Molecular Structure and Ion Exchange of Amidoximated Cellulosic Materials

A. M. A. Nada, Nahla A. El-Wakil

Cellulose and Paper Department, National Research Centre, Dokki, Cairo, Egypt

Received 20 May 2005; accepted 24 October 2005
DOI 10.1002/app.23802
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Modification of lignocellulosic materials, e.g., cotton stalks, bagasse, and rice straw, by incorporation of amidoxime group for ion exchange is investigated. The uptake of metal ions Cu, Cr, Ni, and Fe by these modified lignocellulosic materials is measured. Amidoximated bagasse has higher efficiency toward metal ions uptake than amidoximated cotton and rice straw. The effect of different variables, e.g., metal ion concentration, temperature of metal ion solution, and time of steeping, on the efficiency of the amidoximated (bagasse raw material, unbleached bagasse, and bleached bagasse) ion exchangers toward metal ions uptake is tested. The molecular structure of the prepared amidoxime from bagasse and its pulps is studied by using infrared spectroscopy. New bands appeared at 1661 and 916 cm^{-1} in the spectra of amidoximated bagasse and its pulps ion exchangers due to the formation of C═N and N—OH groups. The thermal properties of these ion exchangers is also studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 303–311, 2006

Key words: structure; ion exchangers; infrared spectroscopy

INTRODUCTION

Ion exchangers are broadly employed for treatment of process water and waste water. Agricultural residues have been examined for potential use as ion exchangers. The lignocellulosic materials themselves have low ion exchange or adsorption property as well as poor physical stability. For this reason, different methods have been developed, such as chemical modifications,[1–4] copolymerization, and crosslinking[5–7] to increase their ion exchange or adsorption efficiency. Also, incorporation of phosphate, sulfate, or carboxylate groups to lignocellulosic materials increases their efficiency toward cation exchangers. Various cellulose derivatives have been used as ion exchangers or chelate resin because of their hydrophilic character. Derivatization of the agricultural residues aimed to produce chelating anoin or cation exchangers. Among these derivatives, cellulose amidoxime can adsorb copper and chromium ions from their solutions.[8,9] Wastewater from dyes manufacturing and textile-dyeing industries, as well as paper and pulp mills contain appreciable amounts of metal ions and/or colored matters. They must be treated so as to lower the level of pollutant content before being disloaded into receiving streams. The processes for color removal from industrial effluent include biological treatment, coagulation, floatation, adsorption, oxidation, and hyperfiltration. Among these treatments, adsorption has attracted a considerable interest as feasible procedure for removing color from the effluent. Many agricultural by-products are able, eventually after chemical treatment, to recover metal ions by adsorption. Recently, recovery of metal ions from wastewater can be achieved by using modified cellulose by complexing group involving an amine functional groups.[10–12]

The purpose of this work was to study the efficiency of amidoximated cotton stalk, rice straw, bagasse, and its unbleached and bleached pulp towards Cu, Cr, Ni, and Fe ions uptake. The molecular structure of some amidoximated materials (bagasse and its pulps) was studied by using infrared spectroscopy. Also, the thermal properties of these materials were studied.

EXPERIMENTAL

The raw materials used in this study were bagasse raw material, unbleached kraft bagasse pulp, bleached kraft bagasse pulp, cotton stalk, and rice straw raw materials. Bagasse raw material and unbleached kraft bagasse pulp were obtained from Edfo Paper Mill, Kenna, Egypt. The chemical analysis of the material are shown in Table I. All samples were ground to 200 μm.

Preparation of cyanoethylated samples

Cyanoethylation of lignocellulosic materials was performed as described previously.[8] The nitrogen content of the cyanoethylated samples was 9.18, 10.49, and 13.63% for bagasse raw material, unbleached kraft bagasse pulp, and bleached kraft bagasse pulp, respectively.

Correspondence to: A. M. A. Nada (amnada46@yahoo.com).

TABLE I
Chemical Constituent of Different Lignocellulosic Materials

Material	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Ash (%)
Bagasse	20.7	27.2	44.8	1.2
Unbleached kraft bagasse pulp	6.8	26.4	63.5	1.07
Bleached kraft bagasse pulp	≤1	25.1	70	1.1
Rice straw	17.5	16.2	39	14.1
Cotton stalks	27	18.4	43	1.55

Amidoximation of the cyanoethylated materials

Amidoximation of cyanoethylated materials was carried out using 10% w/w hydroxylamine at 80°C for 3 h. After the complete reaction, samples were washed with deionized water till neutrality and then dried at 60°C. The nitrogen content of cyanoethylated and amidoximated samples was determined by using Kjeldhal method. The nitrogen content of amidoximated bagasse raw material, unbleached kraft bagasse pulp, and bleached kraft bagasse pulp was 10.78, 12.04, and 13.9%, respectively.

Infrared spectroscopy was carried out using KBr disc technique by JASCO FTIR 3006 (Fourier Transform Spectrophotometer).

Thermal analysis was carried out using a Perkine–Elmer Thermogravimetric Analyzer, TGA-7. All experiments of thermal analysis were conducted under nitrogen atmosphere at a heating rate of 10°C/min.

