

Phosphorylated Cation-Exchangers from Cotton Stalks and Their Constituents

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ABSTRACT: Cation-exchangers were prepared by phosphorylation of cotton stalks and their isolated constituents (lignin, soda-anthraquinone pulp, and bleached cellulose pulp). FTIR spectra of the phosphorylated materials showed new absorption bands at 950–1200 cm^{-1} of the C—O—P bonds as a result of phosphorylation. The adsorption of different heavy metal ions (lead, copper, nickel, cobalt, chromium, and cadmium) at different metal ion concentrations (50–1500 μg) by the phosphorylated cotton stalks was studied. The adsorption of metal ions by the phosphorylated cotton stalks increased by increasing their concentration. The binding capacity of phosphorylated cellulose, lignin,

and soda-anthraquinone pulp was measured at 1000 μg metal ion concentration. The adsorption of the different heavy metal ions by phosphorylated-lignin and -bleached cellulose pulp was higher than that of phosphorylated cotton stalks. Thermogravimetric analysis of the raw and phosphorylated cotton stalks showed that the resistance of the phosphorylated cotton stalks to thermal degradation was higher than that of raw cotton stalks (lower rate of weight loss), despite the lower degradation onset temperature of the phosphorylated cotton stalks. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2950–2956, 2003

INTRODUCTION

Lignocellulosic materials and crop byproducts have been used for the production of ion-exchangers. These ion-exchangers can be used for water treatment. In order to increase the ion exchange capacity of these materials, different methods have been developed, such as chemical modification, copolymerization, and crosslinking.^{1–4} Chelating polymer based on cellulose is more efficient to ion exchange than the usual synthetic polymer due to its fibrous structure, which causes a high hydrophilicity sorption capacity.⁵ Epichlorohydrin is commercially used as a crosslinking agent for the preparation of cation-exchangers.⁶ Also, incorporation of phosphate, sulfate, or carboxylate groups to the lignocellulosic materials increases their efficiency toward cation-exchangers.^{6–9} Also, the efficiency of the agricultural wastes as anion-exchangers can be increased by changing these materials to quaternary ammonium salts.¹⁰ The major fields of application of these polysaccharide ion-exchangers are protein isolation, chromatography, and wastewater treatment.

Cotton stalks are an agricultural residue, which, up until now, have not been effectively utilized on the industrial level. This work was aimed to the prepara-

tion and characterization of phosphorylation of cotton stalks and their isolated constituents, namely soda-anthraquinone pulp (soda-AQ pulp), bleached cellulose pulp (BCP), and lignin. Also, the sodium ion-exchange capacity and the ability of the prepared ion-exchangers to remove heavy metal ions were studied. The thermal properties of the prepared phosphorylated cotton stalks were investigated.

EXPERIMENTAL

Material and reagents

The raw materials used in this work were cotton stalks (collected from the Delta region in Egypt), soda-AQ pulp, BCP, and lignin isolated from cotton stalks. The cotton stalks had the following chemical composition: cellulose 43.1%, hemicelluloses 26.9%, lignin 27.3%, ash 1.3%, and ethanol-benzene extractives 5.6%.

The cotton stalks were ground to pass through a 1.5 mm screen. Soda-AQ pulp was isolated from the cotton stalks by pulping the cotton stalks with 20% NaOH (based on raw material) in the presence of 0.1% anthraquinone.¹¹ The lignin was precipitated and isolated from the waste black liquor by using 10% sulfuric acid.¹² BCP was prepared by bleaching the soda-AQ pulp by a two-stage sodium chlorite bleaching.¹³ Analytical grade phosphorous oxychloride, pyridine, methylene chloride, and metals chloride were used.

Chemical analyses of cotton stalks

The chemical composition of cotton stalks was determined according to the standard methods.¹³

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Phosphorylation

Cotton stalks, soda-AQ pulp, BCP, and lignin were phosphorylated according to the method of Lehrfeld.¹⁴ Five grams of oven-dry materials was suspended in 40 mL of pyridine and cooled to 8°C. Twenty milliliters of dichloromethane containing 5 mL of phosphorus oxychloride was added to the previous mixture and heated at 115°C for 2 h. The mixture was filtered and the phosphorylated material was washed with 0.1N HCl, distilled water, and dried at 65°C.

