

Preparation and Characterization of Cation Exchangers from Agricultural Residues

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ABSTRACT: Cation-exchange systems were prepared by phosphorylation of some lignocellulosic materials, namely, rice straw, cotton stalks, and bagasse. The effect of the particle size of the lignocellulosic materials as well as their chemical constituents on the phosphorylation process was studied by the determination of the phosphorus content of the prepared ion-exchange material. Phosphorus was determined using inductively coupled plasma atomic emission spectrometry. Optimization of the phosphorylation reaction was achieved by studying the effect of the different experimental parameters, namely, the reaction time, temperature, and amount of phosphorus oxychloride added, on the phosphate content of the reaction product. The treatment of the lignocellulosic material with sodium hydroxide was found to improve its phosphorylation. The cation-exchange efficiency of the produced phosphated material toward Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} was examined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 792–800, 2002

Key words: ion exchange; phosphorylation; agricultural residues

INTRODUCTION

Ion-exchange resins are broadly employed for the treatment of process waters and wastewaters. Numerous by-products of agricultural residues have been examined for potential use as ion-exchange materials. Agricultural residues represent a cheap and environmentally safe source of materials for the preparation of ion exchangers that are useful for metal and color removal from

water.^{1,2} The lignocellulosic materials themselves have low ion-exchange or adsorption capacity as well as poor physical stability. For this reason, chemical modification, copolymerization, or cross-linking should be carried out for these materials to achieve efficient ion exchangers.³ Various cellulose derivatives have been used as ion-exchange or chelate resin because of their hydrophilic character. Chelating polymers based on cellulose of agricultural residues have several advantages over those prepared using the usual synthetic polymers. This is due to the fibrous structure and the consequent high hydrophilic sorption capacity of the cellulosic material as compared with

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synthetic polymers.⁴ Derivatization of the agricultural residues can aim to produce chelating anion or cation exchangers. Epichlorohydrin is a commercially used crosslinking agent for the preparation of acid cation exchangers.⁵ Also, the incorporation of certain groups to the lignocellulosic materials is used to increase their efficiency toward their cation-exchange ability, such as phosphonic groups ($-\text{PO}_3\text{H}_2$), sulfonic groups ($-\text{SO}_3\text{H}$), and carboxylic groups ($-\text{COOH}$),⁶⁻⁸ or toward their anion-exchange ability, as 1ry, 2ry, or 3ry amino groups⁹ and quaternary ammonium groups.¹⁰ The major fields of application of these polysaccharide ion exchangers are protein isolation, chromatography, wastewater treatment, capturing of mercury, and removal of ammonia from air.

The present work was devoted to the preparation of ion exchangers from rice straw, bagasse, and cotton stalks as well as from lignin and bleached bagasse pulp, by phosphorylation of these agricultural residues. The experimental parameters affecting the phosphorylation process as well as the ion-exchange efficiency of the produced ion exchanger, including particle size and reaction parameters, were studied. The efficiency of the produced ion exchangers toward uptake of different heavy metals from their solutions was also investigated. The latter was carried out using inductively coupled plasma atomic emission spectrometry (ICP-AES).

EXPERIMENTAL

Materials and Reagents

The raw materials used in this work were rice straw, bagasse (depithed), and cotton stalks, which were dried and ground to different particle sizes ranging from 100 to 400 μm . Lignin was precipitated from waste black liquor produced from the pulping of bagasse with NaOH.¹¹ Bleached bagasse pulp was prepared by three conventional bleaching methods (chlorination, extraction, and hypochlorite).

Analytical-grade (dry) phosphorous oxychloride, pyridin, and methylene chloride were used. For the preparation of standard calibration solution stock, standard solutions (Merck, Darmstadt, Germany) were used.

