



## **Ion exchange properties of carboxylated bagasse**

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### **ABSTRACT**

Bagasse fibers were chemically modified using three different reactions: etherification using monochloroacetic acid, esterification using succinic anhydride, and oxidation using sodium periodate and sodium chlorite with the aim to prepare cation exchanger bearing carboxylic groups. 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 (FTIR) and chemical methods. The ability of the prepared bagasse cation exchangers to adsorb heavy metal ions ( $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Fe}^{+3}$ ), 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 (TGA).

Keywords: Bagasse; ion exchanger; oxycellulose; carboxymethyl; succinic anhydride; thermogravimetric analysis.

### **INTRODUCTION**

Agricultural residues 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 refineries and feed for animals [2, 3].

There is an increasing interest in 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].



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Bagasse has been studied as a raw material for 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 introduce carboxylic groups onto bagasse constituents using three different reactions, which are commonly applied to cellulose. These reactions were oxidation using sodium periodate/sodium chlorite, etherification using monochloroacetic acid, and esterification using succinic anhydride. 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 cross-linked carboxylated bagasse derivatives**

#### **a- Crosslinked oxy-bagasse [15]**

Bagasse (5 g) was first crosslinked using epichlorohydrin at reflux for 3 hours. Crosslinked bagasse (5 g) was mixed with 100 ml of aqueous 10 % NaIO<sub>4</sub> solution. The mixture was stirred gently at room temperature for 24 h. The produced product was further treated with 50 ml of 0.4 M sodium chlorite solution in 2 M acetic acid at room temperature for 48 hours. 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.

#### **b- Crosslinked Carboxymethyl bagasse [16]**

Bagasse (5 g) was first crosslinked using epichlorohydrin at reflux for 3 hours. Crosslinked bagasse (5 g) was etherified with monochloroacetic acid (4 gm) in the



presence of NaOH (15 ml of 40 % solution) in iso-propanol (120 ml) at 50 °C for 3 hours. The product was filtered, stirred in 70 % MeOH, neutralized with acetic acid, filtered and repeatedly washed with the aqueous MeOH till neutrality.

### **c- Crosslinked succinylated lignocellulose [17]**

Bagasse (5 g) was first crosslinked using epichlorohydrin at reflux for 3 hours. Crosslinked bagasse (5 g) was treated with succinic anhydride dissolved in acetone (5 gram in 40 ml acetone), the acetone was evaporated and the residual mixture was heated in an oven at 100 °C for 3 hours. The weight percent gain due to esterification was determined.

### **Fourier transform infrared analysis**

A JASCO 300-E Fourier transform infrared spectrometer was used for 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 hours 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 (ICP-AES), 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 cm<sup>3</sup> / min.