Determination of phosphorous

Phosphorylated material (0.2 g) was digested in 10 mL of concentrated nitric acid. After digestion, the solution was diluted to 100 mL of deionized water in a measuring flask. Phosphorous was determined using an Induced Coupled Plasma spectrophotometer ICP-AES Jobin Yvon J4 185 spectrometer.

Fourier transform infrared (FTIR) analysis

Infrared spectra of cotton stalks, soda-AQ pulp, BCP, and lignin and their phosphorylated derivatives were obtained by using JASCO FTIR 800 E spectrometer. The samples were measured using the KBr disc technique.

Thermogravimetric analysis

A PerkinElmer Thermogravimetric analyzer was used to study the thermal properties of the cotton stalks and their phosphorylated derivatives. The heating rate was set at 10°C/min over a temperature range of 50–500°C. Measurements were carried out in a nitrogen atmosphere, with a rate of flow of 50 cm³/min.

Sodium ion-exchange capacity

Sodium ion-exchange capacity of the phosphorylated derivatives was determined as a measure to the extent of the phosphorylation as follows: For 0.2 g of the phosphorylated material, 10 mL of 0.01N NaOH was added and the mixture was stirred for 2 h and left overnight. Twenty milliliters of 0.01N HCl was added and the mixture left overnight, then the excess HCl was determined using 0.01N NaOH. The sodium ion-exchange capacity was calculated as follows:

Sodium ion-exchange capacity

$$= [(B - V) \times N \times 1000] / W \quad (1)$$

where *B* is the volume of 0.01N NaOH consumed in titration of the phosphorylated sample; *V* is the volume of 0.01N NaOH consumed in titration of the

blank sample, *N* is the normality of NaOH; *W* is the weight of oven-dry sample.

Adsorption of heavy metal ions

The phosphorylated material (0.2 g) was stirred with 25 mL of the aqueous solution of the metal chlorides of chromium, copper, cobalt, nickel, lead, and cadmium at different concentrations (50–1000 μg) for 30 min at room temperature. The suspension was filtered and the metal ions were determined in the filtrate using an ICP-AES Jobin Yvon J4 185 spectrometer.

RESULTS AND DISCUSSION

Phosphorylation of cotton stalks and their constituents

A series of phosphorylated derivatives was prepared from barked and debarked cotton stalks, alkali-treated cotton stalks using 1–6% NaOH, and ethanol-benzene-extracted cotton stalks, in addition to soda-AQ pulp, BCP, and lignin. Figure 1 shows FTIR spectra of cotton stalks, soda-AQ pulp, BCP, and lignin and their phosphorylated derivatives. As shown, the intensity of the OH group band at 3400 cm⁻¹ shows detectable change due to phosphorylation. Broadening and shifting to a lower wave number of the OH band occurred as a result of phosphorylation. Also, the relative intensity of the OH band of the stretching vibration at 3400 cm⁻¹ and the secondary OH bending vibration band at 1325–1160 cm⁻¹, as well as at 1035 cm⁻¹, to that of the 1328 cm⁻¹ band¹⁵ (cellulose ring C—H bending vibration band) was decreased due to phosphorylation. New bands at 1200 and 980 cm⁻¹ appeared because of phosphorylation, and these bands were due to C—O—P bond bending vibration. The relative intensities of these bands to that of the 1328 cm⁻¹ were higher in the case of BCP than in the case of phosphorylated cotton stalks. The relative intensity of C—O—P bands at 1200 and 980 cm⁻¹ was 1.0 and 0.9, respectively, in the case of BCP, while it was 0.91 and 0.59 in the case of phosphorylated cotton stalks. This is in accordance with the higher phosphorous content of the phosphorylated cellulose as shown in Table I. In addition, the relative intensity of the aforementioned bands was slightly higher in the case of phosphorylated lignin than in the case of BCP. Relative intensities of 1.1 and 0.95 for the 1200 and 980 cm⁻¹ bands were found in the case of phosphorylated lignin. Phosphorylation of cotton stalks, BCP, soda-AQ pulp, or lignin resulted in remarkable degradation of these materials as evidenced by the decrease of the relative intensity of the C—O—C band at 1120 cm⁻¹. The relative intensity of the C—O—C band was 1.42 and 1.35 for cotton stalks and phosphorylated cotton