The ion exchangers were steeped in 25-mL solution containing metal ions of different concentrations for different times. Then, after steeping, filtration was carried out. The metal ion absorbed by amidoximated samples, in the filtrate, were measured using ICP-AES.

RESULTS AND DISCUSSION

Metal ion adsorption

The adsorption of metal ions by amidoximation of different agricultural wastes (rice straw, bagasse, and cotton stalks) from their solutions occur at pH 6. This pH is suitable for the amidoximated material for metal ion adsorption.[8,12] The affinity of bleached pulp and cyanoethylated bleached pulp toward metal ions adsorption is nearly nil. So, the amidoximated materials as ion exchangers for metal ions adsorption were studied. The ion exchange properties of the amidoximated materials were studied in a solution containing different metal ions (Cr, Fe, Cu, and Ni) of pH 6. The effect of different variables, e.g., metal ions concentration, metal ions solution temperature, and steeping time, on the efficiency of amidoximated materials toward metal ions adsorption was investigated.

Metal ions uptake of amidoximated different lignocelulosic material

Ion exchangers (0.1 g) were stirred in 25 mL of solution containing mixture of metal ions of 20 ppm for 30 min. After stirring, the mixture was filtered and the remaining metal ions in the filtrate were measured. Table II shows the metal ions uptake by amidoximated rice straw, cotton stalks, and bagasse raw materials. From the table, it is clear that the metal ions uptake by amidoximated bagasse raw material has a higher value than that by amidoximated rice straw and cotton stalks. This may be due to the higher nitrogen content, i.e. higher amidoxime functional groups. On the other hand, the rice straw amidoxime has a lower tendency to absorb metal ion due to its higher ash and lower cellulose content than bagasse and cotton stalks. Also, from the table, it is clear that the different metal ions were adsorbed by ion exchanger with in quantities. So, it is seen from the table that the Fe and Cu ions were adsorbed in higher amounts than the Cr and Ni ions. This adsorbance tendency of these ions is also possibly dependent on the softness of ion species as well as intrinsic and coulombic interaction.[5]

Effect of metal ions concentration on the efficiency of ion exchanger toward metal ion uptake

Figure 1 shows the adsorbed metal ions uptake by different amidoximated bagasse pulps. From the figure, it is clear that the amidoximated bagasse raw material has a lower efficiency for Cr, Fe, Cu, and Ni adsorption than that in the case of amidoximated unbleached and bleached bagasse pulp. This can be due to the higher lignin content, which may decrease cyanoethylation and amidoximation extent of bagasse raw material and also due to the lower nitrogen content, and consequently, the amidoxime content. On the other hand, the amidoximated unbleached bagasse

TABLE II
Metal Ions Uptake by Different Amidoximated Lignocellulosic Materials Ion Exchanger

	Cr (μmol/g)	Fe (μmol/g)	Cu (μmol/g)	Ni (μmol/g)
Amidoximated bagasse	0.6	44.6	31.7	15
Amidoximated cotton stalks	7.2	39.8	26.9	10.9
Amidoximated rice straw	6.1	35	24.1	8.2

