

EFFECT OF DIFFERENT TREATMENTS ON CELLULOSE TOWARD CARBOXYLATION AND ITS APPLICATION FOR METAL ION ABSORPTION

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Carboxylation of cotton linters was investigated relative to its use in ion exchange. The effects of different treatments of cotton linters, such as alkali, acid, and activating agents, e.g. LiCl, on the molecular structure and carboxylation of cotton linters were taken in our consideration. The absence or presence of a crosslinking was considered, and the efficiency of these prepared carboxylated cotton linters toward metal ions uptake, as well as thermal analysis of treated and carboxylated cotton linters, was investigated. It was found that treatment of cotton linters with alkali and activating agent decreased the crystallinity index (band intensity at 1425/band intensity at 890 cm^{-1}). On the other hand, the prepared carboxylated cotton linters had lower crystallinity index than uncarboxylated linters. Thermal analysis of the treated and carboxylated cotton linters allowed calculation of the activation energy of thermally treated materials. It was found that the crosslinked and acid treated cotton linters had a higher activation.

Keywords: Carboxylation; Cotton linter; Infrared; Atomic Absorption; Thermal analysis; Ion exchange

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INTRODUCTION

The effect of different treatments on the swelling of the fine structure of cellulose has been studied (Nada and Sefeun 1986). The degree of polymerization and reactivity of cellulose for different reactions depends on the type of treatment. Cellulose is renewable, and its abundance in nature provides material for cost-effective technologies of ion exchangers (Laszlo and Dintizis 1994; Laszlo 1996; Nada and El-Wakeel 2006; Nada and Hassan 2006).

Preparation of the ion exchangers from agricultural wastes can be carried out by chemical modification (Lehifeld 1996), copolymerization, and crosslinking (Shi et al. 1999; Nada and Adel 2006). To ensure good performance, these materials should be structurally stable under mildly acidic or basic aqueous conditions. Epichlorohydrin is a commonly used crosslinking agent that effectively stabilizes agricultural residues for the preparation of weakly acidic cation exchangers. Cotton linters have been studied as cellulose raw material for the preparation of ion exchange materials. Different chemical modification has been studied to incorporate different functional groups onto cellulose chains to increase its capacity toward metal ion absorption.

Groups that have been considered include phosphate (Nada et al. 2002), sulfate, and phosphosulfonate (Nada et al. 2003), as well as crosslinking (Simkovei and Laszlo 1997). Infrared spectroscopy and thermal gravimetric analysis have been used to follow the molecular structure of cellulose, including the inter- and intra-molecular structure (Antal et al. 1985; Nada et al. 2000).

The aim of this work is to prepare carboxylic cotton linters ion exchangers for heavy metal ions absorption. Also the effects of different treatments for cotton linters on its fine structural were investigated. Preparation of carboxylate cotton linters in the presence or absence of a crosslinking agent (epichlorohydrin) was also studied. The molecular structure of the treated and carboxylated cotton linters was followed by using infrared spectroscopy and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

The raw material used in this work was cotton linters delivered from 81 factory, Egypt which has about 99% of α cellulose and 0.2% ash.

Treatment of Cotton Linters

Cotton linters were treated with 1N NaOH or 1 N HCl under reflux for 1.5 hr. The cotton linters were also treated with 70% LiCl w/w for 1 hr. using a liquid ratio 1: 20. After treatment the mixture was filtered and washed with distilled water until it had a neutral pH. Thereafter it was treated with methanol and air dried.

Degree of Polymerization

The degree of polymerization (DP) of untreated and treated cotton linters was determined according to (Glockner et al. 1968).

Crosslinking

Crosslinking of cotton linters with epichlorohydrin was carried out according to (Laszlo and Dintizis 1994).

Carboxylation

Carboxylation was carried out according to Mackawo and Koshijima (1984). 5 gm of cotton linters was treated with 100 ml 10% sodium periodate at room temperature for 4 hours and then treated with 50 ml of 0.4 M sodium chloride in the presence of 2M acetic acid at room temperature for 48 hrs. Then the solids were filtered and washed with distilled water until it reached a neutral pH, after which it was washed with a solvent.