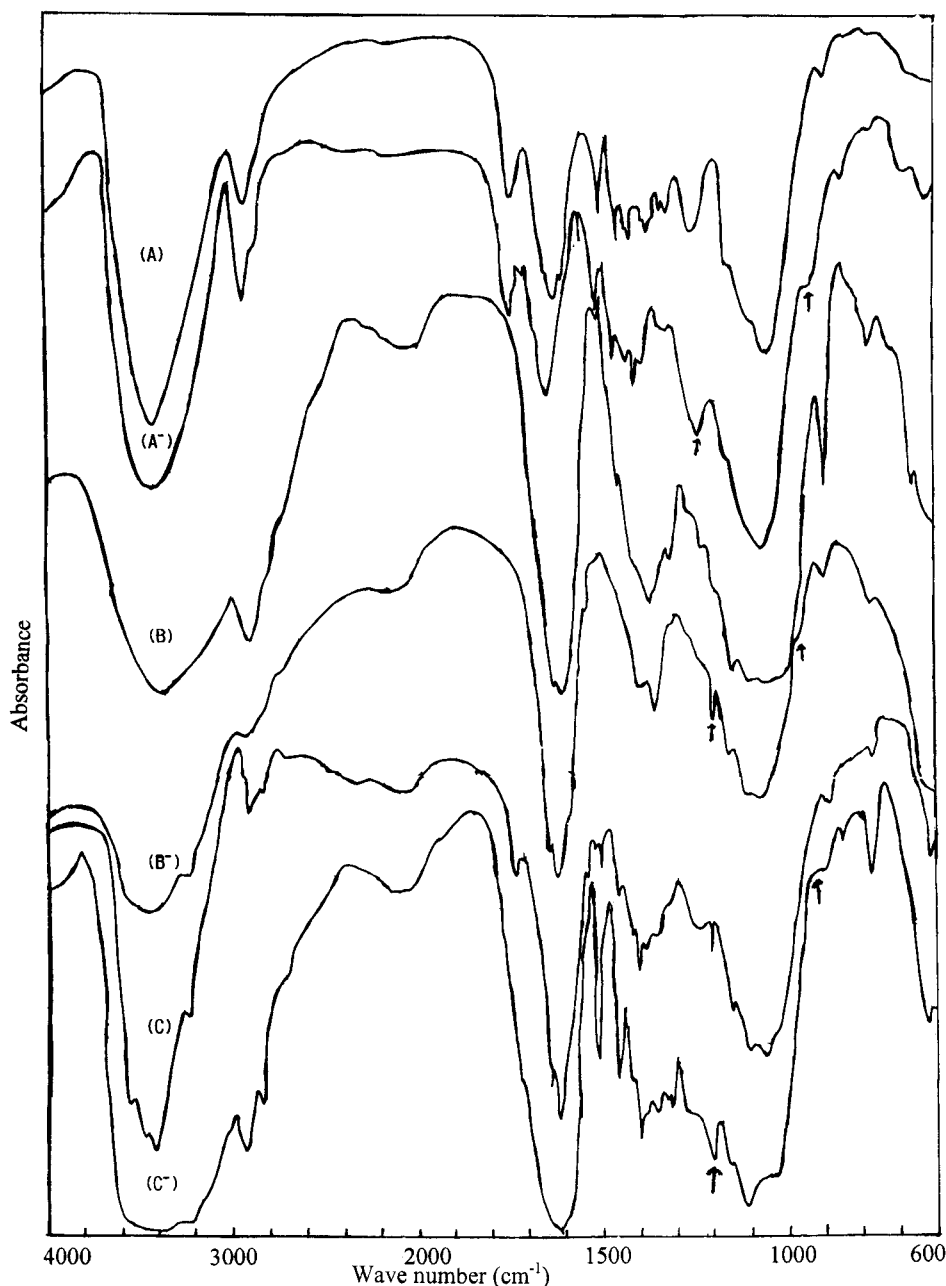


Figure 1 Infrared spectra of (A) cotton stalks raw material, (A⁻) phosphorylated cotton stalks, (B) bleached cotton stalk pulp, (B⁻) phosphorylated bleached cotton stalk pulp, (C) lignin, and (C⁻) phosphorylated lignin.

stalks, respectively, and 1.8 and 1.55 for BCP and phosphorylated BCP, respectively.

