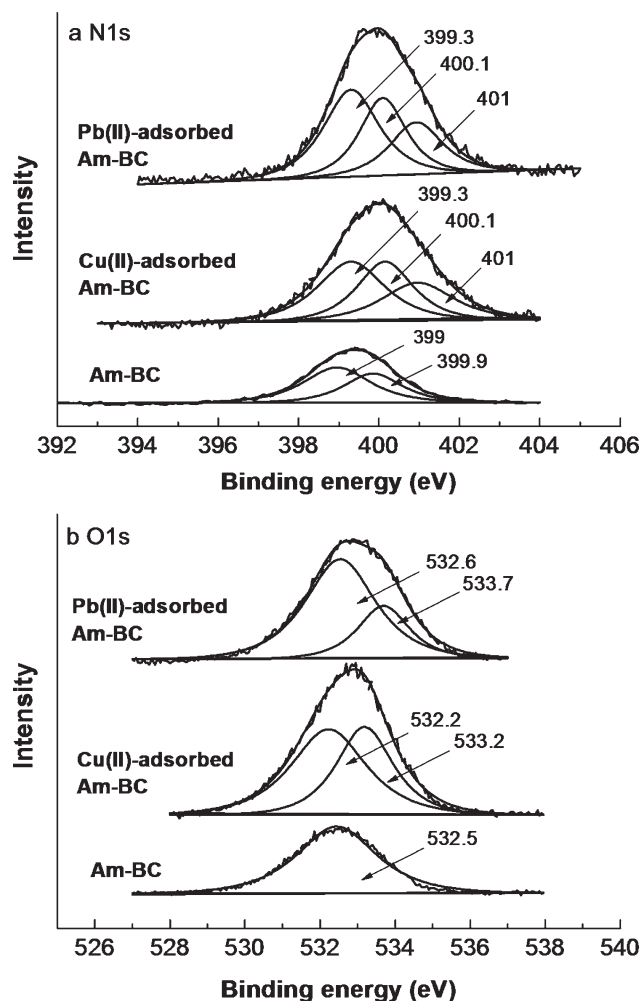


Figure 7 XPS spectra of N 1s (a) and O 1s (b) for Am-BC and Am-BC before and after the adsorption of Cu^{2+} and Pb^{2+} .

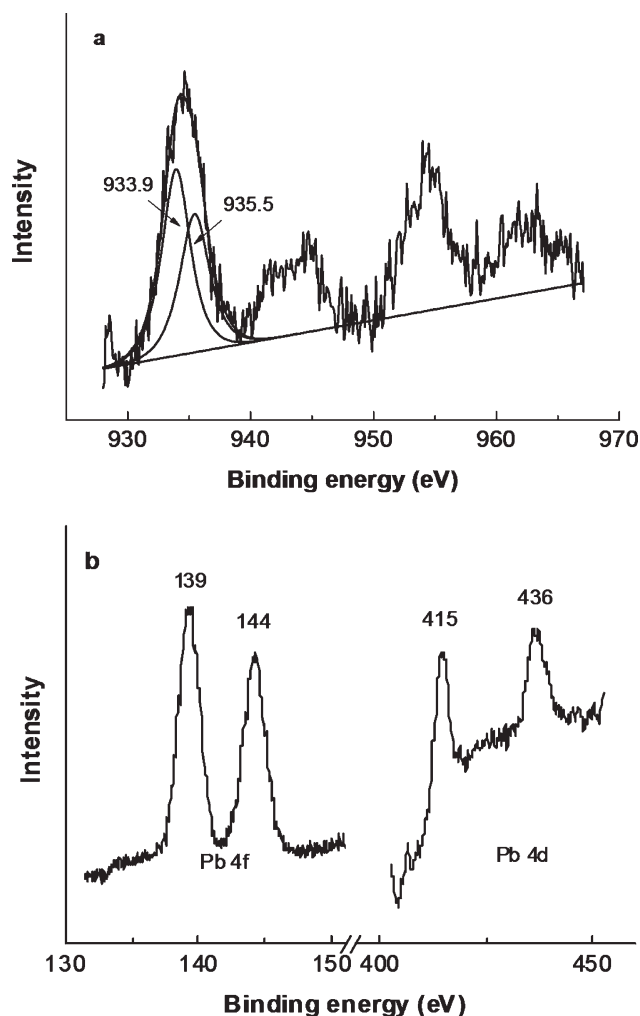


Figure 8 XPS spectra of Cu 2p (a) and Pb 4d and Pb 4f (b) for the Am-BC with Cu²⁺ and Pb²⁺ adsorbed.

