

Heavy Metal Ion Removal by Amidoximated Bagasse

Mohammad L. Hassan, Nahla A. El-Wakil

Cellulose and Paper Department, National Research Center, Dokki, Cairo, Egypt 12622

Received 18 October 2001; accepted 5 May 2002

ABSTRACT: Amidoximated bagasse (Am-B) was prepared by treating sugarcane bagasse fibers with acrylonitrile in the presence of sodium hydroxide followed by aqueous hydroxylamine. Adsorption of some heavy metal ions, namely, Cu(II), Hg(II), Ni(II), Cr(III), and Pb(II) on the prepared Am-B at different metal ion concentration, intervals, and temperatures was studied. Also, the selectivity of the prepared Am-B toward

adsorption of the aforementioned metal ions in an equimolar mixture was studied. The effect of regeneration of Am-B using ethylenediamine tetraacetic acid disodium salt (EDTA), up to five times, on its adsorption capacity of the aforementioned metal ions was investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 666–670, 2003

INTRODUCTION

The removal of heavy metal ions from industrial effluents has been studied extensively because of their well-known hazardous effect on different forms of life. For example, Cu(II) ions from industrial and mining effluents can eliminate all fish and marine plants for miles downstream from the source.¹ Different treatment methods were proposed such as electrolysis, reverse osmosis, and ion exchange.^{2–4}

Lignocellulosic materials and wastes such as peanut skin,⁵ cotton⁶ (the purest natural cellulose), onion skin,⁷ wood saw,⁸ rice hulls,⁹ maize stalks,¹⁰ barks,¹¹ jute fibers,¹² bagasse,¹³ rice straw,¹⁴ corncobs,⁵ and palm kernel husks¹⁶ have received attention in heavy metal ion removal. All lignocellulosic materials contain cellulose, hemicellulose, lignin, and other minor components. So, various functional groups such as carboxylates, phenolic and aliphatic hydroxyls, and carbonyl groups in these materials have the ability to adsorb some metal ions.

To increase the metal ion adsorption of cellulose, it was chemically modified by introducing different complexing groups such as aminoalkyl,¹⁷ 2,2-diaminoethyl,¹⁸ and amidoxime,¹⁹ or an ionic moiety such as phosphate,²⁰ thiolate,²¹ carboxy,²² and carboxymethyl.²³

The purpose of the present work was to introduce amidoxime groups into bagasse constituents and to study the adsorption of Cu(II), Cr(III), Ni(II), Pb(II), and Hg(II) at different conditions on the prepared Am-B. The selectivity of the Am-B toward the adsorption of the aforementioned metal ions was studied. The effect of regeneration of Am-B using EDTA on its adsorption capacity was also studied.

EXPERIMENTAL

Materials

Bagasse, in the form of 2- to 3-cm-long fibers, was supplied by Edfu Pulp Company, Edfu, Egypt. The chemical composition of the bagasse was 21.4% lignin, 25.9% hemicellulose, 78.3% holocellulose, 55.3% alpha cellulose, and 1.4% ash. The fibers were milled using a 20-mesh screen, extracted with ethanol–benzene (2:1 v/v) for 6 h, washed with distilled water, and then left to air-dry. All chemicals and solvents used were reagent grade and used without further treatment or purification.

Preparation of cyanoethyl bagasse

Cyanoethyl bagasse (CE-B) with a nitrogen content of 11.3% was prepared as described previously.²⁴

Preparation of amidoximated bagasse (Am-B)¹⁹

CE-B was treated with an aqueous solution of hydroxylamine hydrochloride (10% wt/v) at pH 9–10; sodium carbonate was used to adjust the pH. The mixture was heated at 80°C for 3 h. The modified bagasse was then filtered, washed with deionized water, and finally dried at 60°C. The amidoxime content (C_A) of Am-B, in millimoles per gram, was calculated as follows:

$$C_A = [(N_2 - N_1)/M_N] \times 10$$

where N_2 is the nitrogen content of Am-B; N_1 is the nitrogen content of CE-B; and M_N is the atomic weight of nitrogen.