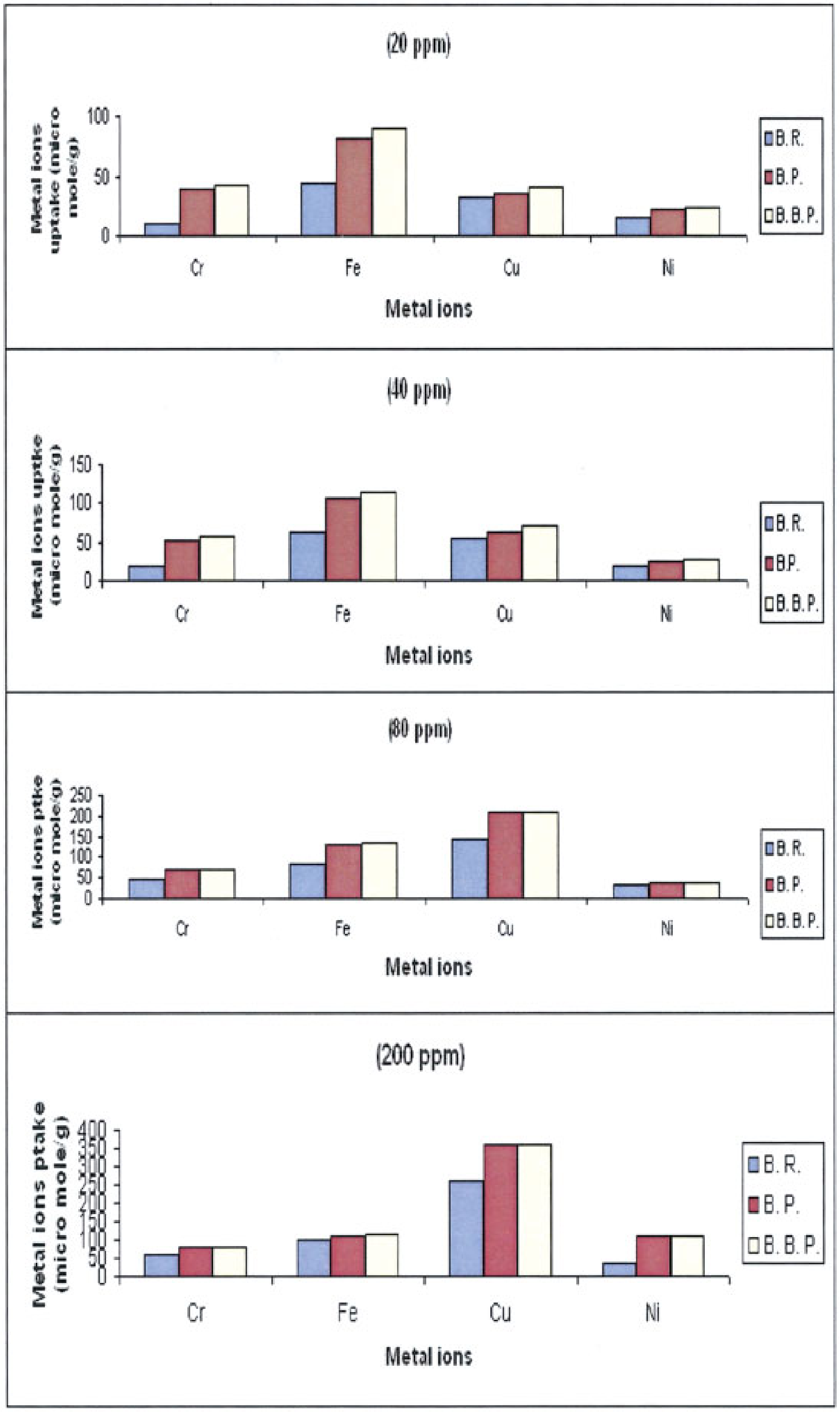

Figure 1 Effect of metal ion concentration on the efficiency of different amidoximated ion exchangers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pulp has a tendency toward metal ions uptake as nearly as that in the case of amidoximated bleached bagasse. From the figure, it can also be shown that the adsorption of metal ions by ion exchangers increases by increasing the concentration of metal ions. The adsorbed amount of metal ions by ion exchangers is different from one metal to another. For example, Fe and Cu are more adsorbed than Cr and Ni. The reduced stability of ion exchangers to bind with the metal ions is probably due to both steric and electronic effect. Boyd et al.[13] concluded that the ion exchanger adsorption affinities are determined by the magnitude