XPS spectra study

Figure 6 shows the typical results of XPS spectra for Am-BC before and after metal adsorption. The peaks at BE of 285 eV, 400 eV, 533 eV correspond to the C 1s, N 1s, and O 1s spectra, respectively, which exist in all samples. It is observed that after Cu²⁺ adsorption, a new peak with a binding energy of 934.3 eV appeared which can be assigned to the Cu 2p_{3/2} orbital. And two new peaks at the BE of about 139 eV and 415 eV appear after Pb²⁺ adsorption, which represent the Pb 4f and Pb 4d orbital. These indicate that Cu²⁺ and Pb²⁺ were adsorbed onto Am-BC.

High resolution spectra of N 1s and O 1s regions for Am-BC and the copper- and lead-adsorbed Am-BC are shown in Figure 7. As seen in Figure 7(a), there are two peaks at the BE of 399 and 399.9 eV of Am-BC, which can be attributed to the nitrogen atoms in NH₂-C and C=N-OH species, respectively.²³ After Cu²⁺ and Pb²⁺ adsorption, a little shift of the BE at both peaks are observed [one peak at

399 to 399.3 eV, another peak at 399.9 to 400.1 eV for copper (II) and lead (II)-adsorbed, respectively], and a new peak at BE of 401 eV appears. The results confirm that Cu²⁺ and Pb²⁺ were adsorbed on the amidoxime groups of the Am-BC. The lone pair of electrons in the nitrogen atoms of the amidoxime group is donated to form a shared bond between a Cu²⁺ or Pb²⁺ and the nitrogen atoms. The O 1s spectra of Am-BC, Am-BC before and after metal ions adsorption are shown in Figure 7(b). The peak at 532.4 eV is assigned to the oxygen in the C-O and OH bonds.³⁸ After the adsorption of Cu²⁺ and Pb²⁺, binding energy shift is observed (532.5 to 532.2 for copper (II) and to 532.6 for lead (II)-adsorbed, respectively) and a new peak appears at 533.2 eV for copper (II) and 533.7 eV for lead (II)-adsorbed. The results indicate that the hydroxyl groups on the surface of the Am-BC also play an important role in the adsorption of the metal ions. The XPS analyzes reveal that Cu²⁺ and Pb²⁺ are adsorbed on the surface of the Am-BC probably due to both nitrogen and oxygen atoms.

Figure 8(a) shows the XPS spectrum of Cu 2p_{3/2} orbital which can be fitted to two peaks at BE of 933.9 eV attributed to nitrogen-bound copper and 935.5 eV attributed to the Cu(II).¹⁹ This demonstrates that chelation plays the main role in the adsorption process though physical adsorption contributes to the overall adsorption process. The XPS spectra of Pb 4d and Pb 4f for the lead-adsorbed onto Am-BC is shown in Figure 8(b). The peak at BEs of 139 eV is attributed to Pb²⁺, however, the well known peaks at the 137 eV and 138.3 eV represent the N-Pb-N or N-Pb-O and Pb-O, respectively, were not observed obviously.¹⁹ So the contribution to the Pb²⁺ adsorption onto Am-BC mainly comes from the participation of both amine and hydroxyl groups in binding Pb²⁺.