Metal Ion Uptake

Ion exchange resin (0.2 g) was stirred for 30 min in an aqueous solution (25ml) containing 20 μ g/ml of Mg, Mn, and Sr. The suspension was then filtrated. The equipment used in the metals determination was a Thermo-Elemental S4 fully automatic Flame

Atomic Absorption Spectrometer. A burner-nebulizer (100 mm with a single slot for air acetylene C₂H₂) was utilized as an absorption cell. The light sources were Thermo-Elemental hollow cathode lamps. The instrumental parameters, including the flow rate of used gas, were adjusted to give maximum sensitivity for all elements. All measurements were the average of three 3s integrations, and a blank measurement was made between each pair of solution measurements.

Infrared Analysis

An infrared spectrophotometer A JASCO 300 t (Fourier Transform) was used to follow the molecular structure change of cotton linters and the produced carboxylated cotton linters. A KBr disc technique was used. The range of wavenumbers was calculated from 4000 to 400 cm⁻¹.

Thermogravimetric Analysis

A thermogravimetric analyzer Perkin Elmer Thermogravimetric TGA – 7 was used. This analysis was conducted under nitrogen atmosphere with heating rate of 10°C per minute.

RESULTS AND DISCUSSION

The molecular structure of cotton linters was affected by different treatments e.g. acid, alkali, and activating agent e.g. 70% LiCl w/w. Table (1) shows the different infrared data and properties of untreated and treated cotton linters (see Figs. 1-3). The degree of polymerization of treated cotton linters was slightly increased by treatment with alkali or with LiCl. This can be attributed to the dissolution of low chain-length cellulose during treatment with alkali or with LiCl. In case of treatment with acid, the degree of polymerization of cotton linters was considerably decreased due to the degradation of cellulose chains, especially the amorphous part of cellulose chains.

Table 1. Infrared Spectra of Untreated and Treated Cotton Linters with Acid, Alkali, and LiCl.

Material	Wavenumber (cm ⁻¹) (OH)	D.P.	CrI *	Mercerized depth	Relative absorbance of O-β-O linkage
Untreated cotton linters	3408	920	1.79	1.086	1.39
Acid treated cotton linters	3342	560	2.05	0.979	1.01
Alkali treated cotton linters	3410	928	1.50	1.1004	1.43
LiCl treated cotton linters	3419	980	0.961	1.232	1.56

* CrI: Crystallinity index

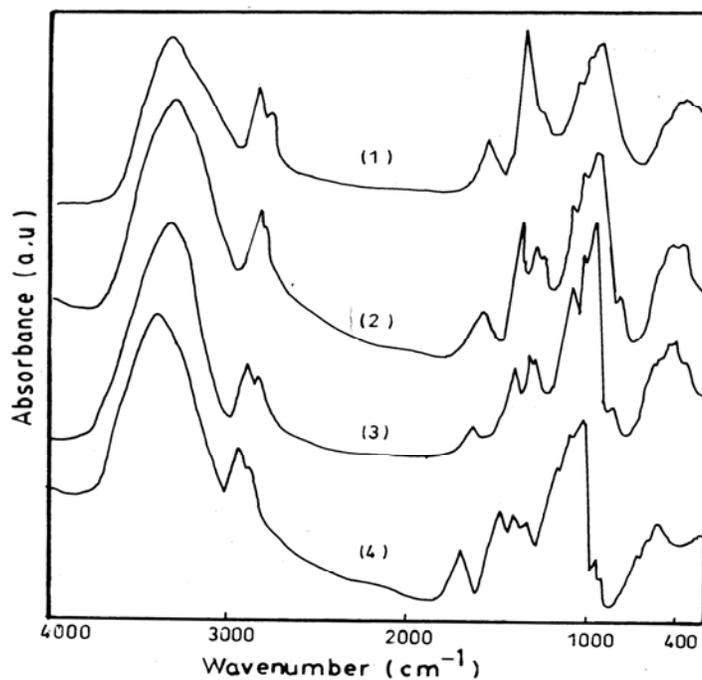


Figure 1. FTIR of cotton linters: (1) blank, (2) 1 N NaOH, (3) 1 N HCl (4), and LiCl agents.