## **RESULTS AND DISCUSSION**

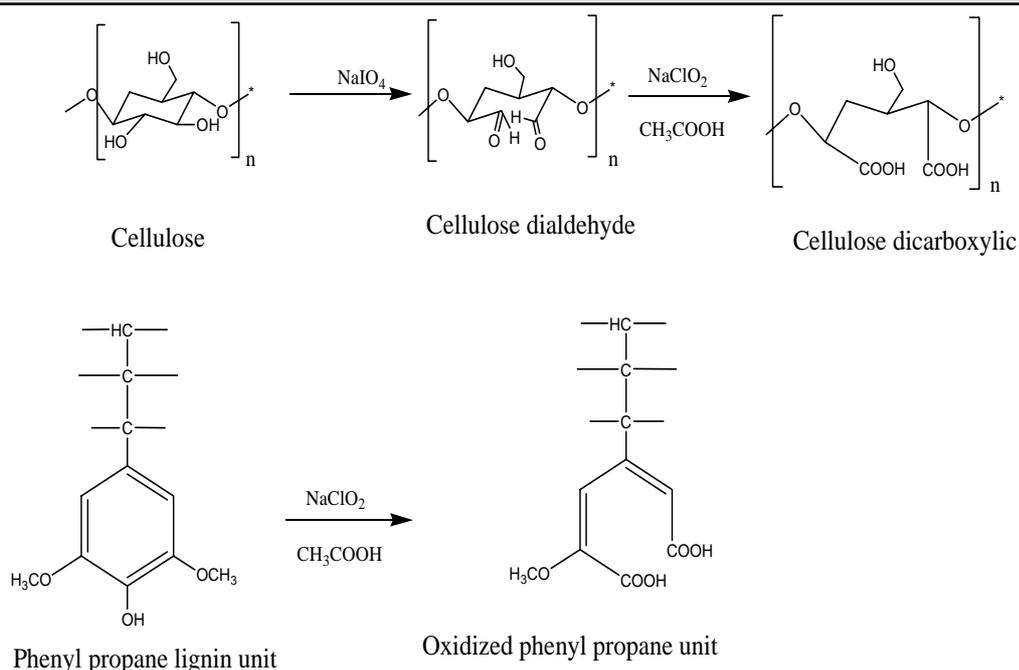


## **Preparation of crosslinked carboxylated bagasse derivatives**

Carboxylated cellulosic materials are of special importance due to 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.

### ***a- Preparation of crosslinked oxy-bagasse***

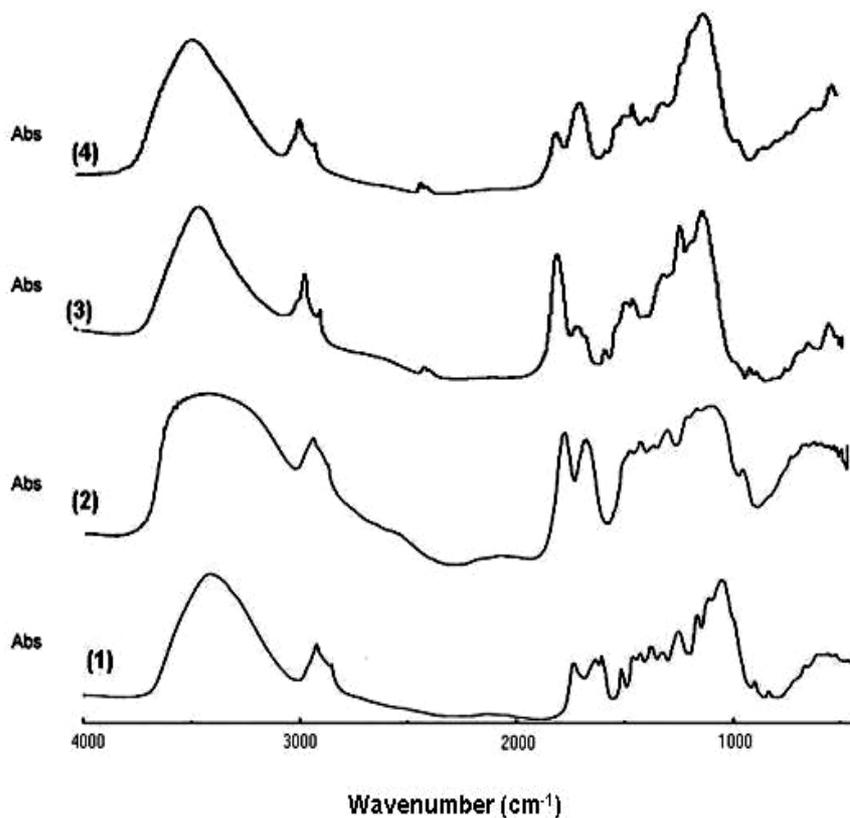
Oxycellulose is one of the well known cellulose derivatives. There are different types of oxycellulose depending on the oxidizing agent used and the hydroxyl groups that are oxidized. Sodium periodate selectively oxidizes the C-2 and C-3 hydroxyl groups of cellulose into cellulose dialdehyde, which on further reaction with sodium chlorite in the presence of acetic acid form 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 de-methylation of methoxy groups of lignin and formation of Ph-OH groups [22] while sodium chlorite oxidation causes benzene ring cleavage and formation of dicarboxylic groups [23] as shown in figure 1.



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

To introduce carboxylic groups onto the different constituents of bagasse, i.e., cellulose, lignin, and hemicelluloses, bagasse was first crosslinked using epichlorohydrin 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 carbonyl group absorption at  $1715\text{ cm}^{-1}$  due to the introduction of the  $\text{COOH}$  groups. Also, reduction of the intensity of the benzene ring absorption at the  $1513\text{ cm}^{-1}$  took place due to the oxidation of lignin benzene rings.



