

## Spectroscopic and ion exchange studies on modified cotton linters

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Cation exchange resin was prepared by phosphorylation of cotton linters. The effect of different treatments (alkali or acid) of cotton linters on phosphorylation process was studied. This treatment increases the efficiency of the produced resin toward metal ions uptake (Cu, Fe, Mn, Ni, Pb, Zn). The effect of pH value of metal ion solution on the efficiency of ion exchanger was investigated. The efficiency of the resin toward metal ion uptake was affected by soaking time and weight of resin. Infrared spectroscopy of the cotton linters and its modification was investigated. A new band was seen at wave number 980  $\text{cm}^{-1}$  and 1194  $\text{cm}^{-1}$  due to the C-O-P band.

**Keywords:** Atomic absorption, Cotton linter, Infrared, Ion exchange

### Introduction

Agricultural residues represent a cheap and environmentally safe source for preparation of ion exchangers that are useful for metal and color removal from water. The lignocellulosic materials have low ion exchange or adsorption capacity as well as poor physical stability. The native exchange capacity and general sorptive characteristic of these materials is derived from their constituents (cellulose, hemicelluloses, lignin). For this reason, chemical modification<sup>1,2</sup>, copolymerization<sup>3</sup> and crosslinking<sup>4</sup> should be carried out to achieve efficient ion exchangers<sup>5</sup>. Various cellulose derivatives have been used as ion exchange or chelate resin because they are hydrophilic and advantageous for such applications<sup>6</sup>. Cellulose is a natural polymer, easily available, which has widely been used as substrate for reactants immobilization with many applications<sup>7</sup>. Derivatization of agricultural residues can aim to produce chelating anion or cation exchangers. Epichlorohydrin is a commercial used cross-linking agent for the preparation of cation exchangers<sup>8,9</sup>. Also, the incorporation of certain groups to cellulose or lignocellulosic molecules is used to increase their efficiency toward their cation or anion exchanges ability<sup>10-12</sup>. Cellulose metal oxide hybrid materials have been used as cation exchangers<sup>13</sup>. The major fields of application of these polysaccharides as ion

exchangers are protein isolation, chromatography, wastewater treatment, capturing of mercury and removal of ammonia from air.

The present work aims to modify cotton linters (CLs) by incorporating a phosphate group to increase its efficiency towards metal ions uptake. The effect of treatment of CLs with alkali or acid before phosphorylation process was carried out. The effect of soaking time, weight of ion exchangers and pH of metal ion solution was studied. Infrared of untreated and phosphorylated CLs was taken into consideration.

### Experimental Procedure

CLs ( $\alpha$  cellulose, 99.3 %; crystallinity 82 %; degree of polymerization, 885) were treated with 10% NaOH or 1% HCl under reflux for 2 h. After reflux, CLs were washed with distilled water till neutrality and then air-dried.

### Phosphorylation of Cotton Linter

In this method<sup>1</sup>, dried CLs (5g) were suspended in dry pyridine (50ml). To the stirred cooled suspension, 5 ml phosphorus oxychloride ( $\text{POCl}_3$ ) in methylene chloride (25ml) were added dropwise for 5 min, and then heated under reflux in an oil bath at 115°C for 2 h. The mixture was cooled and then poured into ice water and filtered, then successively washed with water, 1% HCl, water, and methyl alcohol and finally air-dried. Phosphate group was then determined<sup>2</sup>.