The high phosphorous content of lignin, although it has a relatively lower number of OH groups (1.16 OH group per phenyl propane unit) as compared to cellulose (three hydroxyl groups per glucose unit), may be due to the high surface area of the isolated lignin powder. Also, the higher phosphorous content of the isolated BCP and lignin than that of cotton stalks is expected because cellulose, hemicellulose, and lignin in cotton stalks are associated with each other in the cell wall. Moreover, these polymers have accessibility

for adhesion through hydrogen bonding and, consequently, lower accessible OH groups.

Sodium ion-exchange capacity of phosphorylated cotton stalks

Table I shows the phosphorus content and sodium ion-exchange capacity of the different phosphorylated cotton stalks and BCP derivatives as a measure for the extent of phosphorylation. As shown, sodium ion-exchange capacity of phosphorylated debarked cotton stalks is higher than that of cotton stalks with bark.

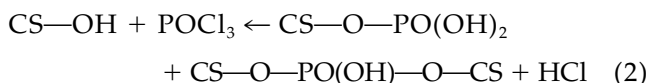
TABLE I
Phosphorus Content and Sodium Ion-Exchange Capacity of the Different Phosphorylated Materials Prepared

Phosphorylated material	mg phosphorus per g material	Sodium ion-exchange capacity (mg eq.)
Cotton stalks	29.4	218.1
6% Alkali-treated cotton stalks	31.2	244.8
Ethanol-toluene extracted cotton stalks	29.7	221
Debarked cotton stalks	29.9	223
Soda-AQ pulp	30.1	
BCP	32.6	
Lignin	33.5	

Phosphorylation conditions were: 5 mL POCl₃ in 20 mL dichloromethane; 5 g cotton stalks or other materials in 40 mL pyridine, reaction temperature 115°C, time 2 h.

This may be due to the presence of waxes and resins in the bark, which decreases phosphorylation of the stalks, and consequently lowers the sodium ion-exchange capacity. Treatment of cotton stalks by 6% NaOH prior to their phosphorylation results in higher phosphorous content and sodium ion capacity than in the untreated cotton stalks. Alkali treatment before phosphorylation may cause partial degradation of the lignin-cellulose-hemicellulose bonds, and hence, it increases the free OH groups for phosphorylation.¹⁶

In other trials, the phosphorylation was carried out in the presence or absence of pyridine after treatment of cotton stalks with 1–6% NaOH and washing to remove excess alkali (Table II). From the table it can be seen that the presence of pyridine was essential for successful phosphorylation; treatment of cotton stalks with alkali prior to phosphorylation cannot substitute for the use of pyridine, which reacts with the hydrochloric acid by-product [eq. (2)]. The liberated HCl causes degradation of the phosphorylated product in the absence of a sufficient amount of base. As a result of the low phosphorylation levels obtained in the absence of pyridine, much lower sodium ion-exchange capacity was noticed (Table II).



where CS refers to cotton stalks.

The phosphorylation of ethanol-benzene extracted cotton stalks resulted in an ion-exchanger with slightly higher sodium ion-exchange capacity than that of nonextracted cotton stalks. The phosphorous content of the former was slightly higher than that of the latter.

Adsorption of heavy metal ions by the phosphorylated derivatives

Adsorption of some heavy metal ions by the prepared phosphorylated derivatives of cotton stalks, soda-AQ pulp, BCP, and lignin was studied. 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 Coulombic interaction. The Coulombic 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 the materials is determined by their surface areas, which can be observed by the effect of different sizes of adsorbents on the adsorption.