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

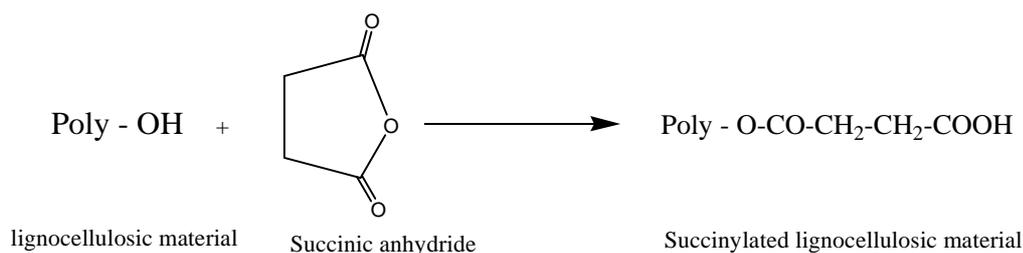
It was noted that a weight loss took place after oxidation of bagasse using sodium periodate and sodium chlorite in spite of the crosslinking step that carried out before oxidation. This may be due to dissolution of non-crosslinked oxidized bagasse constituents.

The carboxylic content of oxy-bagasse was determined by titration using standard sodium hydroxide solution. The carboxylic content of oxy-bagasse was 0.53 mmole / g. On oxidation of cellulose under similar reaction conditions, carboxylic group content of 0.92 mmole / g was obtained. The higher carboxylic content in case of oxidation of cellulose than that in case of bagasse is expected since cellulose, hemicelluloses, and lignin are intimately mixed and crosslinked in bagasse and not all

the hydroxyl groups of the these constituents are accessible. Also, the reaction medium used is a non-swelling one.

### *b- 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].



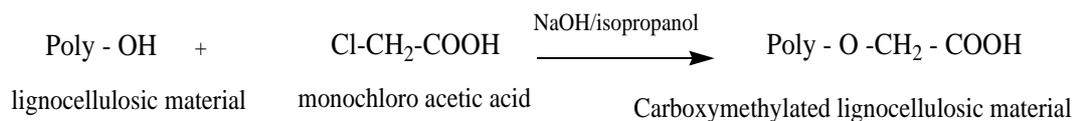
**Figure 3. Reaction of lignocellulosic materials with succinic anhydride.**

Bagasse was first crosslinked using epichlorohydrin then esterified using succinic anhydride. The weight percent gain (WPG) due to esterification was about 37. The carboxylic content determined by sodium hydroxide titration was 1.92 mmole / g. FTIR spectrum of succinylated bagasse (Figure 2) shows significant increase in the carbonyl group absorption at 1715 cm<sup>-1</sup> due to introducing the COOH groups as well as increase in the methylene group absorption at about 2900 cm<sup>-1</sup>.

### *c- 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 a known 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.



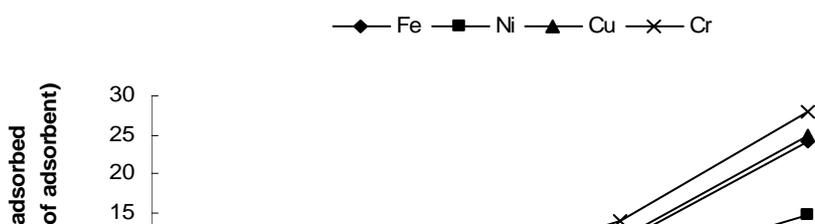
**Figure 4. Reaction of lignocellulosic material with monochloroacetic acid.**

Bagasse was first crosslinked then etherified with monochloroacetic acid. The carboxylic content was determined by titration using standard NaOH solution and was 0.33 mmole / g. On etherification of cellulose under similar reaction conditions carboxylic content of 0.58 mmole was obtained. FTIR spectrum of CM-bagasse (figure 2) shows an increase of the intensity of the carbonyl group band at  $1715\text{ cm}^{-1}$  due to introducing the carboxymethyl groups.