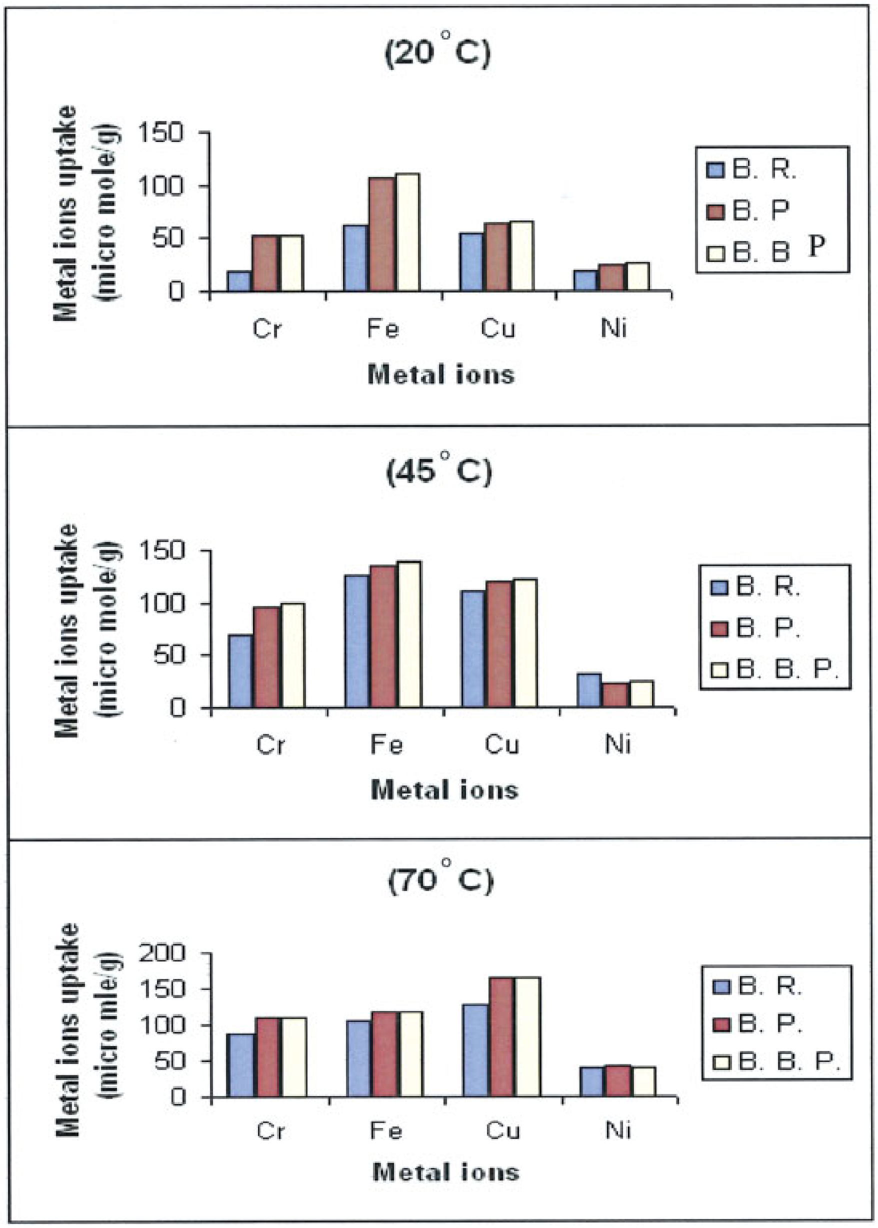

Figure 2 Effect of temperature of metal ions solution on the efficiency of ion exchangers toward metal ions uptake. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the charge and the hydrated radius of metal ions. In addition, a semihard acid of the metal ions has a high effect on its absorption by ion exchangers.

Effect of temperature of metal ions solution on the efficiency of ion exchangers toward metal ions uptake

Figure 2 shows the effect of metal ion solution temperature (20, 45, 70°C) on the absorption efficiency of ion exchangers. It is clear from the figure that, increasing metal ions solution temperature enhances the efficiency of ion exchangers toward metal ions uptake. The temperature of metal ions solution affects two major aspects of adsorption; the equilibrium position in relation with exothermic of the adsorption phenomena and the swelling capacity of the absorbent. So, the increase in the temperature increases the swelling of the ion exchanger and this causes the increase in penetration of metal ions through the fiber of ion exchanger. Also, increase in temperature increases the mobility of metal ions in solution and this causes the increase of metal ions uptake by ion exchangers.

Effect of stirring time

Time of stirring of ion exchange resin in metal ion solution plays an important role on its efficiency to-