### Adsorption of Different Metals

Ion exchange resin (0.2 g) was stirred for 30 min in an aqueous solution (25ml) containing 20 $\mu\text{g}/\text{ml}$  of Cu,

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Table 1— Wavelengths, precision and sensitivity for investigated elements

| Elements | Wavelength, nm | Precision | Sensitivity |
|----------|----------------|-----------|-------------|
| Cu       | 324.8          | 0.3       | 0.10        |
| Fe       | 248.3          | 1.3       | 0.10        |
| Mn       | 279.5          | 0.1       | 0.05        |
| Ni       | 232.0          | 0.1       | 0.12        |
| Pb       | 283.3          | 1.9       | 0.50        |
| Zn       | 213.9          | 0.2       | 0.02        |

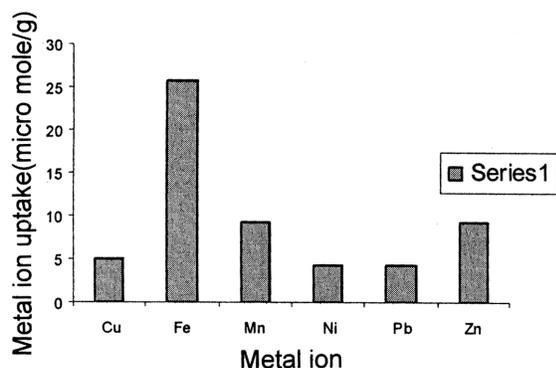


Fig. 1— Metal ions absorbed by phosphorylated cotton linters

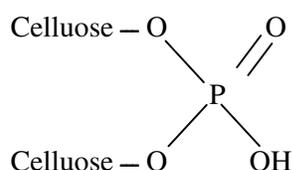
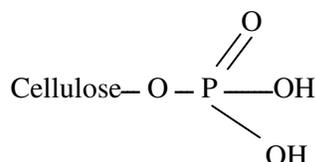
Fe, Mn, Ni, Pb and Zn. The suspension was then filtrated and the elements were determined in the filtrate using Thermo-Elemental S4 full automatic atomic absorption spectrometer equipped with deuterium continuum background corrector. A burner-nebulizer (100 mm with single slot for an air acetylene  $C_2H_2$ ) 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 (Table 1). All measurements were the average of three 3s integrations and a blank measurement was made between every solution measurement.

In another experiment, using different weights (0.1-0.6 g) of resin, the effects of different stirring time, and different pH (1.2-6.3) of the metal ion solution were investigated. Infrared spectroscopy was carried out by Fourier "Transform spectrometer" using the disc technique.

## Results and Discussion

Hydroxyl group of cellulose and its binding ability for metal ions depends on the amorphous and crystalline percent as well as the pH at which the binding is performed<sup>14</sup>. At neutral and acidic pH, the ability of cellulose to absorb cations is increased. On the other hand, the hydroxyl groups of cellulose are available to substitution with a wide variety of the

electrophilic reagents. Multiple functional groups may be placed on.  $POCl_3$  can react at a single site and the product can remain as a dianion or it can react with two sites on the biopolymer backbones, crosslink them, and result on only a mono anion to react with a cation<sup>11</sup>. The phosphorylated cotton linters had higher capacity for iron than other metal ions.



The reduced ability of the produced ion exchanger to bind with metals probably is due to both steric and electronic effects. As compared to other metal ions, Fe and Mn ions have a lower ionic radius, which increases from their absorbance by the ion exchanger. On the other hand, Pb ion has a larger ionic radius than Fe or Mn, which reduces its accessibility to functional groups in the interior matrix. This result is in agreement with Sun & Shi<sup>15</sup>, which concluded that chiefly the magnitude of the charge and the hydrated radius of the ions in solution determines ion exchange adsorption affinities. In addition, Pb is semi hard acid and held less tenaciously by these substituted residues than Fe and Mn, which are hard acids (Fig. 1).

### Effect of Stirring Time

Phosphorylated CLs (0.2 g) were stirred in an aqueous solution (25 ml), which contains  $20\mu\text{g/ml}$  of metal ions (Cu, Fe, Mn, Ni, Pb and Zn) in glass beaker for 20-60 min. The increase of stirring time from 20-45 min slightly increased the quantity of the metal ion uptake by the ion exchanger (Fig. 2). This can be attributed to the increase of the contact time between the surface of the resin and metal ions and consequently the increase in chelation between the metal ions and phosphate groups. Increasing the stirring time (> 45 min) has no remarkable effect on the absorbed quantity of metal ions. Fe and Zn ions have a higher absorption capacity by the resin while Cu and Pb have the lower absorption capacity (Fig. 2).