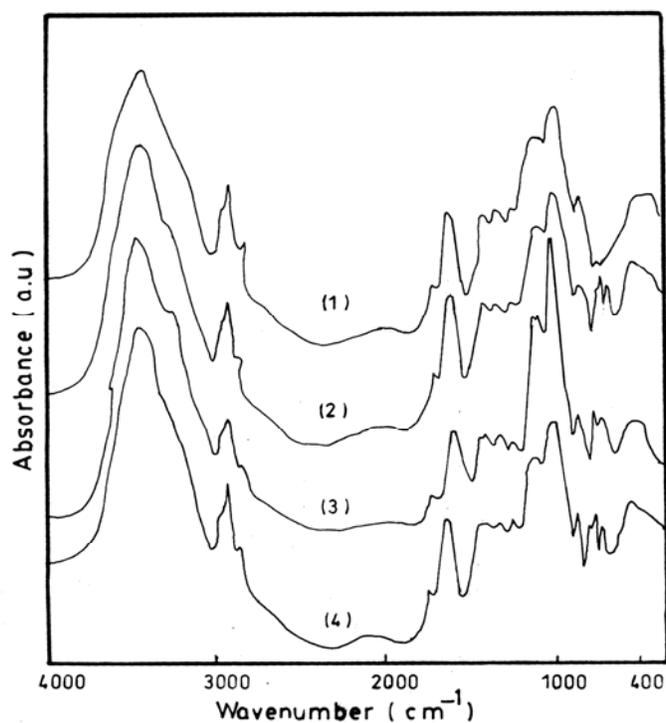


Figure 2. FTIR of cotton linters: (1) blank carboxylated crosslinked, (2) Alkali-treated (carboxylated crosslinked), (3) Acid treated (carboxylated crosslinked), (4) LiCl treated (carboxylated crosslinked).

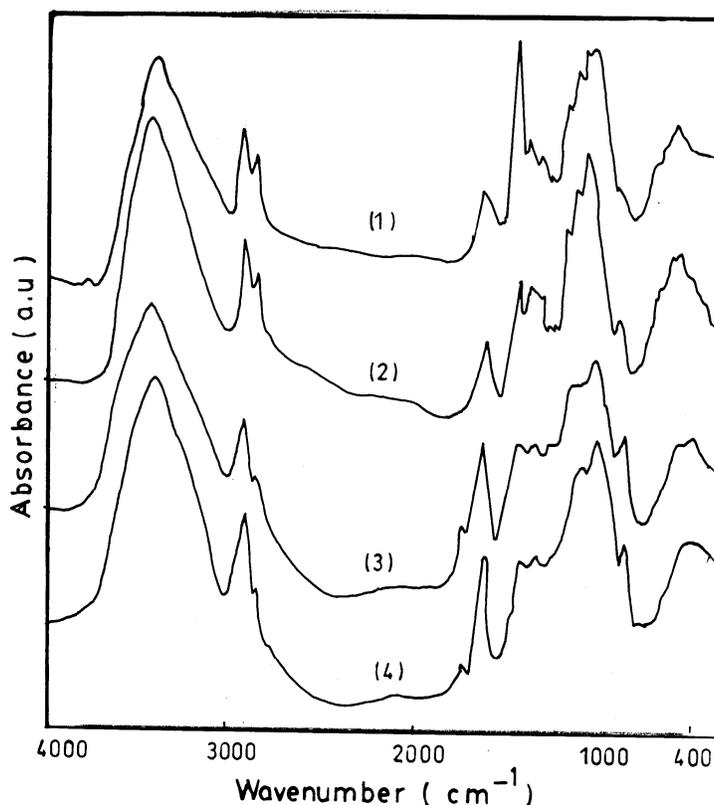


Fig. 3. FTIR spectrum of cotton linters: (1) blank, (2) blank (crosslinked), (3) blank (carboxylated), (4) blank (carboxylated crosslinked)

It is clear also from Table 1 that the relative absorbance (ratio of intensity of any band to intensity of band at 1325 cm^{-1} ; Yuludvek et al. 1967) of 1-4 B-O pyranose linkage at 1120 cm^{-1} was decreased by acid treatment, due to the degradation of this linkage, while it slightly increased with alkali treatment. On the other hand, the CrI (band intensity at $1425/\text{band intensity } 900\text{ cm}^{-1}$) (Nelson and Conner 1964) was increased by treating cotton linters with acid. This was due to the degradation that occurs in the amorphous part of cellulose chains. The crystallinity index of alkali or LiCl treated cotton linters was decreased. This can be attributed to the breakage of hydrogen bonds in the crystalline part of cellulose chains. This can be confirmed by the shift that occurred for OH group at 3408 cm^{-1} to high wave number of treated cotton linters with alkali or LiCl due to the decrease in hydrogen bonds and to low wavenumber in the acid-treated cotton linters due to the increase in the hydrogen bond by degradation of amorphous parts in cellulose chains. Also, from the table, the mercerization depth of treated cotton linters with alkali or LiCl solution was higher than that treated with acid. This can be explained by the increase of swelling of the crystalline part of treated cotton linters with alkali or LiCl solutions.

