

Ion Exchange Properties of Carboxylated Bagasse

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ABSTRACT: Bagasse fibers were chemically modified with the aim to prepare lignocellulosic materials that have the ability to remove heavy metal ions from waste water. Three different reactions were used for the modification: etherification using monochloroacetic acid, esterification using succinic anhydride, and oxidation using sodium periodate and sodium chlorite. Bagasse was crosslinked using epichlorohydrin before chemical modification to avoid loss of its constituents during the chemical modification or application. The structure of the prepared derivatives was proofed using Fourier transform infrared and chemical

methods. The ability of the prepared bagasse cation exchangers to adsorb heavy metal ions (Cu^{2+} , Ni^{2+} , Cr^{3+} , Fe^{3+}), on a separate basis or in a mixture of them, at different metal ion concentration was tested. Thermal stability of the different bagasse derivatives was studied using thermogravimetric analysis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1399–1404, 2006

Key words: bagasse; ion exchanger; oxycellulose; carboxymethyl; succinic anhydride; thermogravimetric analysis

INTRODUCTION

Agricultural residue materials such as sugarcane bagasse and straws are abundant, inexpensive, and readily available as natural resources for chemicals and paper production. The annual world production of bagasse is approximately 234 million tons.¹ Bagasse is a potential source for paper and ethanol production, and as a fuel in the sugar refiners and feed for animals.^{2,3}

There is an increasing interest in the utilization of agricultural residues as a cheap and environmentally save material for preparation of ion exchangers for removal of heavy metal ions and colorants from water.^{4–9} To ensure good performance, these materials should be structurally stable under mildly acidic or basic aqueous conditions (pH 2–12). Epichlorohydrin, a commonly used crosslinking agent, effectively stabilizes agricultural residues for the preparation of weakly acidic cation exchangers.⁵

Bagasse has been studied as a raw material for the preparation of ion exchanger materials. Different chemical modifications have been carried out to introduce different functional groups onto bagasse constituents to increase its ion exchange capacity, such as phosphate,¹⁰ sulfonate and phosphosulfonate,¹¹ amidoxime,¹² quaternized diethylaminoethyl,^{13,14} and crosslinking.⁸

The aim of this work is to prepare lignocellulosic materials to be used in heavy metal ions' removal from industrial waste water. For this purpose, carboxylic groups were introduced onto bagasse constituents using three different reactions, which are commonly applied to cellulose. The use of the prepared carboxylated bagasse in removing some heavy metal ions was tested.

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% hemicelluloses, 78.3% holocellulose, 55.3% alpha cellulose (based on holocellulose), and 1.4% ash. The fibers were milled using a 20-mesh screen. All chemicals and solvents used were reagent grade and used without further treatment or purification.

Preparation of crosslinked carboxylated bagasse derivatives

Crosslinking of bagasse

Bagasse (5 g) was crosslinked using neat epichlorohydrin (100 mL) at reflux for 3 h. The crosslinked bagasse was filtered, washed with ethanol and water, and finally vacuum dried at 65°C for 12 h.

Crosslinked oxy-bagasse¹⁵

Crosslinked bagasse (5 g) was mixed with 100 mL of aqueous 10% NaIO_4 solution. The mixture was stirred

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gently at room temperature for 24 h. The product was further treated with 50 mL of 0.4M sodium chlorite solution in 2M acetic acid at room temperature for 48 h. The produced oxy-bagasse was thoroughly washed with water and left to air dry. The carboxylic content was determined by titration using NaOH standard solution and phenolphthalein indicator.

Crosslinked Carboxymethyl bagasse¹⁶

Crosslinked bagasse (5 g) was etherified with mono-chloroacetic acid (4 g) in the presence of NaOH (15 mL of 40% solution) in isopropanol (120 mL) at 50°C for 3 h. The product was filtered, stirred in 70% MeOH, neutralized with acetic acid, filtered, and repeatedly washed with the aqueous MeOH till neutrality.