Table 2— Effect of resin weight on absorbed metals

| Eelements | Resin |      |      |      |
|-----------|-------|------|------|------|
|           | 0.1g  | 0.2g | 0.4g | 0.6g |
| Cu        | 1.7   | 3.1  | 3.5  | 3.7  |
| Fe        | 14.3  | 15.7 | 16.2 | 17.4 |
| Mn        | 15.9  | 16.0 | 16.4 | 15.9 |
| Ni        | 13.3  | 14.0 | 14.2 | 14.9 |
| Pb        | 0.03  | 0.2  | 1.6  | 1.9  |
| Zn        | 16.8  | 17.1 | 17.4 | 17.7 |

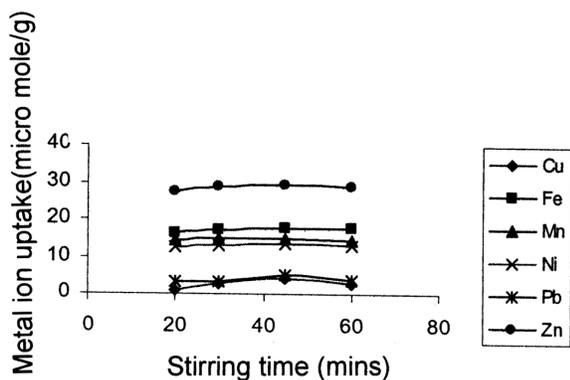


Fig. 2— Effect of stirring time on the efficiency of ion exchanger toward metal ion uptake (micro mole / g)

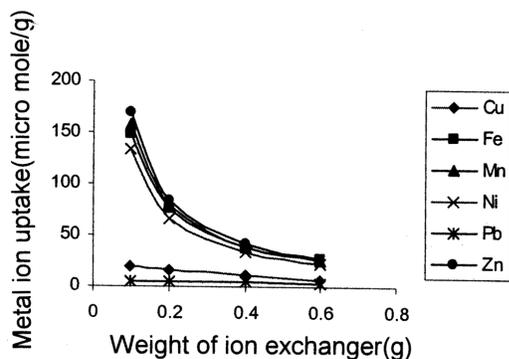


Fig. 3— Effect of weight of ion exchanger on the metal ion uptake(micro mole/g).

**Effect of Ion Exchanger Weight**

Different weights (0.1-0.6 g) of ion exchanger were stirred in 25 ml solution containing 20µg/ml of different metal ions (Cu, Fe, Mn, Ni, Pb, Zn) for 30 min. Absorbed metal ions increase by increasing weight of the ion exchangers (Table 2). This is attributed to the increase of surface of ion exchanger, thereby increasing the functional groups, which absorb the metal ion. The absorbed metal ions per gram of resin, decreases by increasing the weight of resin (Fig. 3).

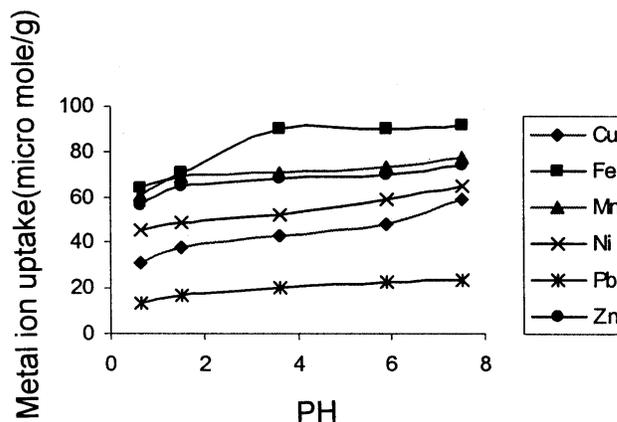


Fig. 4— Effect of pH value of metal ion solution on the efficiency of the ion exchanger toward metal ion uptake