It is concluded from the table that the treatment of LiCl was more effective in the lowering of crystallinity and the increasing of mercerization depth due to the high swellability of cotton linters.

Table 2 shows that carboxylated crosslinked treated cotton linters with LiCl had higher relative absorbance of COOH at 1720 cm^{-1} and CH_2 at 2920 cm^{-1} , as well as mercerization depth, than other treated cotton linters. This is attributed to the increase of swelling of cellulose chains. This enhances the penetration of chemicals through cellulose chains and consequently increases the incorporation of carboxylic groups onto cellulose.

Table 2. Infrared Spectra of Carboxylated Treated Cotton Linters with Different Solutions

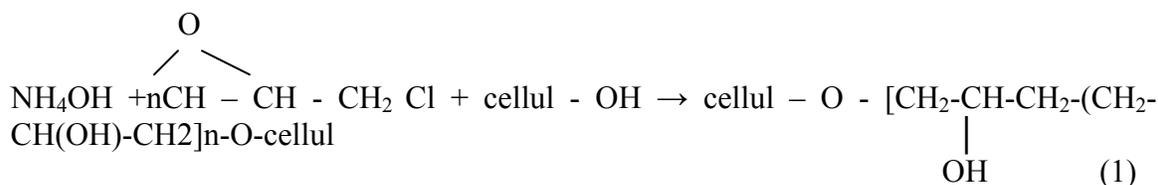
Material	Relative absorbance of			Mercerized depth	CrI *	CH_2/OH 2920/3439
	COOH	OH	CH_2			
Carboxylated cross linked untreated cotton linters	0.686	2.93	1.19	0.791	1.79	0.41
Carboxylated cross linked acid treated cotton linters	0.782	3.317	1.9	0.92	0.836	0.57
Carboxylated cross linked alkali treated cotton linters	0.841	1.63	1.061	1.19	0.907	0.65
Carboxylated cross linked LiCl treated cotton linters	1.183	4.1	2.01	1.38	0.7936	0.49

* CrI: Crystallinity index

From Table (3) it is clear that the crosslinking of cotton linters increased the carboxylation of cotton linters due to the increase of mercerization depth and decrease of crystallinity index. The increase in the carboxylation of crosslinked cellulose can be attributed to the expectation that crosslinking of cellulose with epichlorohydrin would severely depress biodegradation. This can be explained by the closing of macropores in cell walls, resulting in diminished walls penetrability by degradation (Laszlo 1998). The effect of crosslinking epichlorohydrin can be improved by reducing the amount of added water to the reacting mixture (Laszlo 1996). On the other hand, epichlorohydrin treatment brought about a substantial improvement in stability of functional group and the produced cellulose derivative (Laszlo 1996).

Table 3. Relative Absorbance of Different Bands in Untreated, Cross Linked, Carboxylated, and Carboxylated Crosslinked Cotton Linters

Material	Relative absorption of				Crystallinity index
	OH	C=O	COOH	CH_2	
Untreated cotton linters	1.43	—	1.088	1.19	1.79
Crosslinked cotton linters	2.76	0.31	1.30	1.56	1.70
Carboxylated cotton linters	2.28	0.94	0.992	1.21	1.82
carboxylated crosslinked cotton linters	2.39	1.04	1.001	1.43	1.65



The relative absorption of the CH₂ band at 2920 cm⁻¹ of cross linked cotton linters had a higher value than other samples (untreated cellulose and carboxylated cellulose). This is attributed to the epichlorohydrin crosslinking at 3(CH). The crosslinking of cellulose with epichlorohydrin increases the carboxylation process due to the increase of added OH from the crosslinking agent (epichlorohydrin). The relative absorbance of the OH group of crosslinked cellulose decreased by carboxylation due to the oxidation of OH to form COOH groups.

Thermogravimetric Analysis (TGA)

The stability of crosslinked and carboxylated cellulose can be followed by thermal analysis. TGA can be used to determine the onset degradation temperature of cellulose and the loss of weight during thermal treatment. It was found that the thermal stability of cellulose (cotton linters) gives an indication about the durability of cellulose derivatives. Thermal stability can be measured by using TGA (Table 4).