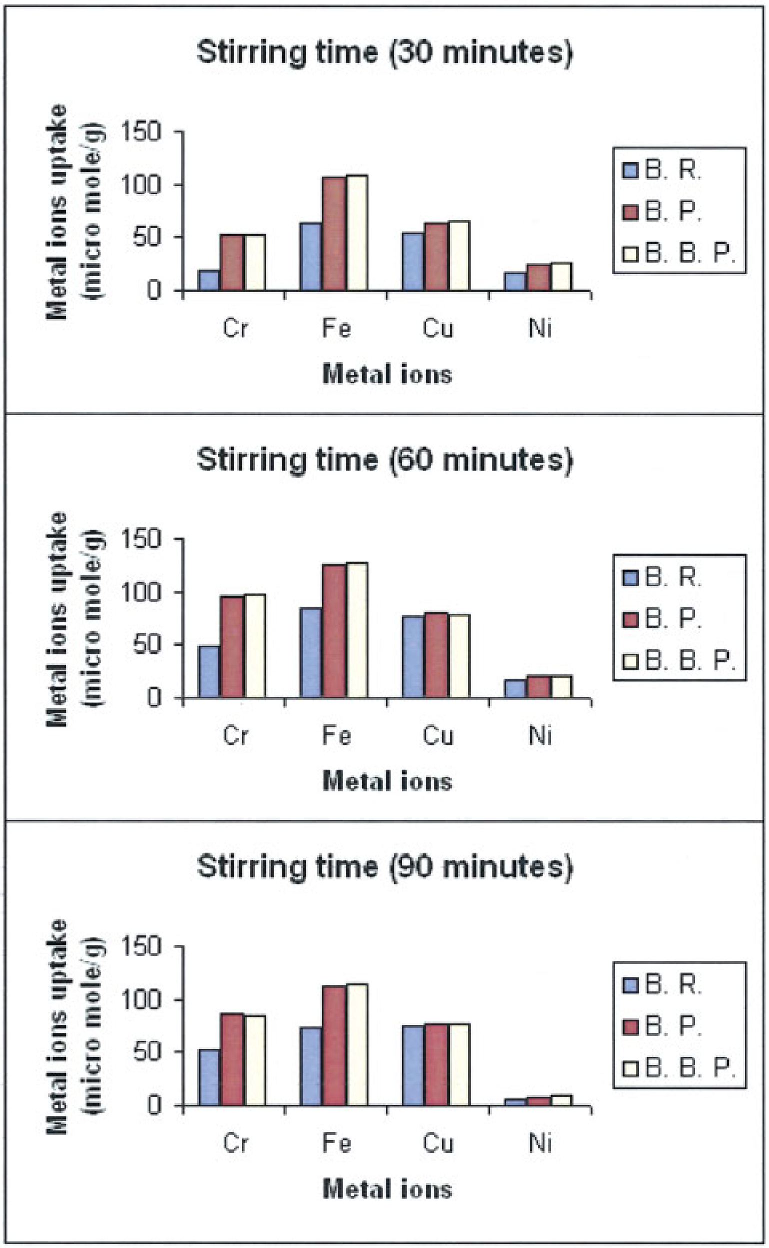

Figure 3 Effect of stirring time on the efficiency of ion exchanger toward metal ion uptake. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ward metal ion uptake. Figure 3 shows the effect of contact time of amidoximated bagasse raw material and amidoximated unbleached and bleached bagasse pulp. The experiment was carried out using metal ion concentration 20 ppm (pH 6) at 20°C and at different time intervals (30, 60, 90 min). From the figure, it can be seen that the increase of steeping time of the resin in metal ions solution from 30 to 60 min increases the metal ions uptake by ion exchangers. This can be attributed to the increase in chelation between the metal ions and amidoximated functional groups. Increasing the steeping time of resin in metal ions solution from 60 to 90 min does not significantly affect the amount of metal ions uptake by the ion exchangers.

Infrared spectra

Infrared spectra of cyanoethylated and amidoximated bagasse pulp

Infrared spectra of bleached bagasse pulp, cyanoethylated and amidoximated bleached bagasse pulp is shown in Figure 4. From the figure, a new band appeared in the cyanoethylated pulp at 2152 cm^{-1}, which is characteristic to cyano group. On the other hand, three new bands appeared at 2152, 1161, and 918 cm^{-1} in the amidoximated bagasse pulp. The bands are characteristic to the —C≡N, —C═N and N—OH groups. The relative absorbance (ratio of band intensity at any wavenumber/band intensity at 1325

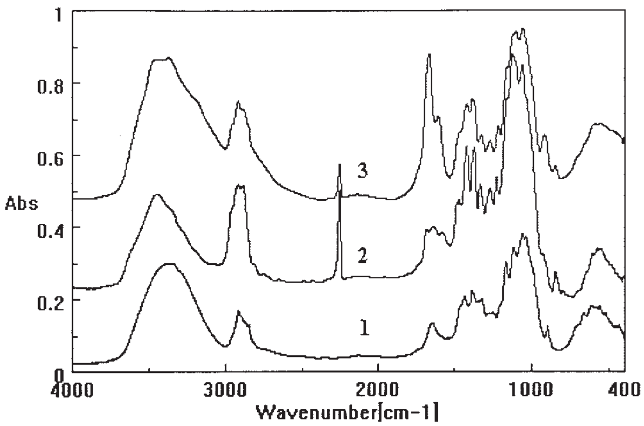

Figure 4 Infrared spectra of (1) bleached bagasse pulp, (2) cyanoethylated bleached bagasse pulp, and (3) amidoximated bleached bagasse pulp.

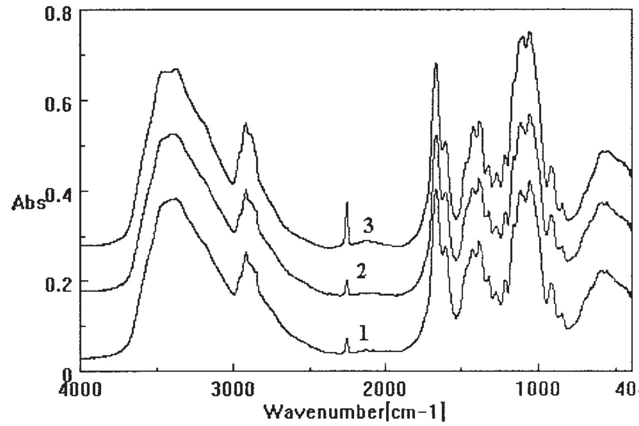

Figure 5 Infrared spectra of (1) amidoximated bagasse raw materials, (2) amidoximated unbleached bagasse pulp, and (3) amidoximated bleached bagasse pulp.

cm^{-1})[12,14] of cyano group in amidoximated pulp (0.8) has a lower value than that in the case of cyanoethylated pulp (1.23) due to the formation of oxime as shown in the following equations:

$$\text{Cell-OH} + \text{CH}_2{=}\text{CH—CN} \rightarrow \text{Cell—O—CH}_2\text{—CH}_2\text{—CN} \quad (1)$$

$$\text{Cell-OH} + \text{CH}_2{=}\text{CH}_2\text{—CN} + \text{NH}_2\text{OH} \rightarrow \text{Cell—O—CH}_2\text{—CH}_2\text{—}\underset{\displaystyle |\atop \displaystyle \text{NH}_2}{\text{C}}{=}\text{N—OH} \quad (2)$$

The ratio of band intensity at 2930 cm^{-1}, characteristic to the CH vibration of CH_2, to band intensity at 3430 cm^{-1}, characteristic to OH group, in case of of cyanoethylated (0.85) and amidoximated (0.8) pulp is higher than that in case of untreated pulp (0.68). This ratio has a lower value in case of amidoximated pulp than the cyanoethylated pulp due to the increase of OH intensity resulted from the formation of oxime C═N—OH. This is clear in the eqs. (1) and (2). Also, the relative absorbance of the band at 1120 cm^{-1}, characteristic to ether linkage, in case of cyanoethylated (0.75) and amidoximated pulp (0.74) is higher than that of the untreated pulp (0.59), as shown in Table III, due to the formation of ether linkage in the cyanoethylated and amidoximated pulp [eqs. (1) and (2)].