Crosslinked succinylated lignocellulose¹⁷

Crosslinked bagasse (5 g) was treated with succinic anhydride dissolved in acetone (5 g in 40 mL acetone); the acetone was evaporated and the residual mixture was heated in an oven at 100°C for 3 h. The weight percent gain (WPG) due to esterification was determined.

Fourier transform infrared analysis

A JASCO 300-E Fourier transform infrared spectrometer was used for Fourier transform infrared (FTIR) analysis to follow up the chemical changes in bagasse by the different reactions. KBr disc technique was used.

Adsorption and determination of heavy metal ions

The different bagasse derivatives (0.2 g) were stirred with 25 mL of the aqueous solution of the metal chlorides of chromium, copper, nickel, and iron at different concentrations (25–200 ppm) for 18 h at room temperature. The suspension was filtered and the metal ions were determined in the filtrate using a sequential inductively coupled plasma atomic emission spectrometer, Jibin Yvon 38S (France).

Thermogravimetric analysis

A Perkin–Elmer Thermogravimetric analyzer was used to study the thermal stability of the different bagasse derivatives. The heating rate was set at 10°C/min over a temperature range of 50–900°C. Measurements were carried out in nitrogen atmosphere, with a rate of flow of 50 cm³/min.

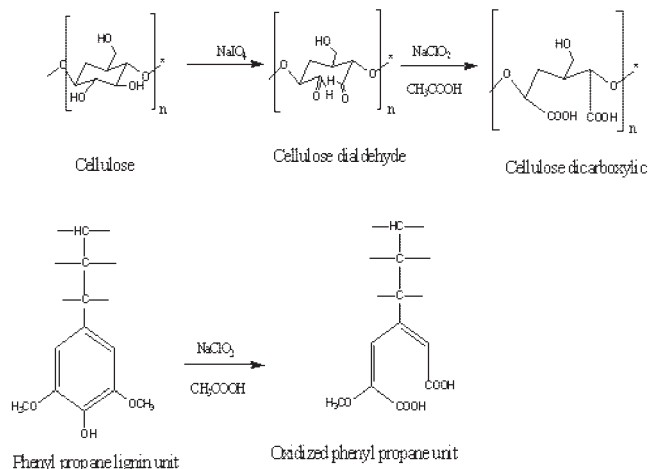


Figure 1 Reaction of cellulose (upper) and lignin (lower) with sodium periodate and sodium chlorite.

RESULTS AND DISCUSSION

Preparation of crosslinked carboxylated bagasse derivatives

Carboxylated cellulosic materials are of special importance because of their wide range of applications as ion exchange materials, adhesives, thickeners, and gels. The introduction of carboxylic groups onto the lignocellulosic materials may impart their constituents, especially cellulose and hemicelluloses, water solubility. So, it is important to apply crosslinking step before the carboxylation to avoid the loss of the carboxylated constituents of lignocellulosic materials. Epichlorohydrin was used as a crosslinking agent. It reacts with the hydroxyl groups of the lignocellulosic constituents and forms crosslinks between them.

Preparation of crosslinked oxy-bagasse

Oxycellulose is one of the well known cellulose derivatives. There are different types of oxycellulose depending on the oxidizing agent used and the hydroxyl groups that are oxidized. Sodium periodate selectively oxidizes the C-2 and C-3 hydroxyl groups of cellulose into cellulose dialdehyde, which on further reaction with sodium chlorite in the presence of acetic acid forms dicarboxylic groups at C-2 and C-3 position as shown in Figure 1.^{18–21} Oxycellulose has different application as ion exchangers and gel materials. Hemicelluloses in bagasse are xylanes which consist mainly of pentoses. They may react with sodium periodate in a similar way to cellulose. On the other hand, lignin (phenyl propane-based polymer) may be oxidized by the sodium periodate and sodium chlorite. Sodium periodate oxidation of lignin results in demethylation of methoxy groups of lignin and formation of Ph—OH groups,²² while sodium chlorite oxidation causes ben-