**Effect of pH**

Most solution of metal ions is acidic (pH, 1.1-1.6). Normally, metal ion absorbents exhibit a drastic decrease in metal ion uptake in low pH conditions because the competition with hydronium ions<sup>16</sup>. On the other hand, an increase in pH of metal ion solution causes a decrease in hydronium ion concentration with a consequent increase in metal ion absorption. However, this takes place up to a certain pH value, above which precipitation of metal ions in the form of hydroxide starts. The metal ion uptake by the ion exchanger increases by increasing the pH of metal ion solution (Fig. 4). Metal ion uptake of the phosphorylated cotton linters (PCLs) ion exchanger was significantly increased for all metal ions by increasing the pH (4). At higher pH (> 4), a slight increase in efficiency was observed. Ion exchanger has a higher efficiency to absorb Fe and the lowest efficiency was that of Pb. The metal ion uptake by the PCLs has the following sequence: Fe > Mn > Zn > Cu > Ni > Pb.

**Effect of Acid and Alkali Treatment on the Phosphorylated Cotton Linters**

In another trials, CLs were treated with acid (1%) or alkali (10%) before phosphorylation process. The incorporated phosphate group in the treated CLs was found higher (acidic 121, alkaline 106 mg/g) than that in case of untreated one (85 mg/g). Because the treated CLs with acid before phosphorylation causes a degradation of cellulose chains and consequently increase the active end groups, which causes an increase of incorporated phosphate groups. In case of treated CLs with NaOH, the increase in amorphous part in the cellulose chains causes an increase in the free OH group. This treatment also increases

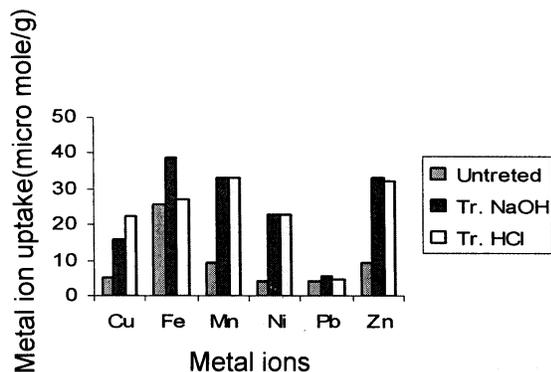


Fig. 5— Histogram shows the effect of different treatment of cotton linters on the efficiency of the produced ion exchanger toward metal ion uptake

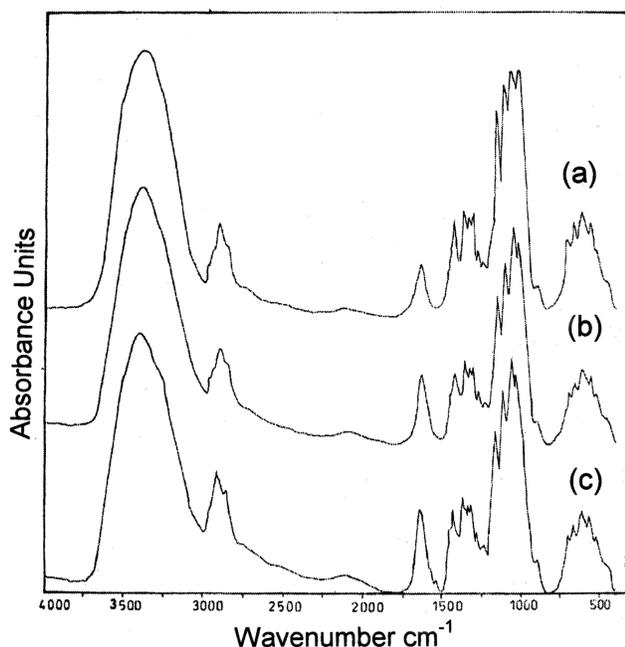


Fig. 6—FTIR spectra of cotton linters: (a) Untreated; (b) Treated with NaOH; (c) Treated with HCl

efficiency of the produced resin toward metal ions uptake (Fig. 5). The resin produced from treated CLs has the higher value of absorbed metal ion than untreated one. Also, acid treated PCLs have higher ability than alkali- treated toward metal ion uptake.