Fourier transform infrared analysis

A JASCO 300-E Fourier transform infrared spectrometer was used for FTIR to follow up the chemical

Correspondence to: M. L. Hassan (mlhassan@eudoramail.com; mlhassan@hotmail.com).

changes in bagasse by cyanoethylation and amidoximation.

Metal-ion adsorption

Am-B fibers (0.2 g) were added to 20 mL of the different buffered metal chloride solutions. The pH was adjusted using a Clark-Lubs buffer solution²⁵ made up of 0.1N HCl, 0.1N NaOH, and 0.1N potassium hydrogen phthalate. The mixture was stirred for different times (0.25–24 h) and at different temperatures (25–70°C) in closed flasks. The fibers were filtered, and the concentration of remaining metal ions in the filtrate was determined by EDTA titration.²⁶

Metal-ion desorption

Am-B (0.2 g) containing adsorbed metal ions was stirred with 10 mL of a standard EDTA solution (0.1N) for 1 h at 80°C, then filtered off and washed with hot distilled water and finally with deionized water.

Selectivity of Am-B toward metal ion adsorption

Am-B (0.4 g) was immersed in 20 mL of a mixture consisting of 0.01M solution of Cu(II), Cr(III), Ni(II), and Hg(II) for 4 h at room temperature. The fibers were filtered, and the filtrate was collected. The residual metal ions in the filtrate were determined as follows: Cr(III), Ni(II), and Cu(II) were determined using a Varian Spectra AA 220 Atomic Absorption Spectrometer. Hg(II) metal ion concentration was determined indirectly as follows: the concentration of Cu(II) and Ni(II) was determined by EDTA in a 20-mL portion of the filtrate using Murexide as an indicator; EDTA forms complexes with Cu(II) and Ni(II) on cold but very slowly with Cr(III) and Hg(II). To another portion of the filtrate, EDTA solution equivalent to Cu(II) and Ni(II) were added, then both Hg(II) and Cr(III) were back-titrated using a standard Cu(II) solution after adding excess 0.01M EDTA and heating the solution near to boiling. PAN was used as an indicator. The concentration of Hg(II) was calculated as follows: Number of millimoles of Hg(II) = total number of millimoles of Hg(II) and Cr(III) determined using EDTA – number of millimoles of Cr(III) determined using the atomic absorption technique.

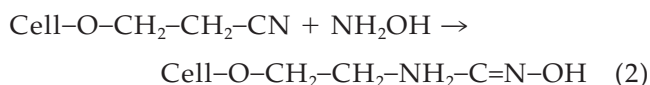
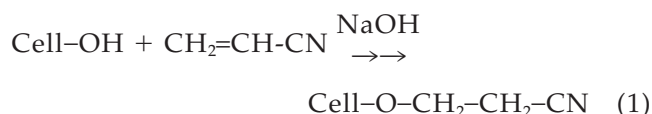
Regeneration of Am-B

After adsorption of the metal ions, Am-B fibers were regenerated by their immersion in 0.1M EDTA solution at 80°C for 1 h and filtered, and the fibers were thoroughly washed with hot distilled water and finally with deionized water.

RESULTS AND DISCUSSION

Preparation and characterization of Am-B

Hydroxyl groups of cellulose or lignocellulosic materials react with acrylonitrile under alkaline conditions to give a cyanoethyl derivative [eq. (1)]. Treatment of the cyanoethyl derivative with aqueous hydroxyl amine or hydroxyl amine hydrochloride whose pH was adjusted at 9–10 by adding sodium carbonate results in the formation of an amidoximated derivative [eq. (2)].



Previous studies have shown that the transformation of the cyano group (CN) of cyanoethyl cellulose to the amidoxime group increases with increasing hydroxyl amine concentration and temperature. Also, this transformation increases sharply with time, then tends toward a steady value after 2 h.^{7,19}

In this study cyanoethyl bagasse (CE-B) having a nitrogen content of 11.3% was prepared using the optimum conditions previously found.²⁴ The Am-B prepared from the CE-B had a nitrogen content of 14.4%; this value is equivalent to an amidoxime content (C_A) of 3.25. In a previous study on the preparation of Am-cellulose,¹⁹ a C_A content of 3.76 (nitrogen content of 15.26%) could be prepared using CE-cellulose having a nitrogen content of about 9.9% under similar reaction conditions to that used for preparing of Am-B.