Table 4. Minor and Major Decomposition Temperatures and Weight Loss of Thermally Treated Cotton Linters and its Derivatives

Material	Minor decomp. temp.	Loss in weight	Major decomp. temp.	Loss in weight
Untreated cotton linters	300	7.5	380	84.9
NaOH treated cotton linters	285	8.5	383	83.4
HCl treated cotton linters	340	6	420	80
Crosslinked cotton linters	320	6.8	400	79
Carboxylated cotton linters	220	7.2	530	78.2
Carboxylated Crosslinked cotton linters	238	7.1	560	76.5

From Table 4 it is clear that the alkali-treated cellulose, carboxylated, and cross linked carboxylated cellulose had the lowest minor decomposition temperature and loss in percent mass. On the other hand, the acid-treated and crosslinked cellulose had the highest minor decomposition temperature. This can be attributed to the increase of compaction of cellulose chains in the case of crosslinked cellulose, and increase in the crystalline part, which has more resistance to thermal treatment (Nada et al. 2006) due to the degradation of amorphous part during acid treatment of cellulose. On the other hand, the acid-treated cellulose, crosslinked, carboxylated, and crosslinked carboxylated cellu-

lose had a higher major decomposition temperature than untreated and alkali-treated cotton linters i.e. they were more resistant to thermal treatment than the untreated cellulose and alkali-treated cellulose. This can be explained by increase of hydrogen bonding, which increases from the formation of crystallinity of cellulose, and consequently this increases cellulose's resistance to thermal treatment. In general the loss in percent mass of the acid, crosslinked, carboxylated, and crosslinked carboxylated cellulose had a lower value than cellulose and alkali-treated cellulose (Figs. 4 and 5).

Metal Ion Uptake

Metal ion uptake by treated cellulose was compared with that of untreated cotton linters in the cases of alkali, acid, and LiCl treatments (Fig. 6). Generally, in the case of native cotton linters (in which hydroxyl groups are present) the binding capacity with metal ion depended on the pH at which the binding capacity was performed. So, at neutral or acidic pH, the ability of pure cotton linters to bind cations is expected to be minimal (Lehifeld 1996). So from Table 5 it is clear that the untreated cotton linters had a lower affinity to metal ions uptake from their solution. On the other hand, it is evident that the treated cotton linters with LiCl solution had a higher affinity toward metal ions uptake than the other cellulosic materials. This can be attributed to a decrease in the crystalline content in cotton linters due to treatment with LiCl. This causes an increase in the proportion of amorphous cellulose. This increase in the amorphous component can be expected to increase the penetration of metal ions solution and consequently the contact between cellulose and metal ions. This causes an increase of the binding of metal with cellulose chains. On the other hand, cellulose treated with acid had a lower affinity toward metal ions uptake than the alkali-treated cellulose. This can be explained by degradation of the amorphous part of cellulose chains, and consequently the crystallinity cellulose increased. This decreased the penetration rate of metal ions solution, and it also decreased the affinity of cellulose for metal ions uptake. However, the crystallinity of acid-treated cellulose chains and its affinity toward metal ions were higher than untreated cellulose, which had lower crystallinity than acid-treated material. Thus is attributed to increased degradation of the treated cellulose chains with acid, and consequently the population of end groups of chains increases, which also increases the affinity toward metal ion uptake.

The affinity of the cellulosic material to absorb metal ion had the following sequence:

Treated cellulose with LiCl > treated with NaOH > treated with acid > untreated cellulose (Lehifeld 1996).

Crosslinking and Carboxylation of Cotton Linters

The incorporation of carboxyl groups onto cellulose chains can be expected to increase their affinity to cations. The pure cellulose contains only OH groups, and its binding capacity depends on pH at which the binding is performed. Some cellulose preparations, however, have appreciable ion binding capacity, which is due to the manner in which the cellulose is prepared. Various types of pretreatment can oxidize the terminal hydroxyl groups, with an accompanying increase in cation binding capacity.