Effect of lignin removal on the spectra of amidoximated pulps

Infrared spectra of amidoximated bagasse raw material, amidoximated unbleached bagasse pulp, and bleached bagasse pulp are shown in Figure 5. From the figure, it is clear that the relative absorbance of the bands at wavenumber 1161 and 917 cm^{-1}, characteristic to oxime group, in the case of amidoximated bleached bagasse pulp has a higher value than that in the case of amidoximated bagasse raw material and unbleached bagasse pulp (Table IV). These results were confirmed by the higher nitrogen content of amidoximated bleached bagasse pulp than the other two amidoximated materials. Also, it is clear from the figure that, the relative absorbance of cyano group at wavenumber 2152 cm^{-1} in case of amidoximated bleached bagasse pulp has a lower value than the other amidoximated pulps. This means that the cyanoethylated bleached bagasse pulp is more reactive toward amidoximation than the cyanoethylated bagasse raw material and unbleached bagasse pulp. Also, it is seen that the relative absorbance of cyano group in amidoximated unbleached bagasse pulp is lower than that in the case of amidoximated bagasse raw material. This is attributed to the higher

TABLE III
Relative Absorbance of Different Bands of Untreated, Cyanoethylated and Amidoximated Bleached Bagasse Pulp

Material	—C≡N 2152 cm^{-1}	—C═N 1161 cm^{-1}	—N—OH 916 cm^{-1}	Ratio of band intensity 2920 CH_2/band intensity 3430 OH	—O— 1120 cm^{-1}
Untreated bleached pulp	—	—	—	0.68	0.59
Cyanoethylated pulp	1.23	—	—	0.86	0.74
Amidoximated pulp	0.8	1.56	0.99	0.80	0.75

TABLE IV
Relative Absorbance and Nitrogen Content of Different Amidoximated Bagasse Pulps Material

	Relative Absorbance			Nitrogen (%)
	$1162\ cm^{-1}$ —C=N	$917\ cm^{-1}$ —N—OH	$2152\ cm^{-1}$ C≡N	
Amidoximated bleached bagasse pulp	1.56	0.996	0.8	13.9
Amidoximated unbleached bagasse pulp	1.48	0.963	0.82	12
Amidoximated bagasse raw material	1.27	0.957	0.873	10.78

lignin content in bagasse raw material (20.6%) than that in the unbleached pulp (6.8%). This higher lignin content causes a retardation of cyanoethylation and amidoximation, because it causes a hardness for the pulp, and consequently, the penetration rate of chemicals through the fiber of bagasse decreases.

Infrared spectra of amidoximated different raw materials

Infrared spectra of different amidoximated raw materials, bagasse, cotton stalks, and rice straw raw materials, are shown in Figure 6. All amidoximated raw materials have two bands at 1161 and 917 cm^{-1} due to the formation of oxime groups C=N and —N—OH. The relative absorbance of these two bands has the highest value in case of amidoximated bagasse (2.1 and 1.01), while it has the lowest value in case of amidoximated rice straw (1.57 and 0.99). In case of amidoximated cotton stalks, the relative absorbance of these two bands lies between 1.93 and 0.89. These results were parallel with the value of nitrogen content of the amidoximated materials. It was 10.78, 8.85, and 6.2% for amidoximated bagasse, cotton stalks, and rice straw, respectively. The low nitrogen content of amidoximated rice straw means that the reactivity of rice straw toward amidoximation is lower than that in the case of bagasse and cotton stalks.

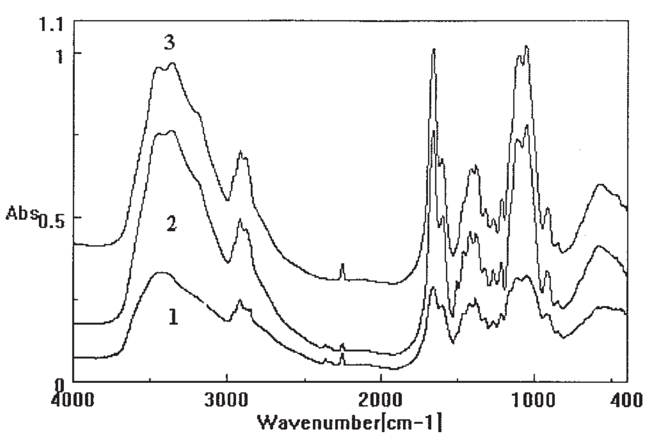

Figure 6 Infrared spectra of (1) amidoximated bagasse raw materials, (2) amidoximated cotton stalks raw materials, and (3) amidoximated rice straw raw materials.