FTIR spectra of Am-B

Figure 1 shows the IR spectra of bagasse and Am-B. A new absorption peak at 1660 cm^{-1} corresponding to the stretching vibration of C=N appeared in the spectra of Am-B. A reduction in the intensity of the C—O band at 1040 cm^{-1} occurred. This may be because the N—O bond of the introduced amidoxime group has an absorption band at the same frequency region of the C—O bond but of a lower intensity because the N—O band has a lower dipole moment than the C—O band. A band of low intensity at 2240 cm^{-1} is still present because of residual cyano groups.

Adsorption of heavy metal ions on Am-B

A previous study showed that both cellulose and cyanoethyl cellulose have no affinity for copper and chromium ion adsorption in the presence of phthalate

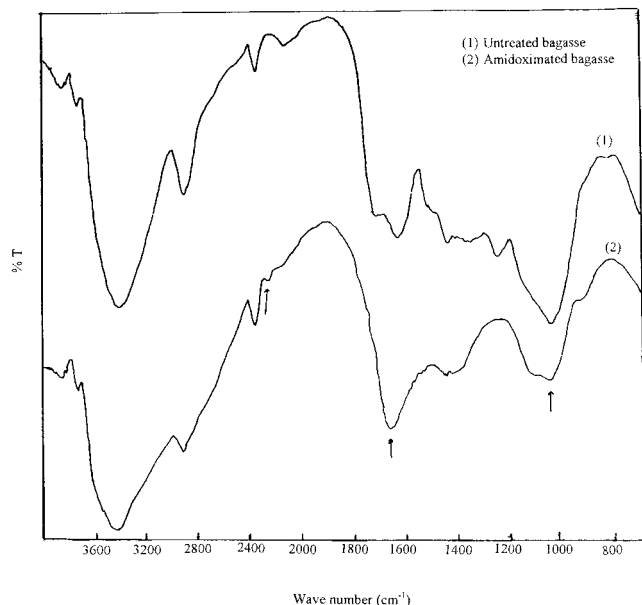


Figure 1 IR spectra of untreated and amidoximated bagasse.

anions at 25°C. On the other hand, Am-cellulose has strong affinity for copper and chromium ion adsorption. A 1:1 octahedral complex of Cr(III) or Cu(II) and Am-cellulose in the presence of phthalate anions was estimated¹⁹; it was also found that the higher the amidoxime content of the Am-cellulose, the higher was the adsorption of the Cr(III) and Cu(II) metal ions. In another study, bagasse in the absence of phthalate was found to adsorb up to about 0.3 mmol of Cu(II) per gram of bagasse.¹³

In this study adsorption of Cu(II), Cr(III), Ni(II), Pb(II), and Hg(II) on the prepared Am-B at different pHs, contact times, metal ion concentrations, and temperatures was studied. Unfortunately, Pb(II) was found to form a precipitate in the presence of phthalate anions. So the study was carried out on the other metal ions.

Factors affecting adsorption of heavy metal ions effect of pH

Figure 2 shows the effect of pH of the metal ion solutions on the residual metal ions and on the amount of the adsorbed metal ions per gram of Am-B after 24 hours contact time. As expected, the higher the acidic conditions, the lower was the adsorption of metal ions; this may be because of the protonation of the amino groups at the acidic conditions. As shown in Figure 1, up to about 86%–92% of Cu(II), Cr(III), or Hg(II) ions could be adsorbed using 0.2 g of Am-B having a C_A of 3.25 and 20 mL of a 0.0025M solution of the metal ions at a pH of 5–6. It was found that 0.1 g of Am-cellulose having a C_A of 3.87 could adsorb completely all the Cu(II) and Cr(III) ions present in 10 mL of 0.01M metal ions solution at pH 6.¹⁹ The lower