#### Infrared Spectroscopy of the Treated Cotton Linters

O'Connor & Coworkes<sup>17</sup> assigned the absorbance band at  $1430\text{ cm}^{-1}$  to crystalline and at  $900\text{ cm}^{-1}$  to amorphous form in origin. The treatment of CLs under reflux for 2 h with 10% NaOH and 1% HCl produced a detectable change in the intensities of these two bands  $1430\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  (Fig. 6) This means that the treatment causes a change in latera order of cellulose I and II. Therefore, the crystallinity

Table—3 The relative absorbance of OH groups

| Sample                           | Cr I | Relative absorbance of OH at $3420\text{ cm}^{-1}$ | Relative absorbance of OH at $1120\text{ cm}^{-1}$ |
|----------------------------------|------|--|--|
| Untreated cotton linters         | 2.34 | 1.8  | 2.28   |
| Treated cotton linters with HCl  | 2.81 | 2.05   | 2.01   |
| Treated cotton linters with NaOH | 2.06 | 1.95   | 2.2  |

index (Cr I) of the treated CLs with HCl is higher than that in case of the untreated one. This can be attributed to the degradation, which occur in the amorphous regions and consequently, the Cr I increases. This can be confirmed by the decrease in the degree of polymerization of the treated CLs with acid (620) while it was more in the untreated one (885). On the other hand, Cr I in the treated CLs with NaOH solution is lower than that in case untreated one. This is due to the swelling, which was produced in the crystalline region of CLs. Moreover, the degree of polymerization of the treated CLs with NaOH is nearly the same (892) as in case of untreated one (Table 3).

The relative absorbance of OH groups ( $3420\text{ cm}^{-1}$ ) were calculated by the ratio of OH band absorbance wave number to a certain absorbance wave number at  $1328\text{ cm}^{-1}$ , which is corresponding to the OH Rocking ring<sup>18</sup>. The relative absorbance of group is higher in case of treated CLs with acid than that in case of untreated and treated CLs with NaOH solution (Table 3). On the other hand, the relative absorbance of ether linkage at  $1120\text{ cm}^{-1}$  in case of treated CLs with acid is lower than that in case of untreated and treated CLs with NaOH (Fig. 7). This is due to the degradation produced by acid treatment in cellulose chains.

The OH groups vibration absorption at about  $3400\text{ cm}^{-1}$  was dramatically diminished after phosphorylation as a result of the esterification of the OH groups. So, OH group intensity at about  $3400\text{ cm}^{-1}$ ,  $1160\text{ cm}^{-1}$  (2<sup>nd</sup> OH) and at  $1044\text{ cm}^{-1}$  (1<sup>st</sup> OH) of untreated CLs has decreased due to the phosphorylation. A new band appeared at  $1194\text{ cm}^{-1}$  and  $980\text{ cm}^{-1}$  in the phosphorylated CLs due to the formation of C-O-P band. The relative absorbance of this band (band intensity at  $1194\text{ cm}^{-1}$ /band intensity at  $1325\text{ cm}^{-1}$ ) was 0.286, 0.43 and 0.293 for PCLs,