This is attributed to the higher ash content of rice straw (13.8%) than bagasse (1.03%) and cotton stalks (1.34%). On the other hand, the relative absorbance of CH_2 band at 2920 cm^{-1} has a lower value in case of amidoximated rice straw (1.307) than that in case of amidoximated cotton stalks (1.381) and amidoximated bagasse (1.412)

Thermal properties of bagasse and its derivatives

TG curves of bleached bagasse pulp and its derivatives

Thermogravimetric curves of bleached bagasse pulp, cyanoethylated bleached bagasse pulp and amidoximated bleached bagasse pulp are shown in Figure 7. From the figure, it is clear that the minor decomposition temperature were 210, 295, and 240°C for bleached bagasse pulp, cyanoethylated bleached bagasse pulp, and amidoximated bleached bagasse pulp with weight loss 7.5, 5.5, and 6%, respectively. The major decomposition temperatures were 330, 390, and 310°C for bleached bagasse pulp and cyanoethylated and amidoximated bleached bagasse pulp, respectively. The weight loss at these major decomposition temperature was 84, 71, and 75%. This means that the cyanoethylation of bleached bagasse pulp increases its resistance toward thermal degradation. The amidoximation of bleached bagasse pulp enhances its resistance toward thermal degradation with lower degree than cyanoethylation. Thus, the amidoximation of bleached bagasse pulp increases its efficiency toward metal ions uptake and its resistance toward thermal degradation. The increase in the thermal stability of cyanoethylated samples is ascribed to the dipole association of side groups and the formation of crosslinks between the cyanoethyl molecules.[15]

Thermal behavior of amidoximated different bagasse pulps

Thermogravimetric curves of amidoximated bagasse raw material and amidoximated unbleached and bleached bagasse pulps is shown in Figure 8. After initial loss of moisture at 100–120°C, loss of actual weight of amidoxime ion exchangers occurred. This

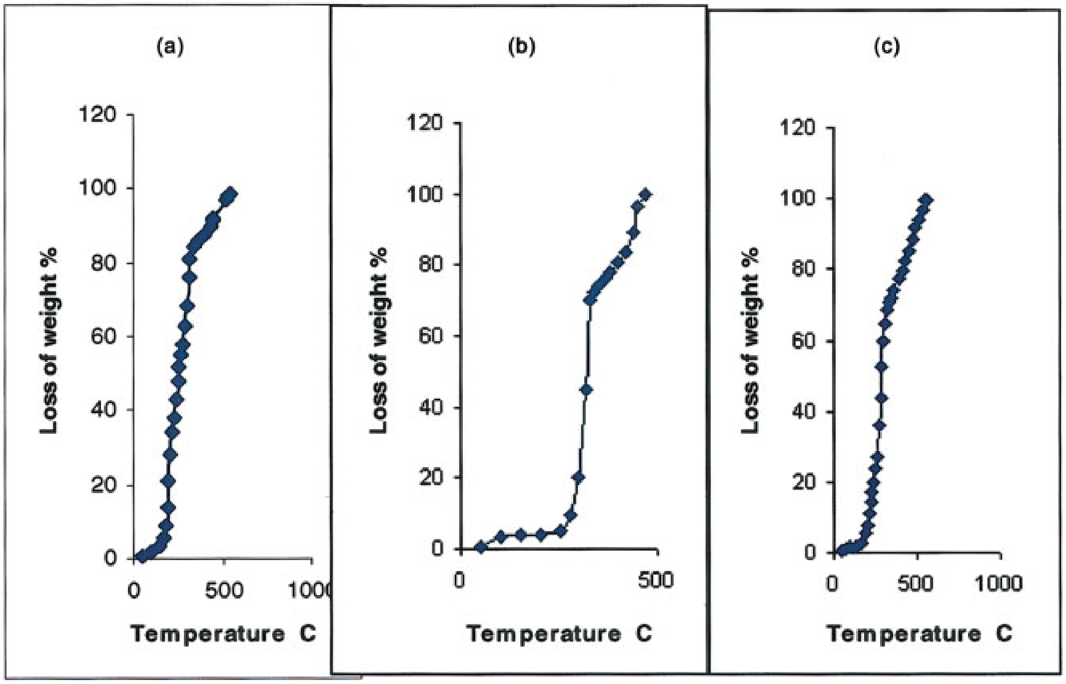

Figure 7 TG curves of (a) bleached bagasse pulp, (b) cyanoethylated bleached bagasse pulp, and (c) amidoximated bleached bagasse pulp. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

loss is attributed to actual pyrolysis by minor decomposition reaction at about 280, 260, and 240°C for amidoxime bagasse raw material, amidoxime unbleached bagasse pulp, and amidoxime bleached bagasse pulp, respectively. The major decomposition degradation proceeded at 340, 325, and 310°C for amidoximated bagasse raw material, amidoximated unbleached and bleached bagasse pulps, respectively. The major and minor decomposition temperatures of amidoximated bagasse raw material are higher than