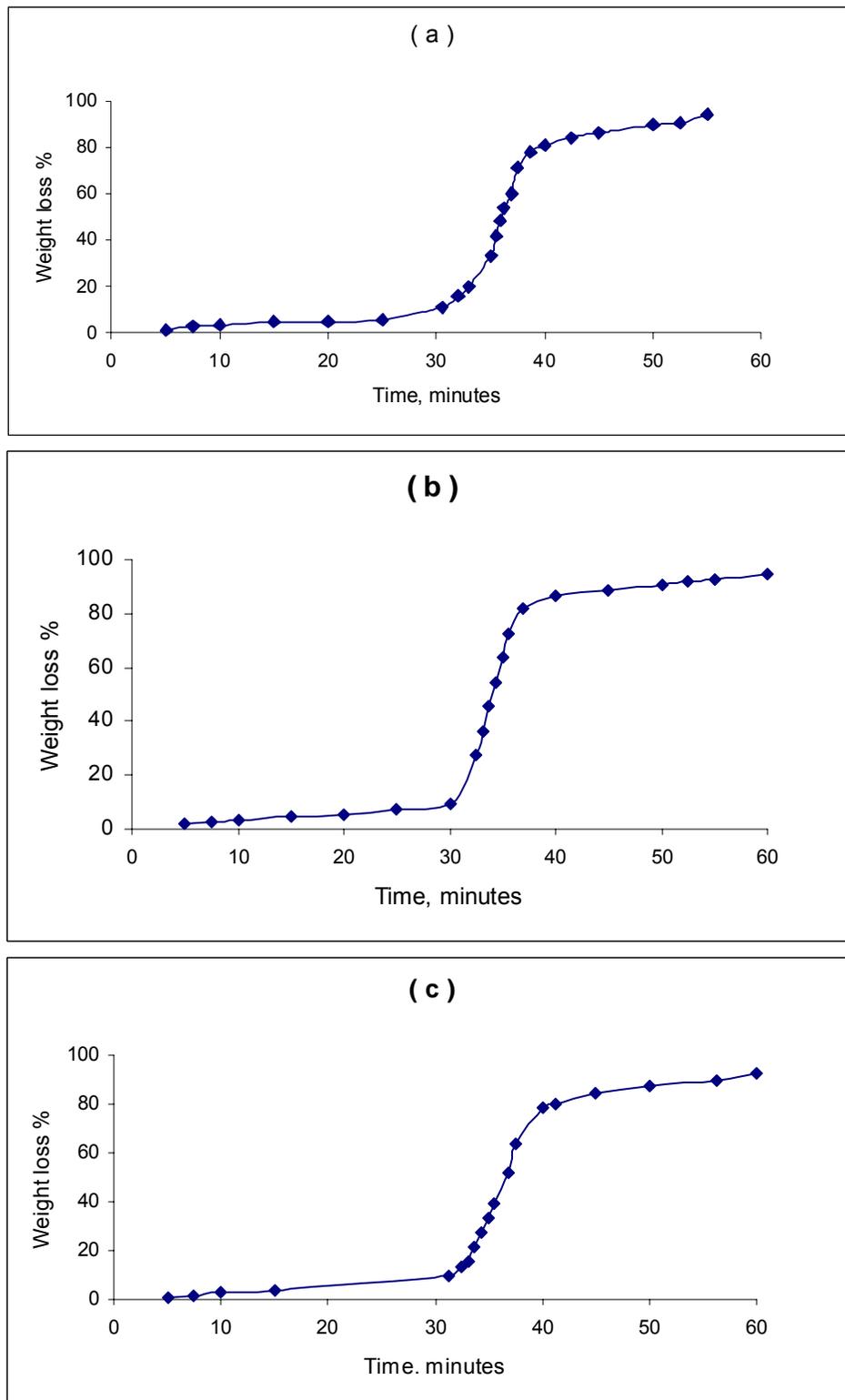


Figure 4. TG curves of thermal treatment of (a) untreated cotton linters, (b) acid, and (c) alkali treated cotton linters.