Methods

Lignin and α -cellulose contents were determined according to Teppi standards T 22205-54 and T

Table I Wavelengths of Analytical Spectral Lines and Their Limits of Detection

Element	Wavelength (nm)	Limit of Detection (ng mL ⁻¹)
Cd	226.502	3.4
Co	228.616	7.0
Cr	267.716	7.1
Cu	327.396	9.7
Fe	259.940	6.2
Ni	352.454	45.0
Pb	220.353	42.0
Zn	213.856	1.8

17m-55, respectively. Hemicellulose was determined according to Jayme and Sarten.¹² Treatment of bagasse (ground) with sodium hydroxide of a concentration varying between 0.5 and 5% was carried out under reflux for 1 h.

Phosphylation

The method used was that described by Lehrfeld.¹³ Five grams of dried residue was suspended in 50 mL dried pyridine. To the stirred cooled suspension, 5 mL phosphorus oxychloride in 25 mL methylene chloride were added dropwise over a period of 5 min, then heated 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, 0.1N HCl, water, and methyl alcohol and finally air-dried.

Absorption of Different Metal Ions

For the determination of the affinity of the phosphorylated cation exchanger for the absorption of metal ions, 1 g of the prepared material was stirred with 50 mL of an aqueous solution containing 20 $\mu\text{g mL}^{-1}$ of different elements for 30 min. The suspension was then filtered and the elements were determined in the filtrate using ICP-AES. The elements investigated were Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn.

The ICP equipment used was a sequential Jobin Yvon JY 38S spectrometer, equipped with a holographic grating of 2400 grooves mm^{-1} . Table I gives the wavelengths of the spectral lines selected for the determination of the elements under investigation and their limits of detection. The selection of the spectral lines was based on

Table II Phosphate Group Content in Phosphated Agricultural Residues

Raw Material	Phosphate Group Content (mg/g)
Rice straw	40.5
Bagasse	112.2
Cotton stalks	87.0

their power of detection as well as on their freedom from line overlap interference.

Determination of Phosphorus

For the determination of phosphorus in the prepared cation exchanger, the following procedure was followed: The sample, 0.2 g, HF, 5 mL, and concentrated HNO₃, 5 mL, were brought together. The mixture was heated in a PTFE beaker on a hot plate and evaporated to near dryness. Another 5 mL HNO₃ was added and the mixture again evaporated until the volume of the acids was about 2 mL. Deionized water was then added to the residue, which then dissolved to a clear solution. The solution was transferred into a 100-mL measuring flask and the volume made up with deionized water. Phosphorus was determined in the solution using ICP-AES.

RESULTS AND DISCUSSION

Phosphorylation of Agricultural Residues

A series of cation-exchange resins was prepared from the agricultural residues under investigation, namely, rice straw, bagasse, and cotton stalks, by the incorporation of phosphate groups into the complex polysaccharide matrix of these materials. The phosphate group content of the prepared materials was calculated from the measured phosphorus concentration. The obtained results are presented in Table II, which shows the ability of these agricultural residues to form phosphate ester groups.

Comparing these results with those obtained from the determined chemical constituents of these residues (Table III), it is clear that the reaction of phosphorus oxychloride with the different materials depends on the kind of material and its chemical structure, that is, the percent of cellulose, lignin, hemicellulose, extractives, and ash content. Rice straw has the lowest ability toward phosphorylation. Its phosphate derivative has a much lower phosphate ester content than that of bagasse and cotton stalks. This can be attributed to its chemical composition, as it has the relatively highest ash content and the lowest content of lignin and α -cellulose as compared with bagasse and cotton stalks. Accordingly, due to the low lignin and α -cellulose content of rice straw, its ability toward the formation of phosphate ester groups is low. In addition, its high ash content, providing the cemented material for cellulose, hemicellulose, and lignin, would decrease the penetration efficiency of chemicals through the cellulose chain.

On the other hand, comparing the behavior of bagasse and cotton stalks toward phosphorylation (Table II), it can be seen that the ability of bagasse to form phosphate ester groups is much higher than that of cotton stalk. This is due to the relatively higher α -cellulose content of bagasse. Moreover, cotton stalks contain barks and a higher content of alcoholic extractive materials that cause less penetration efficiency of chemicals toward the cellulose chains.