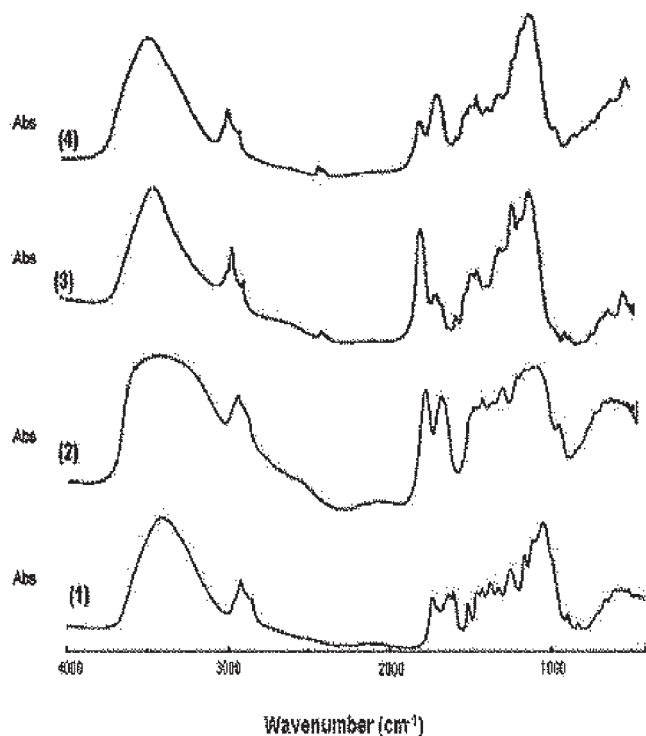


Figure 2 FTIR spectra of (1) bagasse, (2) oxy-bagasse, (3) succinylated bagasse, and (4) carboxymethylated bagasse.

zene ring cleavage and formation of dicarboxylic groups²³ as shown in Figure 1.

To introduce carboxylic groups onto the different constituents of bagasse, i.e., cellulose, lignin, and hemicelluloses, bagasse was first crosslinked using epichlorohydrin, and then oxidized using sodium periodate and sodium chlorite.

Figure 2 shows the FTIR spectrum of bagasse oxidized with sodium periodate and sodium chlorite (so called oxy-bagasse) as well as the other carboxylated bagasse derivatives. The IR spectrum of oxy-bagasse shows a clear increase in the carboxyl group absorption bands at about 1715 cm^{-1} and 1690 cm^{-1} due to the introduction of the COOH groups. Also, reduction of the intensity of the benzene ring absorption at the 1513 cm^{-1} took place because of the oxidation of lignin benzene rings. It was noted that a weight loss took place after oxidation of bagasse using sodium periodate and sodium chlorite in spite of the crosslinking step that carried out before oxidation. This may be due to dissolution of noncrosslinked oxidized bagasse constituents.

The carboxylic content of oxy-bagasse was determined by titration using standard sodium hydroxide solution. The carboxylic content of oxy-bagasse was 0.53 mmol/g . On oxidation of cellulose under similar reaction conditions, carboxylic group content of 0.92 mmol/g was obtained. The higher carboxylic content in case of oxidation of cellulose than that in case of

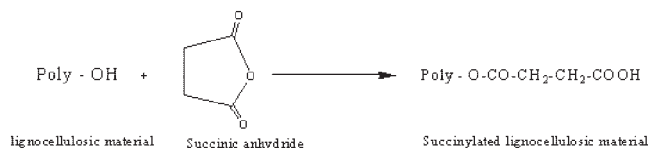


Figure 3 Reaction of lignocellulosic materials with succinic anhydride.

bagasse is expected, since cellulose, hemicelluloses, and lignin are intimately mixed and crosslinked in bagasse and not all the hydroxyl groups of these constituents are accessible. Also, the reaction medium used is a nonswelling one.

Preparation of crosslinked succinylated bagasse

Another method of introducing carboxylic groups onto the lignocellulosic materials is through their esterification reaction with the acid anhydrides in the absence of solvent as shown in Figure 3.¹⁷

Bagasse was first crosslinked using epichlorohydrin, and then esterified using succinic anhydride. The WPG due to esterification was about 37. The carboxylic content determined by sodium hydroxide titration was 1.92 mmol/g . FTIR spectrum of succinylated bagasse (Fig. 2) shows significant increase in the carbonyl group absorption at 1725 cm^{-1} due to introducing the COOH groups as well as increase in the methylene group absorption at about 2900 cm^{-1} .