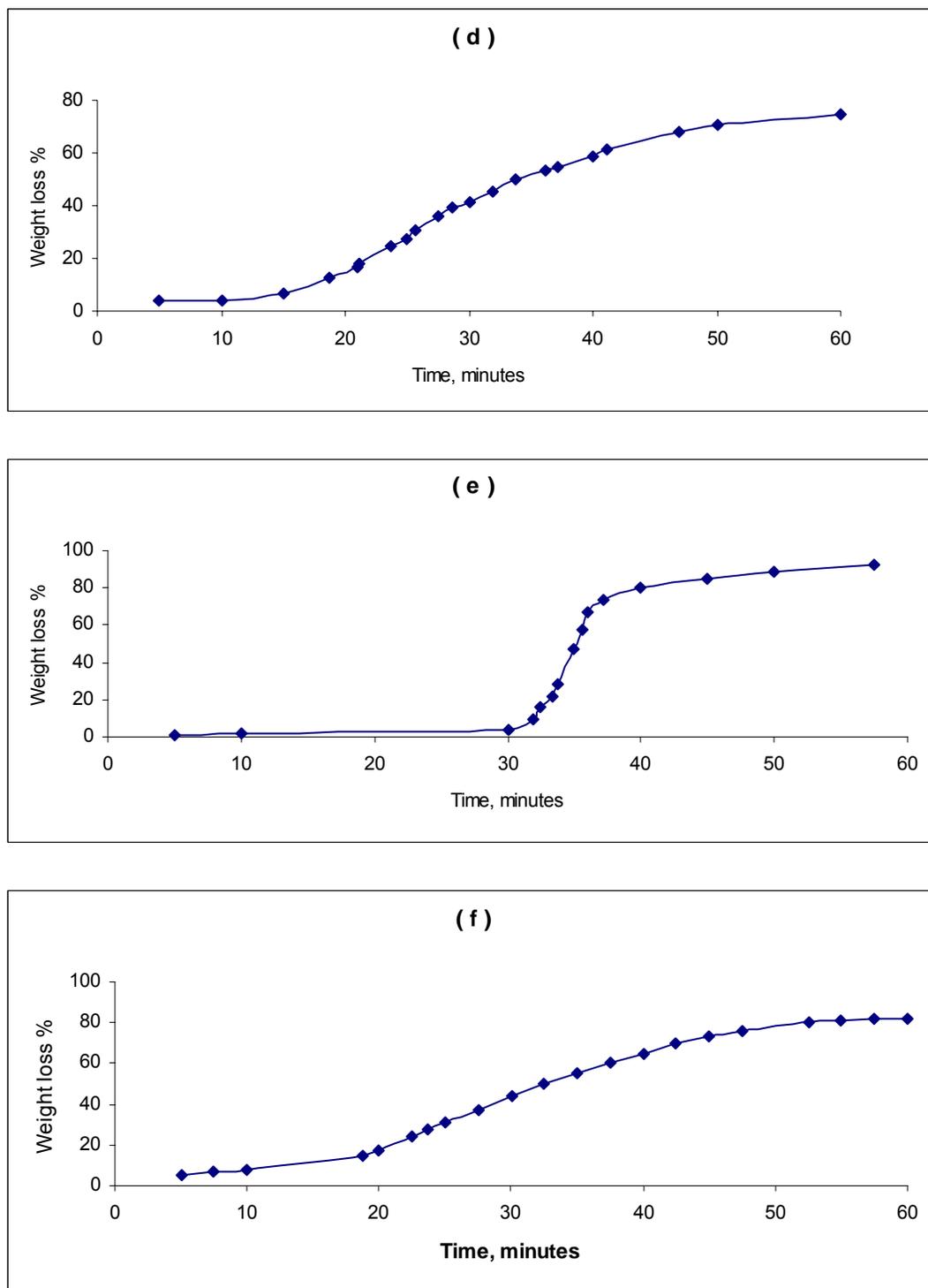


Figure 5. TG curves of (d) carboxylated cotton linters, (e) crosslinked cotton linters, and (f) crosslinked carboxylated cotton linters.

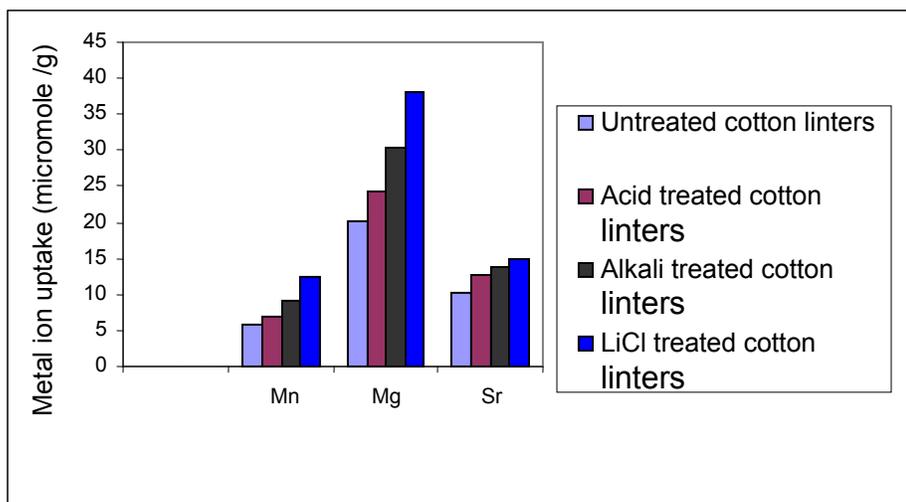


Figure 6. Effects of different treatment of cotton linters on the efficiency on the produced ion exchanger toward metal ion uptake.