TABLE II
Effect of Alkali Treatment and Presence of Pyridine on Phosphorylation of Cotton Stalks and Their Sodium Ion-Exchange Capacity

Material	mg phosphorus per g material	Sodium ion-exchange capacity (mg eq.)
6% Alkali-treated cotton stalks + pyridine ^a	31.2	244.8
6% Alkali-treated cotton stalks without pyridine ^b	0.36	29.4
3% Alkali-treated cotton stalks + pyridine ^a	29.9	209.2
3% Alkali-treated cotton stalks without pyridine ^b	0.30	26.7
1% Alkali-treated cotton stalks + pyridine ^a	26.3	186.9
1% Alkali-treated cotton stalks without pyridine ^b	0.21	13.3

^a Phosphorylation conditions were: 5 mL POCl₃ in 20 mL dichloromethane; 5 g cotton stalks in 40 mL pyridine, reaction temperature 115°C, time 2 h.

^b Phosphorylation conditions were: 5 mL POCl₃ in 20 mL dichloromethane; 5 g cotton stalks, reaction temperature 115°C, time 2 h.

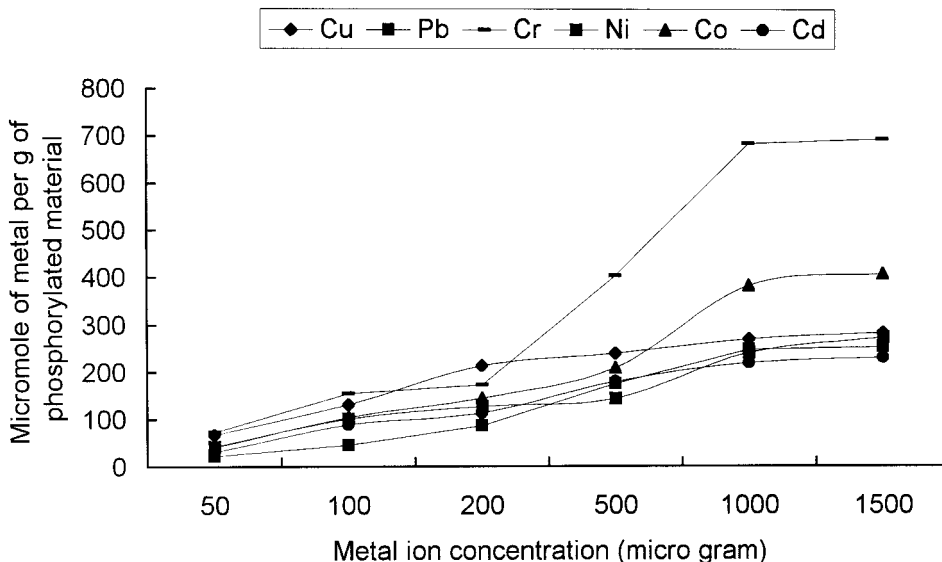


Figure 2 Effect of metal ion concentration on quantity of metal ion adsorption by phosphorylated cotton stalks.

Figure 2 shows the adsorption of the different heavy metal ions by phosphorylated cotton stalks at different metal ion concentrations. As shown, the adsorption of the different metal ions increased by increasing the concentration up to 1000 μg . A slight increase in metal ion adsorption took place on increasing the metal ion concentration to 1500 μg . Generally, the highest adsorption was for chromium metal ions while the lowest adsorption was for lead and cadmium. Lead ion has the largest radius followed by cadmium, while the charge of lead ion is softer than that of cadmium because cadmium is in the fourth period while lead is in the fifth period. Chromium ion (Cr^{+3}) contains three positive charges while the other metal ions contain two positive charges, so chromium has higher

ion-exchange affinity than the other metal ions. At metal ion concentration up to 200 μg , copper ions have comparable adsorption to that of chromium, but at higher metal ion concentration there was no significant increase in adsorption of copper ions. The adsorption of the different metal ions was generally in the following order: $\text{Cr} > \text{Cu} > \text{Co} > \text{Ni} > \text{Cd} > \text{Pb}$, except at a metal ion concentration of 1000 and 1500 μ where Co metal ions had more adsorption than Cu metal ions and lead metal ions had more adsorption than cadmium.