Cation-exchange Efficiency of Phosphated Agricultural Residues

The efficiency of the cation exchanger depends not only on the reacted phosphate ester group, but also on the chemical composition of the phosphated agricultural residue. Figure 1 shows a histogram of the quantity of metal ions that were picked up by the prepared phosphated agricultural residues from solutions containing a mixture of these elements, each at a concentration of

Table III Chemical Constituents (%) of Rice Straw, Bagasse, and Cotton Stalks

Raw Material	α -Cellulose	Lignin	Hemicellulose	Ash	Alcoholic Extractive
Rice straw	37.2	12.2	21.2	14.10	4.6
Bagasse	46.2	20.2	26.8	1.02	3.2
Cotton stalks	42.8	27.3	25.4	1.30	5.1

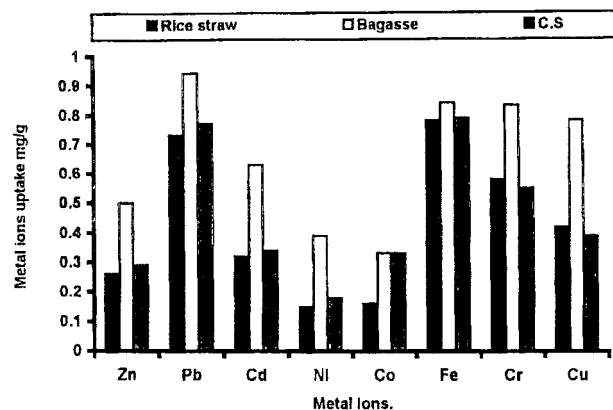


Figure 1 Histogram of metal ion uptake by cation exchangers produced from different raw materials.

$20 \mu\text{g mL}^{-1}$. From the histogram, it can be seen that the phosphated rice straw has, for all investigated elements, the least picking-up efficiency. This can be attributed to its low content of phosphate groups, as well as to the high ash content of rice straw. The latter affects the hornification of the phosphated rice straw and, consequently, reduces the efficiency of penetration of metal ions through it. It is also clear that the efficiency of phosphated cotton stalks toward the picking up of metal ions is lower than that of the phosphated bagasse. This can be due to its lower content of phosphate groups. Also, the high alcoholic extractive material, namely, resin and waxes, decreases the penetration of the metal ions and, consequently, their contact with the ion-exchange sites.

From the histogram, it can be seen that the picking-up tendency of the prepared ion exchangers depend on the ion. Pb and Fe have the highest binding efficiency, while Co and Ni ions are picked up the least. This can probably be attributed to both steric and electronic effects. The ion-exchange affinity is also related to the charge and the hydrated radius of the metal ion.¹⁴ In addition, the binding ability of the different metal ions to the ion exchanger is affected by the semihard acid.¹⁵

Effect of Particle Size on the Properties of the Prepared Ion Exchangers

The size of the particles of the ion exchanger can affect its efficiency. For this reason, the raw materials of the agricultural residues under investigation were ground and first passed through a sieve of 1.5-mm bore diameter. The materials

were then sieved to different particle sizes ranging from 100 to 400 μm before phosphorylation. The effect of particle size on the ion-exchange affinity of the different phosphated agricultural residues is shown in Figure 2(a–c). For bagasse, the relation has a maximum at a particle size of 250 μm for all metal ions investigated. For rice straw, the maximum occurs at about 315 μm , while for phosphated cotton stalks, the ion-exchange efficiency decreases with an increasing particle size. This can be attributed to the number of functional groups incorporated into the prepared ion exchanger that varies also with the particle size. Figure 3 shows the variation of the amount of the phosphate group with the particle size for the different materials. It is clear that these relations have maxima at the same values of the particle size for which the ion-exchange efficiency is at maximum.

From Figure 2, it can also be seen that the efficiency by which metal ions are removed from their solution mixture depends on the metal ion as well as on the ion exchanger. The efficiency of the different ion exchangers varies with the metal ions as follows:

For bagasse: $\text{Fe} > \text{Co} > \text{Cr} > \text{Pb} > \text{Cd} > \text{Cu} > \text{Zn} > \text{Ni}$
 For rice straw: $\text{Fe} > \text{Pb} > \text{Cr} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Co} > \text{Ni}$
 For cotton stalks: $\text{Fe} > \text{Pb} > \text{Cr} > \text{Cu} > \text{Ni} > \text{Cd} > \text{Zn} > \text{CO}$.