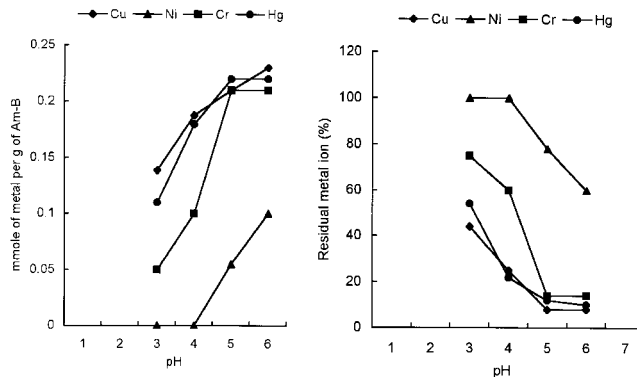
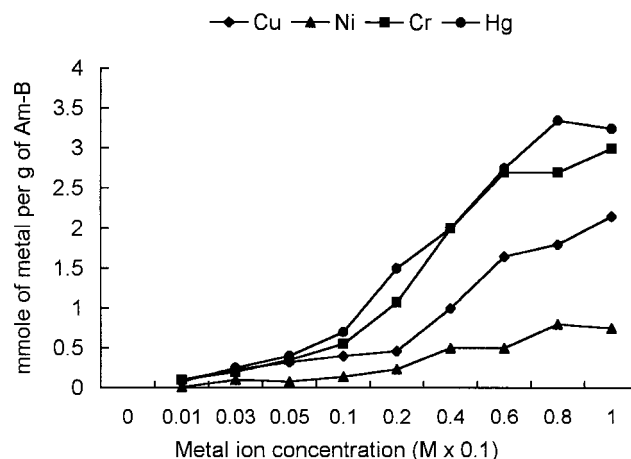


Figure 2 Effect of pH on adsorption of metal ions on amidoximated bagasse.

adsorption capacity of Am-B may be attributed to the presence of branched hemicelluloses and the three-dimensional structure of lignin, which may inhibit the formation of the complex between the metal ions and the amidoxime groups.

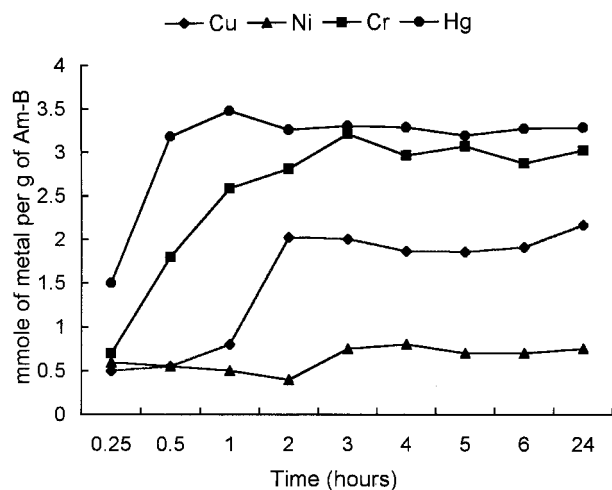
Effect of metal ion concentration

Figure 3 shows the effect of metal ion concentration on the adsorption of the different metal ions at pH 6. The figure shows that the quantity of metal ions adsorbed increased with an increasing concentration and then tended to level off. The maximum millimoles per gram of metal ions adsorbed were 3.35, 3.0, 2.15, and 0.8 for Hg(II), Cr(III), Cu(II), and Ni(II), respectively. These values are close to the amidoxime content (C_A) of Am-B only for Hg(II) and Cr(III); the C_A of Am-B used was 3.25. Generally, the adsorption of the metal ions by Am-B was in the order: Hg > Cr > Cu > Ni. This order may be because of the different stability of complexes between the different metal ions and the amidoxime groups. At the present time no data are avail-



Contact time 24 hrs; pH 6

Figure 3 Effect of metal ion concentration on quantity of metal ions adsorbed on amidoximated bagasse.



0.1 M metals ions solutions; pH 6

Figure 4 Effect of contact time on quantity of metal ions adsorbed on amidoximated bagasse.

able about the stability constants of complexes formed between the metal ions studied and the amidoximated derivatives.