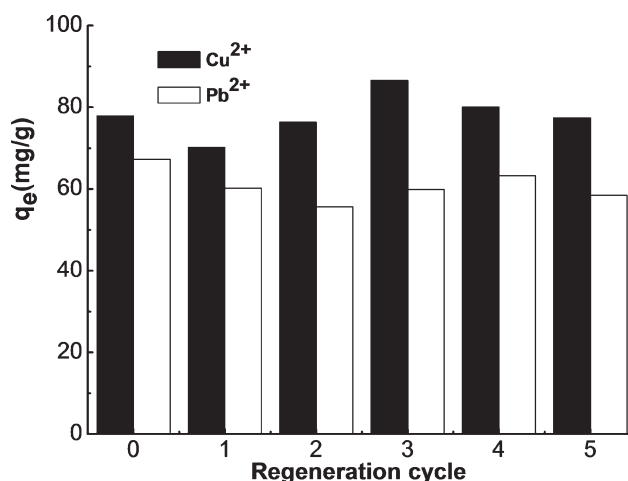


Figure 9 Effect of regeneration of Am-BC using EDTA on its adsorption capacity. Initial concentration of metal ions 200 mg/L, contact time 1 h, pH 5 ± 0.1.

Adsorption mechanism

In review of the results mentioned above, Cu^{2+} and Pb^{2+} adsorption on Am-BC was found to be strongly pH-dependent and to display a maximum and a minimum uptake capacity in the pH range of 2–7. Am-BC had positive ζ -potentials at $\text{pH} < 6.6$, and the adsorption performance cannot be simply explained through an electrostatic interaction. Complexation, ion exchange, and electrostatic interactions are all identified to play a role in adsorption on Am-BC, but their relative importance varies with solution pH values. The present work shows that the only adsorption sites for Cu^{2+} and Pb^{2+} are amidoxime or hydroxyl groups of the Am-BC. Both nitrogen and oxygen atoms have a lone pair of electrons that can bind a proton or a metal ion through an electron pair sharing to form a complex. In FTIR spectra, the variation of peaks suggests the existence of interactions between metal ions and the nitrogen atoms in the amidoxime groups or the oxygen atoms in the hydroxyl groups, indicating the complex formed between metal ions and the O or N atom. The results were further supported by the XPS studies. It is demonstrated that the electrostatic interactions also contribute to the adsorption process. The XPS results explained that the adsorption mechanism for Cu^{2+} can be mainly attributed to the formation of metal complexes with both the nitrogen atoms in the amidoxime groups and the oxygen atoms in the hydroxyl groups on the Am-BC. However, the adsorption mechanism for Pb^{2+} mainly comes from the precipitation.

Regeneration of Am-BC

Desorption of Cu^{2+} and Pb^{2+} from Am-BC was carried out using 0.1M EDTA solution at 25°C for 1 h. The effect of five adsorption–desorption consecutive cycles on the efficiency of the individual adsorption of Cu^{2+} and Pb^{2+} on Am-BC was studied. As shown in Figure 9, it was found that the Cu^{2+} and Pb^{2+} adsorbed on Am-BC were easily desorbed. The regenerated Am-BC was highly effective in the readorption of Cu^{2+} and Pb^{2+} , even the adsorption ability of Am-BC was kept constant observed to be the same after several repetitions of the adsorption–desorption cycles. Am-BC can be regenerated by EDTA because the efficiency of the adsorption for Cu^{2+} and Pb^{2+} did not significantly decrease after repeated desorption.

CONCLUSION

In conclusion, Am-BC was successfully prepared by modifying the BC and its microporous-network structure remained intact after modification. This

new material was used for the removal of Cu^{2+} and Pb^{2+} under different pH values and its regeneration was investigated. Under the maximum adsorption condition, the adsorption mechanism for Cu^{2+} can be mainly attributed to the formation of metal complexes with both the nitrogen atoms of the amine groups and the oxygen atoms of the hydroxyl groups on the Am-BC. However, the adsorption mechanism for Pb^{2+} mainly comes from the precipitation. Though electrostatic interactions play a role in both Cu^{2+} and Pb^{2+} adsorption onto Am-BC, yet the contribution to the adsorption mechanism for Pb^{2+} mainly comes from precipitation. The used Am-BC could be regenerated successfully without significantly affecting its adsorption efficiency. It can be concluded that Am-BC has potential applications as an adsorbent for heavy metal ions from aqueous solutions or wastewater.

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