Preparation of crosslinked Carboxymethylated bagasse

One of the well-known methods to introduce carboxylic groups onto cellulose is through etherification using monochloroacetic acid to form the very famous cellulose derivative carboxymethyl cellulose (CMC). CMC is known as a weak cation exchanger.

Monochloroacetic acid can react with the hydroxyl groups of cellulose, lignin, and hemicelluloses to form the corresponding etherified derivatives as shown in Figure 4.

Bagasse was first crosslinked and then etherified with monochloroacetic acid. The carboxylic content was determined by titration using standard NaOH solution and was 0.33 mmol/g . On etherification of cellulose under similar reaction conditions, carboxylic content of 0.58 mmol was obtained. FTIR spectrum of

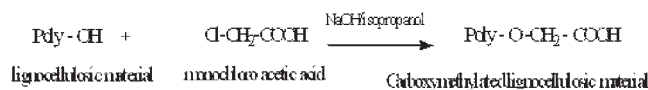


Figure 4 Reaction of lignocellulosic material with monochloroacetic acid.

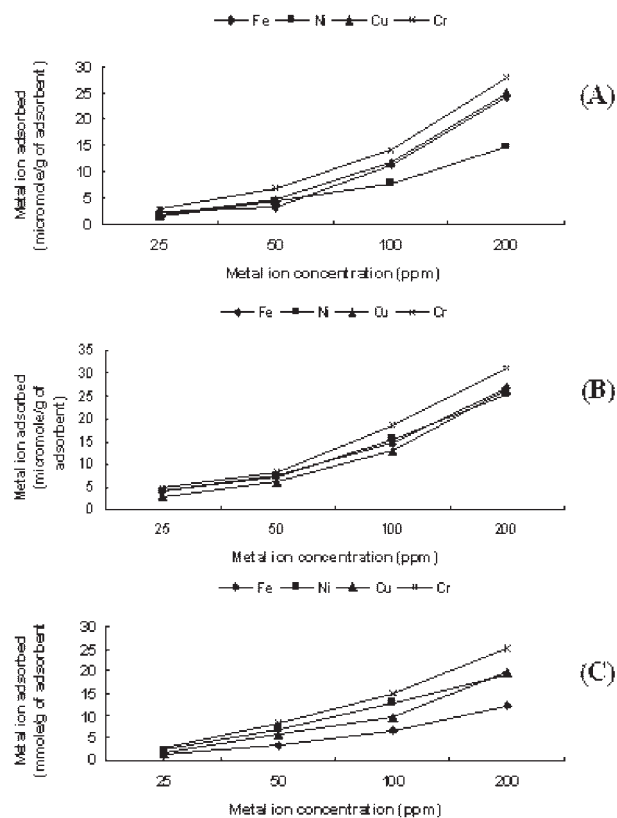


Figure 5 Heavy metal ions adsorption by (A) oxy-bagasse, (B) CM-bagasse, and (C) succinylated bagasse.

CM-bagasse (Fig. 2) shows an increase of the intensity of carboxylate group bands at about 1690 and 1725 cm^{-1} due to the introduction of the carboxymethyl groups. Weight loss, similar to that noted in case of oxidation of bagasse using sodium periodate and sodium chlorite, took place after etherification of bagasse using monochloroacetic acid/sodium hydroxide in spite of the crosslinking step that carried out before etherification. The extent of this weight loss was smaller in case of the etherification than that in case of oxidation. This is expected since sodium periodate/sodium chlorite may cause oxidation and dissolution of lignin in addition to the action of the acidic medium on short chain cellulose and hemicelluloses. In case of carboxymethylation, sodium hydroxide may dissolve hemicelluloses and short-chains cellulose.