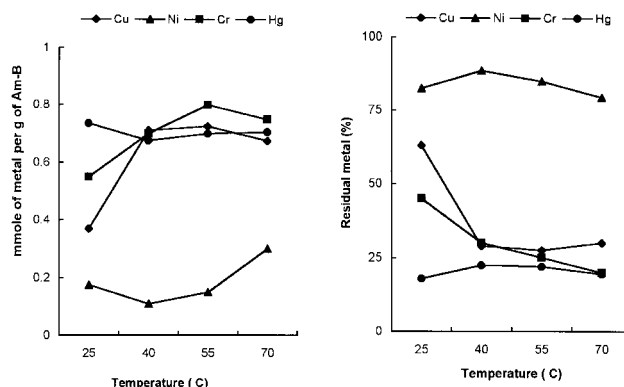
Effect of contact time

Figure 4 shows the effect of contact time on the amount of metal ions adsorbed per gram of Am-B at pH 6. As shown, the adsorption of the metal ions sharply increased during the first few hours of immersion, and the adsorption did not significantly increase after about 2–3 h.

Effect of temperature

The stability of complexation is dependent on temperature. Although it is generally known that for low-molecular-weight complexes the stability constant becomes larger as the temperature is lowered—that is, the higher the temperature, the lower the adsorption—it was found that increasing the temperature may not affect the adsorption of some metal ions on aminoalkyl cellulose derivatives and is also dependent on the concentration of the metal ions.¹⁷ For adsorption of Cu(II) on corncobs,¹³ a slight increase in adsorption was found on increasing the temperature from 25°C to 35°C.

Figure 5 shows the effect of temperature on the quantity of adsorbed metal ions on Am-B using 0.01M metal ions solutions at pH 6. Increasing the temperature from 25°C to 40°C resulted in a significant increase in the adsorption of both Cu(II) and Cr(III), whereas no significant change in the adsorption of Ni(II) and Hg(II) occurred on increasing the temperature. As also shown in Figure 5, on increasing the temperature from room temperature to 40°C, the re-



20 ml of 0.01 M metals ions solutions; pH 6; contact time 3 hours.

Figure 5 Effect of temperature on metal ions adsorption on amidoximated bagasse.

sidual metal ions of Cr(III) and Cu(II) could be decreased from about 42% and 62% to about 10% and 30%, respectively, when 20 mL of 0.01M metal ion solutions and 0.2 g of Am-B were used.

Selectivity of Am-B

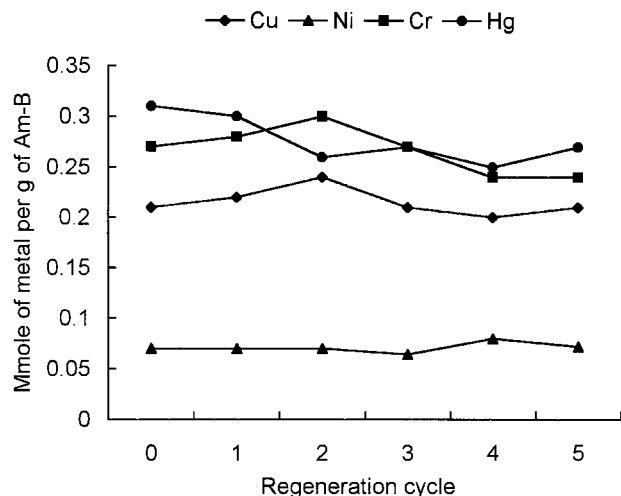
In the previous sections the adsorption of each of the heavy metal ions on Am-B was studied individually. In this part, the adsorption behavior of Am-B toward the metal ions in a mixture containing equal metal ions concentration (0.0025M) was studied. The results are shown in Table I. The millimoles per gram of adsorbed metal ions on Am-B were 0.12, 0.11, 0.08, and 0.04 for Cu, Hg, Cr, and Ni, respectively. This means that Cu(II) ions were selectively adsorbed on Am-B.

Regeneration of Am-B

Desorption of the different metal ions from Am-B was carried out using 0.1M EDTA solution at 80°C for 2 h. The effect of five adsorption–desorption consecutive cycles on the efficiency of the individual adsorption of the different metal ions on Am-B was studied. The results are shown in Figure 6. The efficiency of the adsorption of the different metal ions did not significantly decrease because of repeated desorption by EDTA at 80°C.