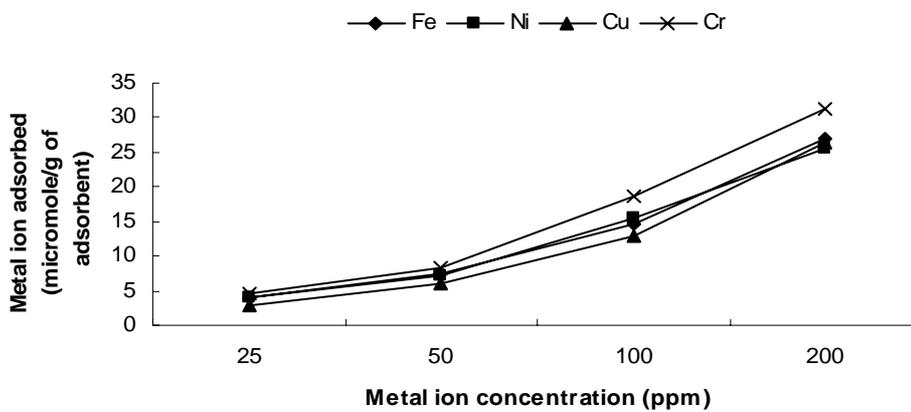
Weight loss, similar to that noted in case of oxidation of bagasse using sodium periodate and sodium chlorite, took place after etherification of bagasse using monochloroacetic acid / sodium hydroxide in spite of the crosslinking step that carried out before etherification. The extent of this weight 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**

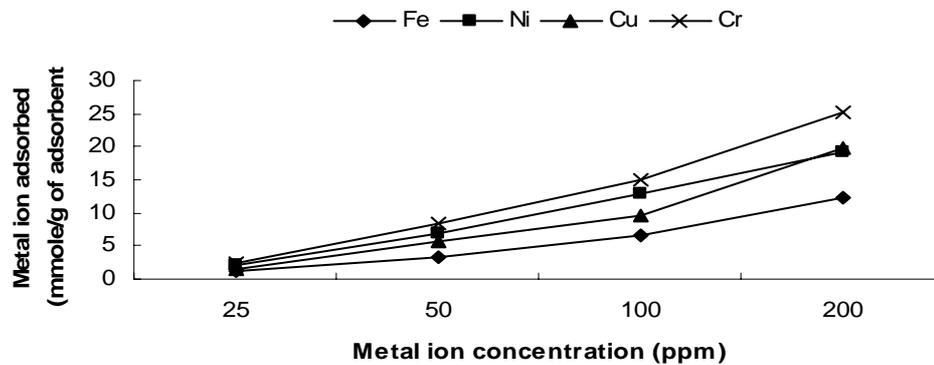
The different carboxylated bagasse derivatives (oxy-, succinylated, and carboxymethylated bagasse) were tested for the removal of heavy metal ions of iron, copper, nickel, and chromium using metal ions concentration from 25 to 200 ppm and contact time of 18 hours (at equilibrium) on a separate basis.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



(A)



(B)



(C)

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

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



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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 mean that the mechanism of ion exchange properties of modified lignocellulosic materials is not that straight forward.

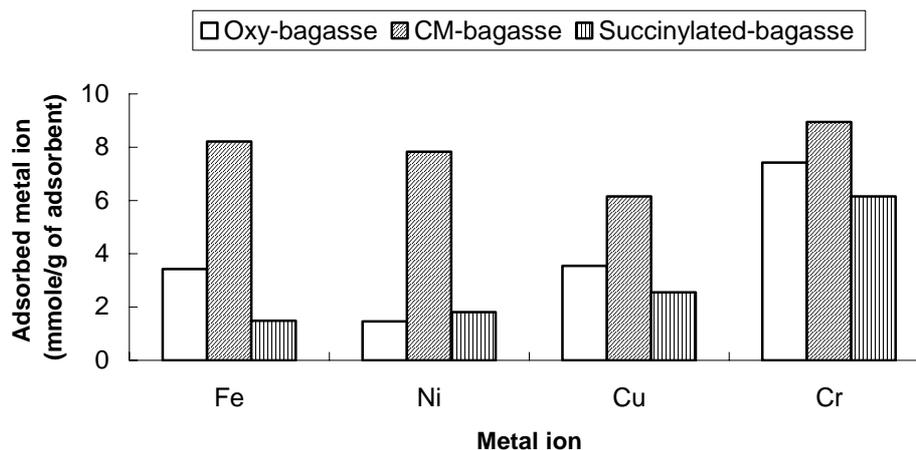
Carboxymethylated bagasse had generally the highest adsorption capacity followed by oxy- and succinylated derivatives in spite of its lowest carboxylic groups' content. This indicates that the method of the preparation of carboxylated bagasse derivatives has a strong effect on its adsorption capacity. 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 consequently no fiber swelling is expected to occur. The adsorption of the different bi- and tri-valent 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 but 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 above-mentioned 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 towards 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 figure 7.