Ion exchange properties of the oxy-, succinylated, and carboxymethylated bagasse

The different carboxylated bagasse derivatives (oxy-, succinylated, and carboxymethylated bagasse) were tested for the removal of heavy metal ions of iron, copper, nickel, and chromium using metal ion concentration from 25 to 200 ppm and contact time of 18 h (at equilibrium) on a separate basis. The results are represented in Figure 5. The figure shows that although

the three cellulose derivatives are essentially carboxylated derivatives, their affinity toward the different metal ions was different. Chromium metal ions were the highest adsorbed ions in case of the different carboxylated bagasse derivatives. Nickel metal ions were the least adsorbed ions in case of oxy-bagasse, while copper and iron metal ions were adsorbed to about the same extent in spite of the higher valency of iron. Iron metal ions were the least adsorbed metal ions in case of succinylated bagasse followed by copper and nickel in spite of that iron ions have three positive charges. Carboxymethylated bagasse showed about equal affinity towards copper, nickel, and iron metal ions. Usually, the ion exchange affinity is related to the charge and the hydrated radius of the metal ion. Also, adsorption of metal ions onto the ion-exchanger can be attributed to two terms: intrinsic adsorption and Columbic interaction. The Columbic term results from the electrostatic energy of interactions between the adsorbents and adsorbates. The charges on the substrates, as well as the softness or hardness of the charge on both sides, are mostly responsible for the amount of adsorption. The intrinsic adsorption of the materials is determined by their surface areas, which can be observed by the effect of different sizes of adsorbents on the adsorption. The above results indicate that the mechanism of ion exchange properties of modified lignocellulosic materials is not that straight forward.

Carboxymethylated bagasse had generally the highest adsorption capacity followed by oxy- and succinylated derivatives in spite of its lowest carboxylic groups' content. This indicates that the method of the preparation of carboxylated bagasse derivatives has a strong effect on its adsorption capacity. Although succinylated bagasse had the highest carboxylic groups content, it showed the lowest metal ions adsorption capacity. Succinylated-bagasse was prepared in the absence of solvent. This means that the majority of modification is at the surface of the fibers and conse-

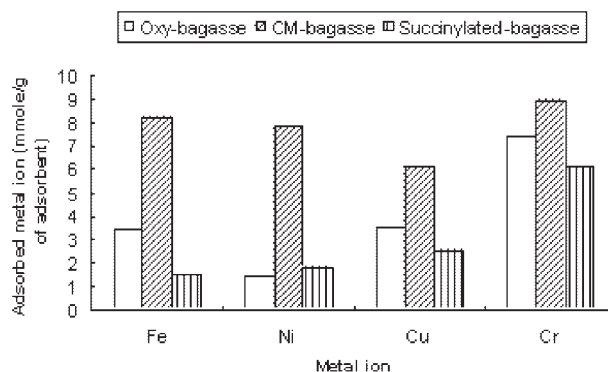


Figure 6 Heavy metal ions adsorption of the different bagasse derivatives in a mixture of the metal ions (the concentration was 50 ppm with respect to each metal ion).

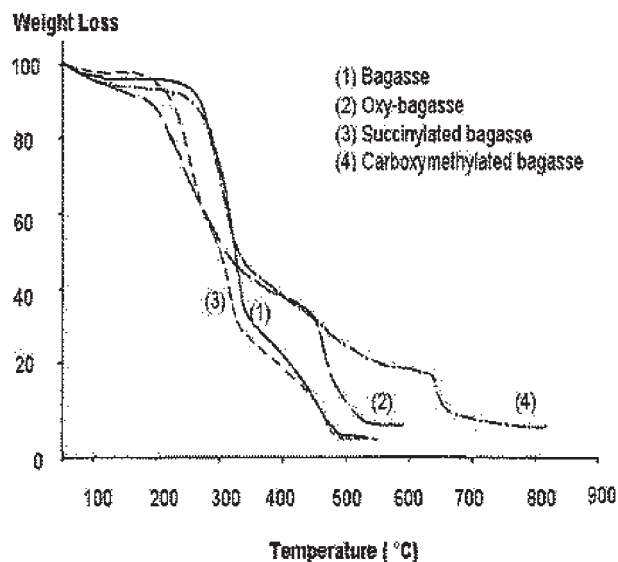


Figure 7 TGA curves of (1) bagasse, (2) oxy-bagasse, (3) succinylated bagasse, and (4) carboxymethylated bagasse.