Figure 3 also shows the adsorption of the different metal ions by phosphorylated derivatives of cotton stalks, alkali-treated cotton stalks, soda-AQ pulp, BCP, and lignin at constant metal ion concentrations

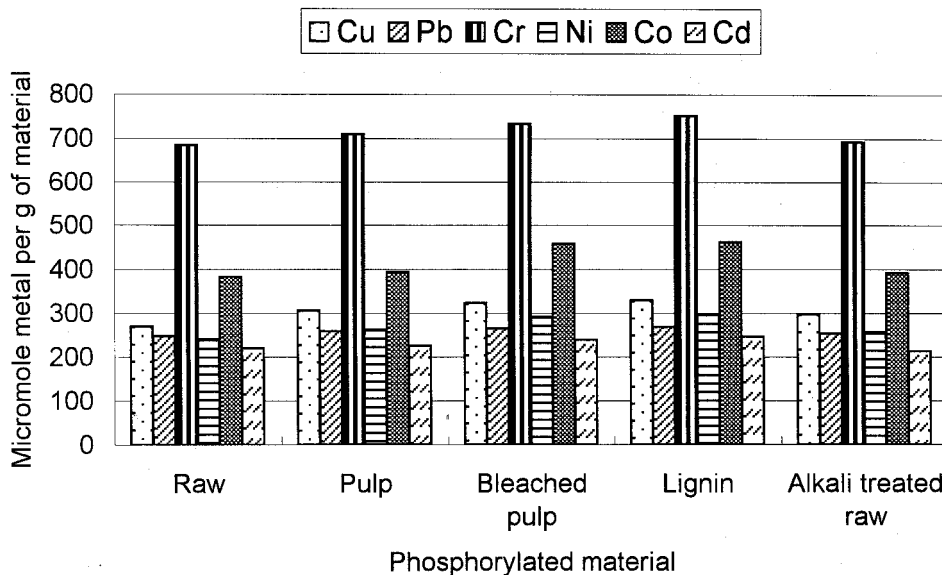


Figure 3 Metal ion adsorption of the different metal ions by different phosphorylated materials.

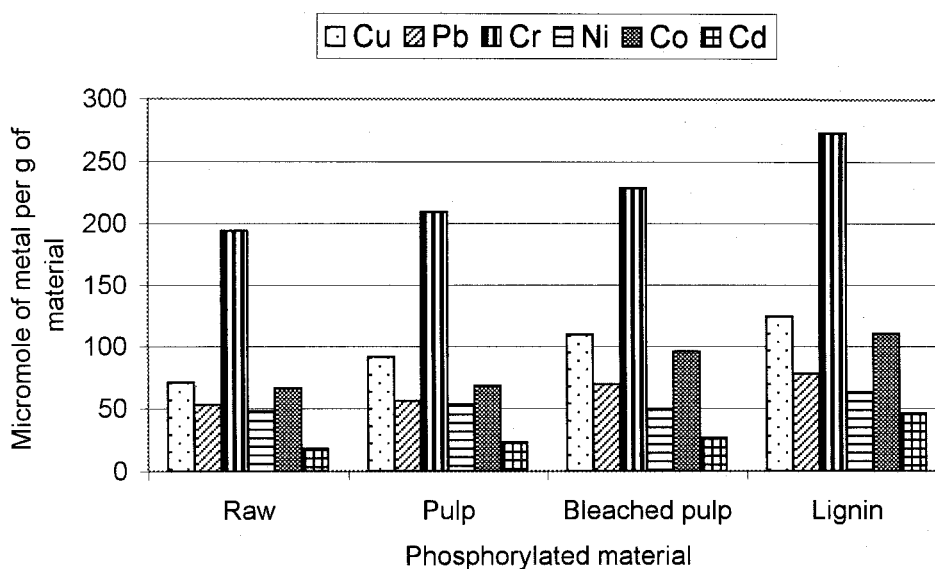


Figure 4 Adsorption of the different metal ions from a mixture of them by different phosphorylated materials.

(1000 μg). Also, chromium metal ions were the highest adsorbed metal ions by the different phosphorylated derivatives. The general order of the adsorption capacity of the different phosphorylated derivatives was as follows: lignin > BCP > soda-AQ pulp > alkali-treated cotton stalks > cotton stalks. This is in accordance with the phosphorous content, that is, the phosphate groups, of these derivatives. Lignin had the highest phosphorus content in addition to its very high surface area compared to the other materials used. The adsorption of the different metal ions by the different phosphorylated derivatives (alkali-treated cotton stalks, soda-AQ pulp, BCP, and lignin) was generally in a similar order to that found in the case of using the phosphorylated cotton stalks.