Phosphorylation of Bagasse and Its Constituents

From the results obtained in this investigation, it was found that bagasse produces a phosphated ion exchanger that has the highest efficiency compared to rice straw and cotton stalks. For this reason, it was found of interest to devote more experimental work to maximize this efficiency. In this respect, the phosphorylation of bagasse and its constituents, namely, cellulose and lignin, was investigated. The obtained results are given in Table IV. From the table, it can be seen that the phosphorylation process in the case of both separated cellulose and lignin is higher than that in the case of bagasse raw material. The relatively low amount of phosphate ester groups in bagasse can be attributed to the fact that the bagasse constituents, namely, cellulose, lignin, hemicellulose, and extractable materials, are all associated with each other in the plant. In the cell wall,

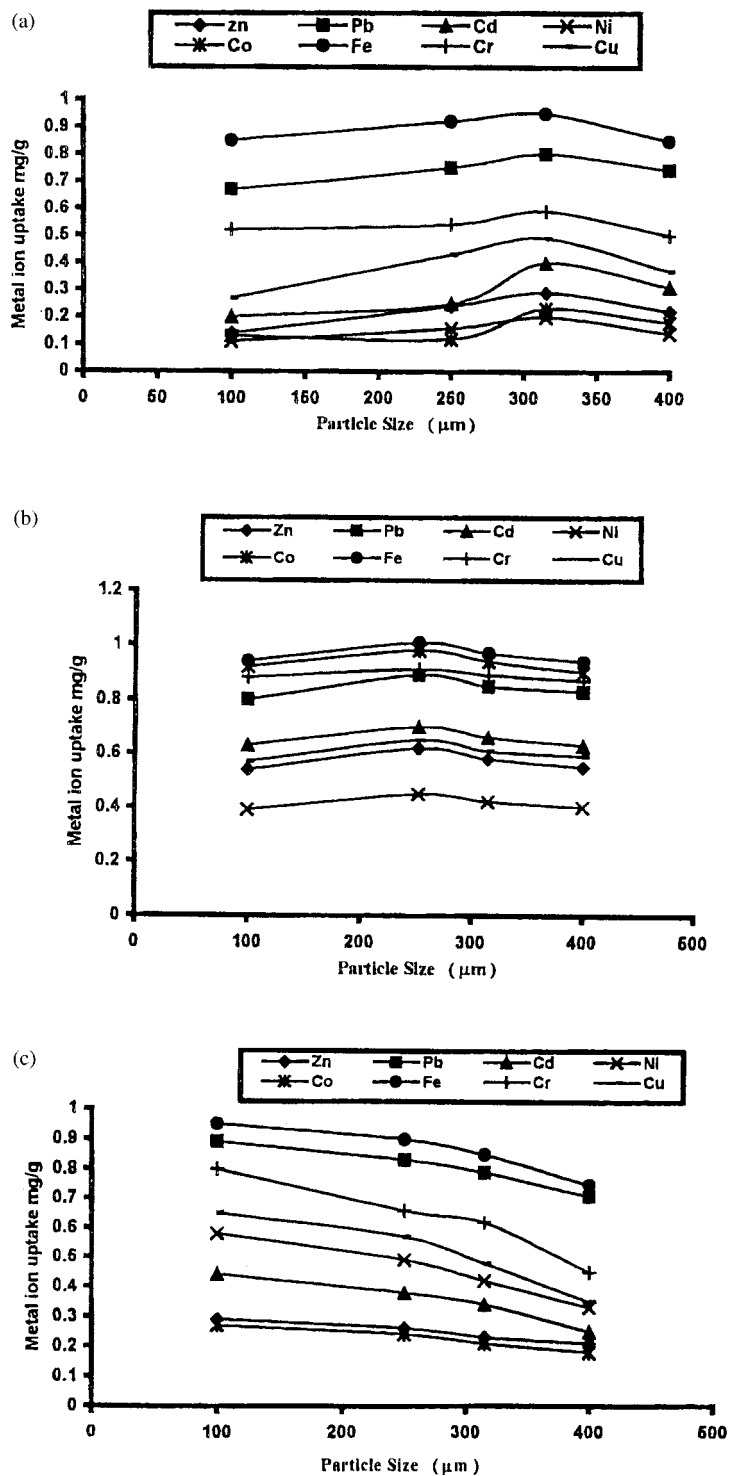


Figure 2 (a) Metal ion uptake (mg/g) by cation exchanger produced from phosphated rice straw of different particle size. (b) Metal ion uptake (mg/g) by cation exchanger produced from phosphated bagasse of different particle size. (c) Metal ion uptake (mg/g) by cation exchanger produced from phosphated cotton stalks of different particle size.

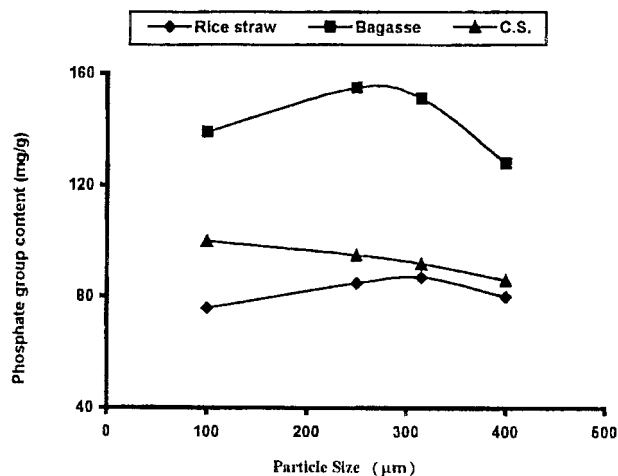


Figure 3 Effect of particle size of raw material on phosphate group content of prepared ion exchangers.

hemicellulose appears to be associated with both lignin and cellulose and may form an intermediate layer between lignin and cellulose.¹⁵ Moreover, in the plant, these materials have accessibility for adhesion through hydrogen bonding. However, lignin is thought to flow and surround the hemicellulose bonds, protecting them from water.¹⁶