From Table 5 it is clear that carboxylation of cotton linters increased its affinity toward metal ion uptake. Also, the treatment of cotton linters with epichlorohydrin as crosslinker increased its affinity toward metal ion uptake. This can be attributed to an increase in the number of function groups on crosslinked cellulose, and also the increase of branched chains, which increase the absorption of metal ions. Besides this, epichlorohydrin, which is commonly used as a crosslinking agent, effectively stabilizes cellulosic materials for the preparation of weakly acidic cation exchangers. The carboxylation of the treated cotton linters with LiCl had the best results for metal ions uptake. This can be attributed to the higher percent of carboxylic groups, and also the increase of the amorphous part in comparison to pure cellulosic materials. The increase of amorphous cellulose causes an increase of incorporated carboxyl groups onto cellulose due to the increase in contact between chemicals and OH groups of cellulose chains. The increase in carboxyl groups incorporated onto treated cellulose with LiCl causes an increase of absorbed metal from the solution. On the other hand, the crosslinked carboxylated cellulose with epichlorohydrin produces an ion exchange material that has higher affinity toward metal ions uptake than carboxylated cellulose only. This can be attributed to the increase of carboxylated cellulose stability, which prevents its swelling in the metal solution, and consequently the metal ions absorption decreases.

From Table 5 it is also clear that the absorbed amounts of different metals by ion exchange materials were not the same. This can be because the hydroxyl functionality in cellulose chains had its origin in a variety of electrophilic reagents. So, the different treatments of cellulose, as listed in Table 1, are expected to result in different amounts of incorporated carboxyl groups. However, some reactive sites may lead to some degree of selective rejection of cations having large ionic radii due to steric hindrance factors or selectivity of ion absorption due to polydentate bonding. The reduced ability to bind the different metals probably is due to both steric and electronic effects. So from the table, the derivatized carboxylate cotton linters had a higher capacity for Mg in all samples. The

reduced capacity for the Mn and Sr ions may be due to their larger ionic radii in comparison to Mg. The high radius of Mn and Sr reduces their access to functional groups in the material matrix. Also, Boyd et al. (1947) concluded that the magnitudes of ion exchange absorption affinities are determined chiefly by the magnitude of the charge and the hydrated radius of the ion in solution.

Table 5. The Effect of Different Treatment of Cotton Linters on the Efficiency on the Produced Ion Exchanger toward Metal Ion Uptake

Samples	Concentration of metal ion uptake ($\mu\text{mole/g}$)		
	Mn	Mg	Sr
Untreated cotton linters	5.7	20.1	10.2
Acid-treated cotton linters	6.8	24.3	12.8
Alkali-treated cotton linters	9.1	30.4	13.7
LiCl-treated cotton linters	12.3	38.1	14.8
Crosslinked cotton linters	14.6	74.1	18.4
Carboxylated cotton linters	16.9	79.3	20.0
Carboxylated crosslinked cotton linters	19.6	96.6	21.8
Acid-treated (carboxylated cross-linked) cotton linters	14.6	80.8	21.2
Alkali-treated (carboxylated cross-linked)cotton linters	21	88.5	22.6
LiCl-treated (carboxylated cross-linked)cotton linters	22.8	92.6	23.5

CONCLUSIONS

1. From infrared spectra, it was found that crystallinity index of cotton linters decreased with LiCl solution treatment, while it increased following treatment with HCl.
2. Crosslinking of untreated and treated cotton linters with epichlorohydrin increased the relative absorbance at 1715 cm^{-1} , due to the C=O group of COOH.
3. From thermal analysis data, it is concluded that treatment of cotton linters with soda decreased the minor decomposition temperature as well as loss in percent mass, while the major decomposition temperature was practically unaffected.

4. Treatment of cotton linters with acid increased the minor and major decomposition temperature, with lower loss in percent mass than untreated cotton linters.
5. Carboxylation of untreated and treated cottons linters increased the efficiency of metal uptake of cotton linters. In addition, carboxylation of crosslinked cotton linters led to higher affinity towards metal ion uptake than untreated and carboxylated cotton linters.
6. The absorption of metal ions by an ion exchanger depends on selectivity and properties of metal ions, as well as on incorporated functional groups.

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