Selectivity of the phosphorylated derivatives

The selectivity of phosphorylated-cotton stalks, -soda-AQ pulp, -BCP, and -lignin toward adsorption of the different heavy metal ions from a mixture containing these metal ions at 1000 μg concentration was investigated. As shown in Figure 4, the highest adsorption was found for chromium followed by copper metal ions. The general order of selectivity was as follows: $\text{Cr} > \text{Cu} > \text{Co} > \text{Ni} \gg \text{Pb} > \text{Cd}$. Also, phosphorylated lignin had the highest metal ion adsorption, followed by BCP, soda-AQ pulp, and then cotton stalks.

Thermal properties of phosphorylated cotton stalks

Figure 5 shows the thermogravimetric curves of cotton stalks and phosphorylated cotton stalks. After water evaporation at 100–120°C, two main weight loss stages were observed. The first weight loss stage,

which was probably due to generation of noncombustible gases such as CO, CO₂, formic acid, and acetic acid,¹⁷ started at about 180°C and 160°C for cotton stalks and phosphorylated cotton stalks, respectively. The maximum weight loss rate of this stage was at 232°C and 171°C, for cotton stalks and phosphorylated cotton stalks, respectively, as shown from the differential thermogram curves. The second weight loss stage, which indicates the onset of pyrolysis and generation of combustible gases,¹⁷ started at 260°C and 250°C for cotton stalks and phosphorylation cotton stalks, respectively. The lower onset weight loss temperature of the first stage in the case of phosphorylated cotton stalks may be due to de-esterification of the phosphate groups and formation of phosphoric acid, which may degrade cotton stalk constituents. However, a lower rate of decomposition is clear for the phosphorylated cotton stalks; the first stage weight loss was 58 and 41% for cotton stalks and phosphorylated cotton stalks, respectively. Also, the second stage ended at about 650°C and 550°C for cotton stalks and phosphorylated cotton stalks, respectively. Phosphorylated cellulose and other phosphorylated derivatives are known to have fire-retardant properties.

CONCLUSIONS

Cotton stalks can be used to prepare phosphorylated cation exchanger in addition to lignin, soda AQ-pulp, and BCP. The cation-exchanger showed high affinity toward chromium and copper metal ions. In a mixture of the different heavy metal ions, the different phosphorylated materials prepared showed high selectively toward chromium metals ions. Phosphorylated lignin showed the highest ion-exchange capacity followed by phosphorylated BCP, soda-AQ pulp, and finally cotton stalks.