**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).**

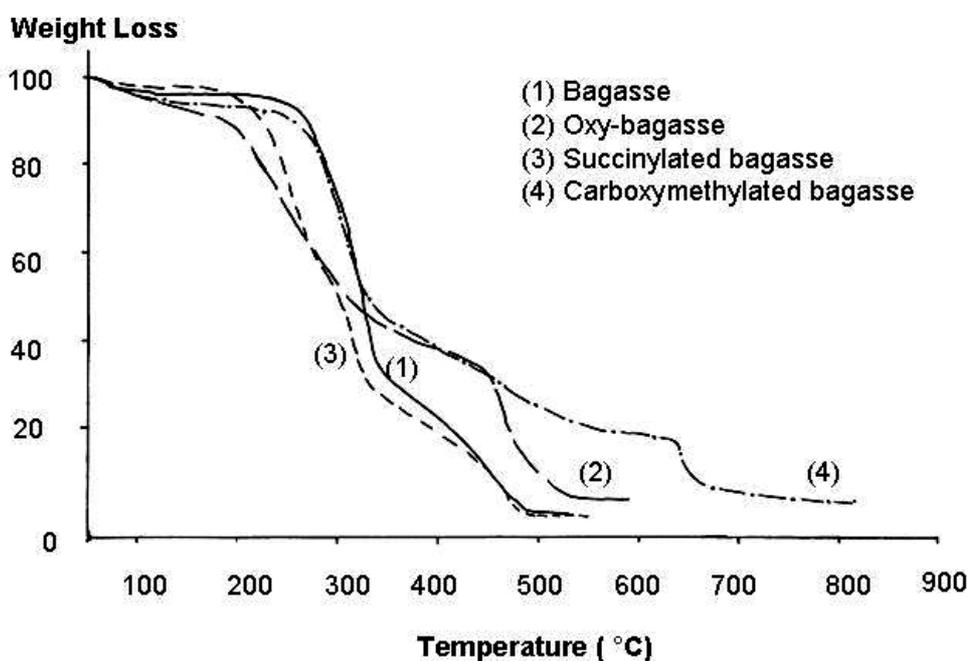


Figure 7. TGA curves of the different carboxylated bagasse derivatives.

Table 1 shows the TG data obtained from the TG and DTG (differential TG) curves. The TG curves shows that the chemical modifications of bagasse resulted in a decrease in the onset degradation temperature compared to untreated bagasse. The onset degradation temperatures were 235, 178, 205, and 165 °C for untreated bagasse, oxy-bagasse, carboxymethyl bagasse, and succinylated bagasse, respectively.

TABLE 1. TGA data of the different carboxylated bagasse derivatives.

	Onset degradation temperature	Maximum weight loss temperature of the first stage* (°C)	Second-stage onset degradation temperature (°C)	Second-stage maximum weight loss temperature* (°C)	Third-stage onset degradation temperature (°C)	Third-stage maximum weight loss temperature* (°C)	Charring temperature (°C)
Bagasse	235	325	355	463	--	--	505
Oxy-bagasse	178	235	336	--			550
Succinylated bagasse	165	251					490
Carboxymethylated bagasse	205	304		474			620

\* Obtained from the first derivatives of the TG curves (DTG curves).



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However, the degradation of untreated bagasse was in some cases faster than bagasse carboxylated derivatives. For example, untreated bagasse almost completely degraded after 50 minutes of heating (at 500 °C, heating rate 10 °C/min) while carboxymethyl and oxycellulose almost completely degraded after 55 - 82 minutes of heating (charring temperatures about 550 and 820 °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. 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.

### **Conclusion**

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 depends 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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