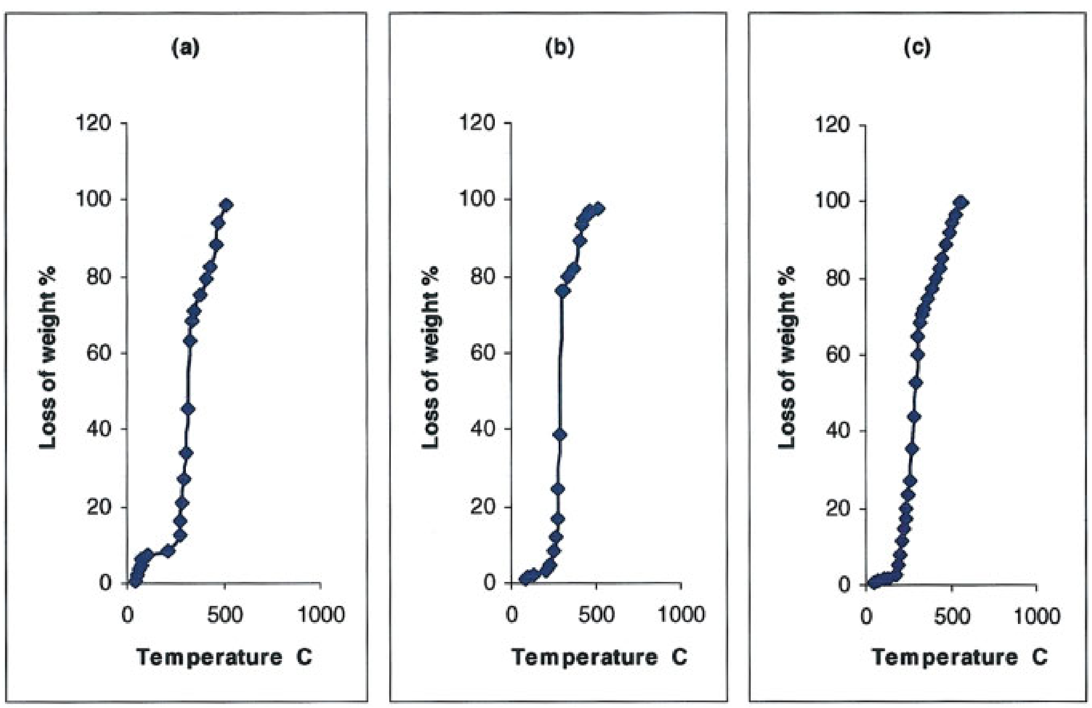

Figure 8 TG curves of amidoximated (a) bagasse raw material, (b) unbleached bagasse pulp, and (c) bleached bagasse pulp. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that in case of amidoximated bagasse pulp. This can be attributed to the presence of high lignin content in amidoximated bagasse raw material (20.4%), which causes a crosslinking between the chemical constituents of bagasse (cellulose, hemicellulose, and lignin). Moreover, lignin is considered a cemented and adhesive materials, which increases the adhesion force between cellulose and hemicellulose.

CONCLUSIONS

Three new bands in the infrared spectra at wavenumber 2152, 1161, and 917 cm^{-1} were formed due to amidoximation of lignocellulosic materials.

Cyanoethylation and amidoximation increase the resistance of lignocellulosic material toward thermal degradation.

The amidoximated bagasse resin has a higher efficiency toward metal ions uptake than amidoximated rice straw and cotton stalks.

Adsorption of Fe and Cu ions by ion exchangers (unbleached and bleached bagasse pulp) is more than Cr and Ni.

References

1. Nada, A. M. A.; Eid, M. A.; El-Bahnsawy, R. M.; Khalifa, M. N. J Appl Polym Sci 2002, 85, 792.
2. Nada, A. M. A.; Eid, M. A.; Sabry, A.; Khalifa, M. N. J Appl Polym Sci 2003, 90, 250.
3. Nada, A. M. A.; Hassan, M. L. J Appl Polym Sci 2003, 89, 2950.
4. Lehrfeld, J. J Appl Polym Sci 1996, 61, 2099.
5. Sun, G.; Gu, X. Ind Eng Chem Res 1997, 36, 808.
6. Wu, H.-S.; Jone, H.-C.; Hwang, J. W. J Appl Polym Sci 1997, 63, 89.
7. Eid, K. A.; Naa, A. M. A. Egypt J Appl Sci 2004, 19, 507.
8. Saliba, R.; Gauthier, H.; Gauthier, R.; Petit-Romel, M. J Appl Polym Sci 2000, 75, 1624.
9. Saliba, R.; Gauthier, H.; Gauthier, R.; Petit-Romel, M. Cellulose 2002, 9, 183.
10. Daly, W.; Manir, A. J Appl Polym Sci 1984, 22, 975.
11. Smith, J. A.; Van Gvieken, R. E. Anal Chem 1980, 52, 479.
12. Hassan, M. L.; El-Wakil, N. A. J Appl Polym Sci 2003, 87, 666.
13. Boyd, G.; Schubert, J.; Adamson, A. W. J Am Chem Soc 1949, 69, 2818.
14. Yu Levdek, K. I.; Inshakova, M. D.; Miyurov, E. P.; Nikitin, N. V. Trvses Nauch Issled Inst Tselyl Burn Prom 1967, 52, 109.
15. Sefain, M. Z.; Naoum, M. N.; Fadl M. H.; El-Wakil, N. A. Thermochim Acta 1994, 231, 257.