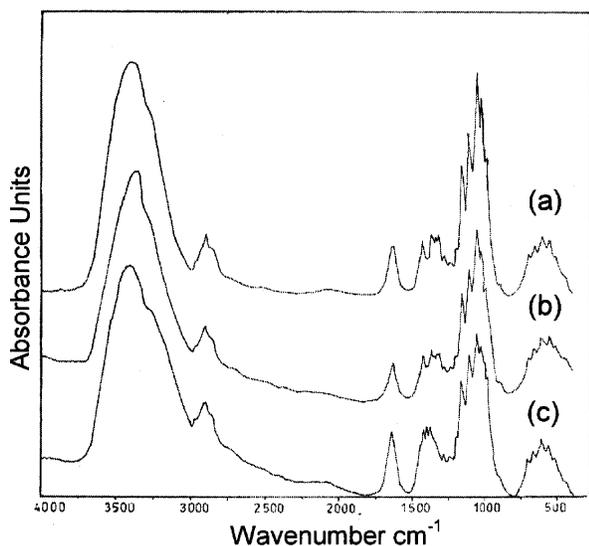


Fig. 7—FTIR spectra of phosphorylated cotton linters: (a) Untreated; (b) Treated with NaOH; (c) Treated with HCl

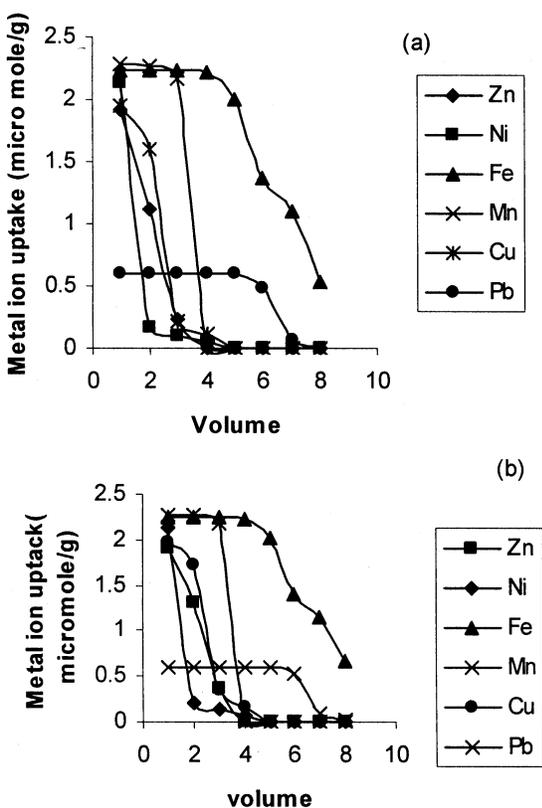


Fig. 8—Metal ion uptake by phosphorylated cotton linter treated with NaOH (a) unactivated with 1N HCL (b) activated with 1N HCL

phosphorylated acid treated CLs and phosphorylated alkali treated CLs respectively. Thus, the acid treated CLs were the more phosphorylated than the untreated

and alkali treated CLs. This can be confirmed by the quantity of the incorporated phosphate groups, which were 60, 95 and 69 mg/g for the untreated, acid treated and alkali treated CLs respectively.

#### Application of the Produced Phosphorylated Cotton Linters Ion Exchangers

Of two columns, each column (10 mm diam) was packed with PCLs (2g). One of the columns was activated with 1% HCl (50 ml) and then the two columns were thoroughly washed with distilled water. Through the two columns, 200 ml of solution containing a mixture of metal ions (20 ppm) was passed through the column with flow rate of 10 ml/min.

The activation of PCLs ion exchanger by 1% HCl increased its efficiency toward metal ion uptake (Fig. 8). This can be attributed to washing and activation of the ion exchangers, which removed any contaminations that have been produced during its preparation. Besides, the ion exchanger brought into hydrated conditions that provided adequate accessibility to ionized sites of the molecules for the metal ion to be adsorbed. Moreover, washing and activation of ion exchangers help and permit coarse particles of resin to orient themselves as they come to rest on the rising surface of the packed materials. For activated and unactivated PCLs, the highest uptake was obtained in case of Fe and Pb and the lesser-absorbed amount was achieved in case of Ni (Fig. 8). This difference in the absorbance of the metal ion by ion exchanger is due to the steric and electronic effects of the metal ions. The binding ability of the metal ions to the ion exchangers was also affected by the semi hard acid<sup>19</sup>.