quently no fiber swelling is expected to occur. The adsorption of the different bi- and trivalent metal ions by the carboxylic groups on bagasse surface seems to be limited by orientation of the carboxylic groups on the surface. Although both carboxymethyl- and oxy-bagasse were prepared in an aqueous medium, the first was prepared in the presence of sodium hydroxide, a swelling agent for cellulose, while in case of the second, the medium was acidic, i.e., no swelling of fibers is expected. This may explain the significantly higher adsorption capacity of carboxymethylated bagasse over that of oxy-bagasse.

The selectivity of the different bagasse derivatives in removing the aforementioned metal ions in a mixture of them was tested. The results are represented in Figure 6. As shown in the figure, both oxy- and succinylated bagasse had significantly higher selectivity in removing chromium ions over the other metal ions, while carboxymethylated bagasse did not have high selectivity toward a specific metal ion.

Thermal stability of carboxylated bagasse derivatives

Thermal stability of cellulosic materials is an important property, since it gives an indication about the long-run durability and thermal stability of the derivatives. Thermogravimetric analysis (TGA) technique was used to study the thermal stability of oxy-, carboxymethylated, and succinylated bagasse derivatives. TG curves of the different bagasse derivatives are shown in Table 1.

Table I shows the TG data obtained from the TG and DTG (differential TG) curves. The TG curves show that the chemical modifications of bagasse resulted in a decrease in the onset degradation temperature when compared with untreated bagasse. The onset degradation temperatures were 235, 178, 205, and 165°C for untreated bagasse, oxy-bagasse, carboxymethyl bagasse, and succinylated bagasse, respectively. However, the degradation of untreated bagasse was in some cases faster than that of bagasse carboxylated derivatives. For example, untreated bagasse almost completely degraded after 50 min of heating (at 500°C, heating rate 10°C/min), while carboxymethyl and oxycellulose almost completely degraded after 55–68 min of heating (charring temperatures about 550 and 680°C). Untreated bagasse showed two main degradation steps, while the other carboxylated derivatives showed more complicated degradation pattern. The thermal stability of the different carboxylated bagasse derivatives was in the order: carboxymethylated bagasse > oxy bagasse > succinylated bagasse (Figure 7). The higher onset degradation temperature of carboxymethylated bagasse may be due to the ether bond nature of the carboxymethyl groups, while succinylated bagasse has ester-bonded carboxyl groups which (the ester bond) is of lower thermal stability. Carboxymethylated bagasse showed also the lowest rate of thermal degradation followed by oxy- and succinylated bagasse.

TABLE I
TGA Data of the Different Carboxylated Bagasse Derivatives

	Onset degradation temperature	Maximum weight loss temperature of the first stage (°C) ^a	Second-stage onset degradation temperature (°C)	Second-stage maximum weight loss temperature (°C) ^a	Third-stage onset degradation temperature (°C)	Third-stage maximum weight loss temperature (°C) ^a	Charring temperature (°C)
Bagasse	235	325	355	463	–	–	505
Oxy-bagasse	178	235	336	–	445	465	550
Succinylated bagasse	165	251	290	319	335	471	490
Carboxymethylated bagasse	205	304	350	474	610	641	680

^a Obtained from the first derivatives of the TG curves (DTG curves).

CONCLUSIONS

Bagasse could be converted into cation exchanger material through the introduction of carboxylic function groups using oxidation, esterification, and etherification reactions. The ion exchange capacity of the different carboxylated bagasse derivatives was dependent on the method of preparation. Carboxymethylated bagasse showed the highest metal ion adsorption capacity over that of succinylated and oxy-bagasse. Also, carboxymethylated bagasse showed the highest thermal stability.

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