Also, the extractive materials present in the raw material can physically block any adhesion form that surrounds lignin, cellulose, and hemicellulose.¹⁷ For this reason, the OH groups of the cellulose, lignin, and hemicellulose are not as free as in the case of the separated cellulose and lignin. In addition, these hydroxyl groups are attached to each other by hydrogen bonds. This is one reason for the fact that the reactivity of bagasse raw material toward phosphorylation is lower than that of separated cellulose and lignin. Moreover, the number of free hydroxyl groups is higher in the case of separated cellulose and lignin. This is because, during the separation of cellulose and lignin from bagasse by pulping and bleaching processes, the OH groups of cellulose that were attached to the lignin and hemicellulose become free. In addition, pulping and bleaching decrease the degree of polymerization and, consequently, increase the chain ends. Accordingly, the active sites toward phosphorylation in the separated cellulose increase. With respect to lignin separated after bagasse pulping, a depolymerization of the lignin matrix occurs that causes an increase in the phenolic OH group, providing the reason for the increase of the reactivity of the separated lignin toward phosphorylation.

The increase in the phosphate ester groups in the material enhances its ability toward ion exchange. This is clear from the histogram shown in Figure 4, which shows the results obtained for the efficiency of bagasse, cellulose, and lignin for the removal of different elements from an aqueous solution containing a mixture of $20 \mu\text{g mL}^{-1}$ of each element. From the histogram, it can be seen that, for all the elements, the efficiency of phosphated bagasse for elemental removal is lower than that of cellulose and lignin. This result is in good agreement with that obtained for the amount of the phosphate group incorporated into the different materials (Fig. 3). On the other hand, phosphated lignin and cellulose have nearly the same ion-exchange efficiency, although lignin has a low amount of phosphate ester groups. This may be due to the smaller particle size of lignin and the consequent higher surface contact area with the solution.