#### Reuse of Column

The activated and unactivated PCLs column were washed with 1% HCl (50 ml) to elutes absorbed metal ion and then washed with distilled water till neutrality. These two columns were used again by passing 200 ml of solution of the mixture of metal ion (10 ppm). The solution passing through the column was analyzed, and the amount of the packed up elements was detected (Fig. 9). For most of the metal ions investigated, the reuse eluted ion exchanger was more efficient in taking up metal ions than were fresh ones (Fig. 8). This is attributed to the increase in removal of contaminated materials as well as the increase in porosity of the ion exchangers. In another experiments, three columns were picked up with 2 g

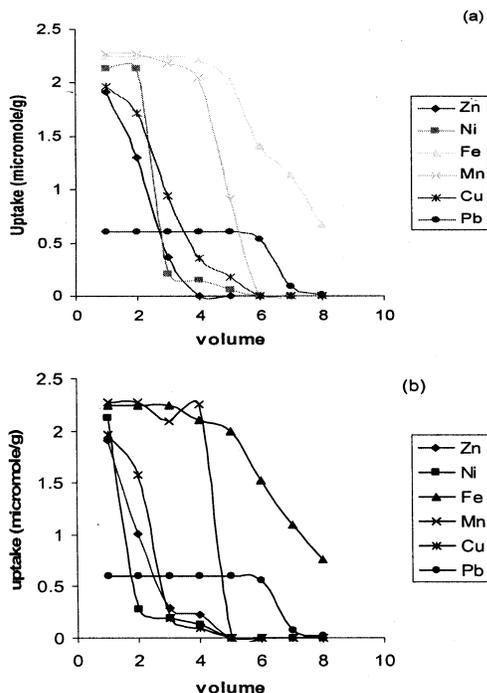


Fig. 9— Metal ion uptake by phosphorylated cotton linter treated with NaOH activated with 1 N HCL (a) before elution (b) after elution

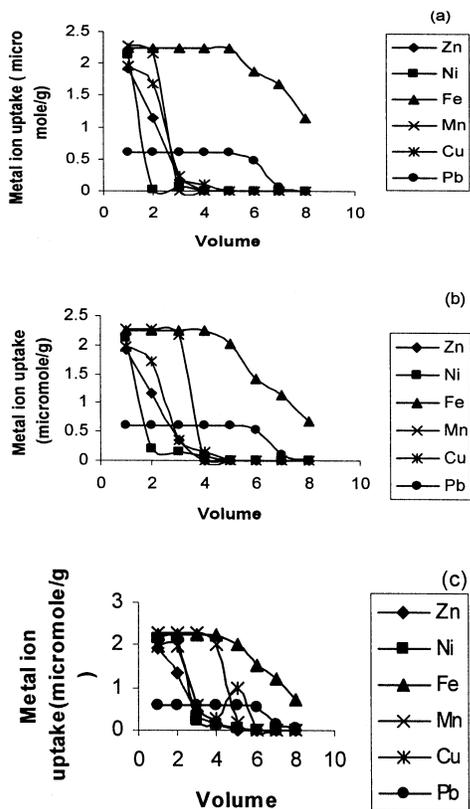


Fig. 10— Metal ion uptake by phosphorylated cotton linter (a) untreated (b) treated with NaOH (c) treated with HCL

of activated PCLs, PCLs treated with 1% NaOH and the third one with PCLs treated with 1 % HCL. Through the three columns, 200 ml of solution containing a mixture of metal ions (10ppm) was passed. The column, which contains PCLs treated with 1%HCl, has a higher accessibility to absorb metal ions than the other two ion exchangers (Fig. 10). This is due to the higher phosphate content of the PCLs treated with 1% HCl than the other two ion exchangers. Also, the efficiency of this ion exchanger was more than the other two ion exchangers.

### Conclusions

Metal ion uptake by CLs can be increased by incorporation of phosphate group. Treatment of CLs with acid or alkali before phosphorylation process causes increase in the incorporated phosphate group onto cellulose and consequently enhances their efficiency towards metal ions uptake. The pH, weight of resin and soaking time show high effects on the absorption of metal ions uptake by the produced resin. A new band was observed in the infrared spectra of the PCLs at  $980\text{ cm}^{-1}$  and  $1194\text{ cm}^{-1}$  which related to the C—O—P.