TABLE I
Quantities of Millimoles of Metal Ions Adsorbed on Am-B from 20-mL Mixture Containing 0.0025M of Each Metal Ion

Metal ion adsorbed per gram of Am-B (mmol)	
Cu(II)	0.12
Hg(II)	0.11
Cr(III)	0.08
Ni(II)	0.04



20 ml of 0.025 M metal ion solution; contact time 24 hrs; pH 6

Figure 6 Effect of regeneration of Am-B using EDTA on its adsorption capacity.

CONCLUSIONS

Bagasse fibers could be used directly without removing lignin or hemicelluloses to prepare a heavy-metal chelating derivative. The adsorption of the metal ions from an equimolar mixture of them occurred in this order: Cu > Hg > Cr ≫ Ni. The prepared Am-B could be regenerated successfully without significantly affecting its adsorption efficiency.

References

- Randall, J. M.; Reuter, F. W.; Friedman, M. *J Appl Polym Sci* 1975, 19, 1563.
- Bolto, B. A.; Pawlowski, L. *Waste Water Treatment by Ion Exchange*; Chapman and Hall: New York, 1987.
- Barcicki, J.; Pawlowski, L.; Cichocki, A.; Zagulski, L. In *Physicochemical Methods for Water and Wastewater Treatment*; Pawlowski, L., Ed.; Pergamon: London, 1980; p 237.
- Geckler, K. E.; Shkinev, V. M.; Ya, B. Spivakov, *Sep Purif Methods* 1988, 17, 105.
- Randall, J. M.; Hantala, E.; Mc Donald, G. *J Appl Polym Sci* 1978, 22, 379.
- Shukla, S. R.; Sakhardande, V. D. *J Appl Polym Sci* 1992, 44, 903.
- Kumar, P.; Dara, S.S. *J Polym Sci Polym Chem Ed* 1981, 19, 397.
- Morita, M.; Higuchi, M.; Sakata, I. *J Appl Polym Sci* 1987, 34, 1013.
- Suemitsu, R.; Uenishi, R.; Akashi, I.; Nakano, M. *J Appl Polym Sci* 1986, 31, 75.
- Okeimen, F. E.; Maya, A. O.; Oriakhi, C.O. *Int J Environ Anal Chem* 1988, 32, 23.
- Seki, K.; Saito, N.; Aoyama, M. *Wood Sci Technol* 1997, 31, 441.
- Shukla, S. R.; Sakardande, V. D. *Dyes Pigments* 1991, 17, 101.
- Nelson, C. F.; Ana, A. W.-H.; Edgardo, A. G.-P. *Intern. J Polymeric Mater* 1996, 34, 211.
- Shet, R. T.; Zeronian, S. H. *Cellulose Chem Technol* 1984, 18, 41.
- Costa, H. T.; Winkler-Hechenleitner, A. A.; Gomez-Pineda, E. A. *Separation Sci Technol* 1995, 30, 12, 2593.
- Ongbu, J. A.; Iweanya, V. I. *J Chem Ed* 1990, 67, 19, 800.
- Shigo, N.; Masato, A.; Yasuo, S.; Toshihiko, S. *J Appl Polym Sci* 1992, 45, 265.
- Smits, J. A.; Van Grieken, R. E. *Anal Chem* 1980, 52, 1479.
- Saliba, R.; Gauthier, H.; Gauthier, R.; Petit-Ramel M. *J Appl Polym Sci*, 2000, 75, 1624.
- Padilha, P. M.; Rocha, J. C.; Moreira, J. C.; Campos, J. T. S.; Federici, C. C. *Talanata* 1997, 45, 317.
- Tashiro, T.; Shimura, Y. *J Appl Polym Sci* 1982, 27, 747.
- Maekawa, G.; Koshijima, T. *J Appl Polym Sci* 1984, 29, 2289.
- Hosny, W. M.; Hadi, A. K. A.; El Saied, H.; Basta, A. H. *Polym Int* 1995, 37, 93.
- Hassan, M. L.; El-Wakil, N. A.; Sefain, M. Z. *J Appl Polym Sci* 2001, 79, 1955.
- Clark, W. M.; Lubs, H.A. *J Biol Chem* 1916, 25, 479.
- Cecil L. W., David W. W., *Comprehensive Analytical Chemistry*; Elsevier Publishing Company, 1960; Vol. IB, p 288–385.