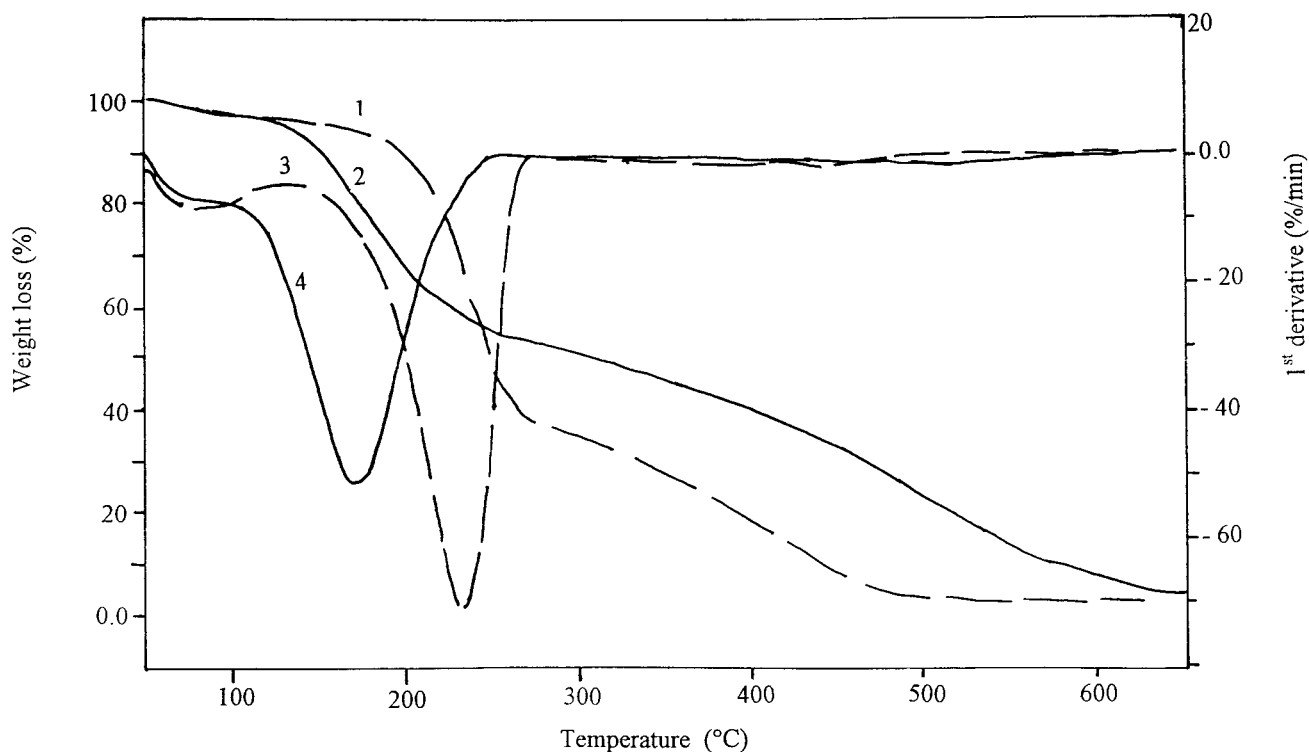


Figure 5 Thermogravimetric analysis of untreated and phosphorylated cotton stalks. (1) Untreated cotton stalks, weight loss. (2) Phosphorylated cotton stalks, weight loss. (3) Untreated cotton stalks, first derivative. (4) Phosphorylated cotton stalks, first derivative.

Phosphorylated cotton stalks have a lower rate of thermal degradation than raw cotton stalks.

References

- Nada, A. M. A.; Eid, M. A.; El-Bahnasawy, R. M.; Khelifa, M. N. *J Appl Polym Sci*, to appear.
- Helann, Z. R.; Volesky, B.; Prasetyo, I. *Biotechnol Bueng* 1993, 41, 819.
- Sun, G.; Gu, X. *Ind Eng Chem Res* 1997, 36, 808.
- Wu, H.-S.; Jone, H.-C.; Hwang, J.-W. *J Appl Polym Sci* 1997, 63, 89.
- Simokovic, I. *Ind Crops Prod* 1996, 10, 164.
- Vishalakshi, B. *J Polym Sci Polym Chem* 1995, 33, 365.
- Nada, A. M. A.; Badry, M.; Abdel-nour, K. N. *Polym Degrad Stab* 1992, 36, 22.
- Nada, A. M. A.; Eid, M. A.; Sabry, A.; Khalifa, M. N. *J Appl Polym Sci*, submitted.
- Mackawa, E.; Koshijima, T. *J Appl Polym Sci* 1984, 29, 2289.
- Simokovic, I.; Miynar, J.; Alfaldi, J. *Carbohydrate Polym* 1992, 17, 285.
- Nada, A. M. A.; El-Saied, H.; El-Ashmawy, A. E. *Holzforshung* 1986, 40, 43.
- Nada, A. M. A.; Fadly, M.; Badry, M. *Int J Polym Mater* 2000, 47, 42.
- Browning, B. L. *Methods of Wood Chemistry*, Vol. 2; Interscience: New York, 1967.
- Lehrfeld, J. *J Appl Polym Sci* 1996, 61, 2099.
- Fengel, D.; Wegener, G. *Wood Chemistry, Ultra-Structure and Reactions*; Walter de Gruyter: New York, 1884.
- Yu, L.; Inshakova, M. D.; Miyurov, E. P.; Nikitinun, T. *Narch Issied, Institute Tselyle, Pourn Prom* 1967, 52, 109.
- Le Van, S. L. In *Concise Encyclopedia of Wood and Wood-Based Materials*; Scniewind, A. P., Ed.; Pergamon Press: New York, 1989; p 271.