### References

- Lehrfeld J, Conversion of agricultural residues onto cation exchange materials, *J Appl Polym Sci*, **61** (1996) 2099-2104.
- Nada A M A, Eid M A, El- Bahnsawy R & Khalifa M N, Preparation and characterization of cation exchangers from agricultural residues, *J Appl Polym Sci*, **85** (2002) 792-800.
- Abo- shosha M & Ibrahim N A, Synthesis and characterization of cellulose/N-methylo lacrylamid/ glycidyl methacrylate/methacrylic acid cation exchange resin, *Die Angewaude Makromal Chem*, **226** (1995) 23-37.
- Nada A M A, El- Masry, Torky A M & El-Faied Y, Infrared spectroscopy of cellulose grafted with different monomers, *The 5<sup>th</sup> Arab Int Conf Polym Sci Technol*, V.1 133-149, 18-22 September 1999, Luxor Aswan, Cairo.
- Nada A M A, Eid A M, Sabry A & Khalifa M N, Preparation and some applications of phospho-sulfonated bagasse and wood pulp cation exchangers, *J Appl Polym Sci*, **90** (2003) 97-100.
- Aoki N, Fukushima K, Kurakata H, Sakamoto M & Furuhashi K-I, Deoxy-6-mercaptocellulose and its s-substituted derivatives as sorbent for metal ions, *React & Function Polym*, **42** (1999) 223-233.
- Acemoglu M, Kusters E, Baumann J, Hernandez I & PongMark C, Synthesis of regioselectivity substituted cellulose derivatives and applications in chiral chromatography, *Chirality*, **10** (1998) 294-306.
- Mackawa E, Koshyima T, Preparation of 2,3 dicarboxy cellulose combined with various metal ions, *J Appl Polym Sci*, **29** (1984) 2289-2293.

- 9 Eid K & Nada A M A, Preparation and spectrometric of clulosan ion exchangers, *J Appl Sci*, **19** (2004) 517- 528.
- 10 Laslo J A, Preparing an ion exchange resin from sugar canes bagasse to remove reactive dye front wastewater, *Text Chem Color*, **28** (1996) 13-19.
- 11 Nada A M A & Hassan M L, Phosohorylated cation exchangers from cotton stalks and its constituents, *J Appl Polym Sci*, **89** (2003) 2950-2956.
- 12 Simokovic I, Preparation of anion exchangers from beech sawdust and wheat straw, *Indus Crops Prod*, **10** (1999) 167-173.
- 13 Alfaya R V S & Gushikem Y, Aluminum oxide coated cellulose fibers modified with n- propylpyridinium chloride silsequioxane polymer, *J Col & Interface Sci*, **213** (1999) 438-455.
- 14 Baouab M, Gauthier R, Gauthier H, Chabert B & Rammah M, Immobilization of residual dyes onto ion exchanger cellulosic materials, *J Appl Polym Sci*, **77** (2000) 171-183.
- 15 Sun G & Shi W, Sunflower stalks as adsorbents for the removal of metal ions from wastewater, *Ind Eng Chem Res*, **37** (1998) 1324-1328.
- 16 Fengel I D & Nagener G, *Wood Chemistry, Ullrustructure, Reactions* (Walter de Gruyter, New York) 1984, .94-107.
- 17 O, Conner R T, Dupre E F & Mitchan D, Infrared spectra of maltigasaccharides, *Text Res*, **28** (1958) 328.
- 18 Yu Ledvek Inshakova M D, Miyurov E P Nikitiinvn & Trvses Narch Issied, *Instit Tesell Burmprom*, **52** (1967) 109.
- 19 Kubota H & Shigehisa Y, Introduction of amidoxime groups into cellulose and its ability to absorb metal ions, *J Appl Polym Sci*, **56** (1996) 147-151.