Effect of Pretreatment of Bagasse with Sodium Hydroxide on the Prepared Phosphated Ion Exchanger

According to the foregoing experimental results, it was found of interest to investigate the effect of the treatment of bagasse with different sodium hydroxide concentrations (0.5–5.0 %) before the phosphorylation process. This would cause partial degradation of the bonds between lignin and cellulose as well as hemicellulose and, hence, increase the number of free OH groups in the cellulose and lignin of the lignocellulose material. Accordingly, the rate of phosphorylation would increase. In addition, sodium hydroxide treatment causes partial dissolution of wax and resin extractive material, thus inducing an increase in the softness of lignin and cellulose as well as an increase in the porosity of the lignocellulose material. Figure 5 shows the relation between the dependence of the efficiency of the phosphated pretreated bagasse toward elemental removal

Table IV Phosphate Group Content of Phosphated Bagasse, Cellulose, and Lignin

Material	Phosphate Group Content (mg/g)
Bagasse	37.4
Cellulose	46.0
Lignin	43.0

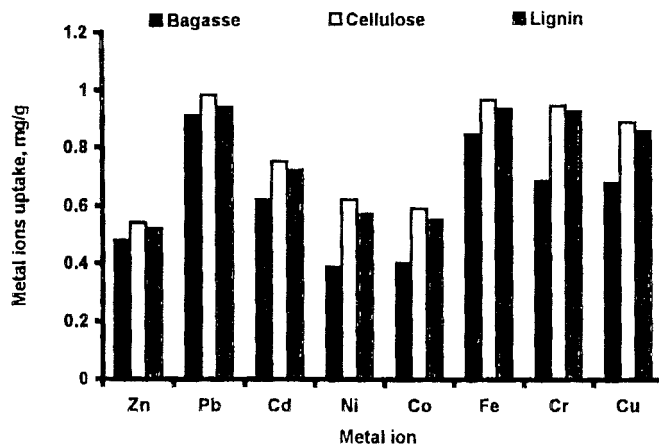


Figure 4 Histogram of metal ions absorbed by cation exchangers prepared from phosphated bagasse, lignin, and cellulose.

and the concentration of sodium hydroxide. From the figure, it is clear that the treatment of bagasse with sodium hydroxide before phosphorylation increases its ion-exchange efficiency.

Effect of Experimental Variable on the Phosphorylation Process

The phosphorylation process depends on a number of experimental variables, namely, the reaction time, reaction temperature, and concentration of phosphorus oxychloride. For the optimization of the phosphorylation process, the effect of each variable on the ion-exchange efficiency of the phosphated bagasse was studied while keeping the rest of the variables constant.

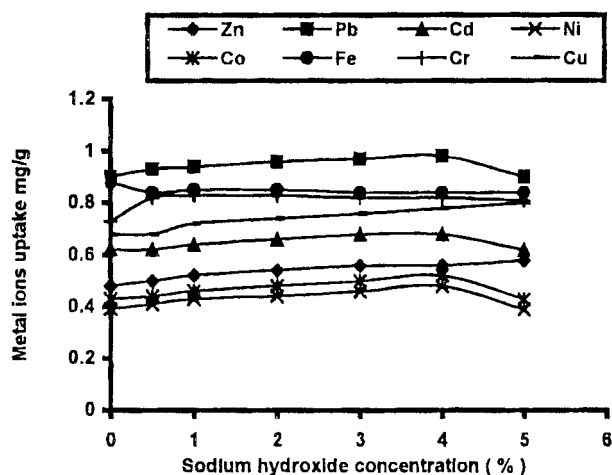


Figure 5 Effect of sodium hydroxide treatment on the efficiency of phosphated bagasse cation exchanger.

Effect of Phosphorus Oxychloride

In this experiment, the amount of phosphorus oxychloride added to the chemicals of the previously described phosphorylation reaction was varied between 3 and 15 mL. Meanwhile, the reaction time and reaction temperature were kept at 3 h and 115°C, respectively. The relation between the ion-exchange efficiency of the produced ion exchangers and the amount of added phosphorus oxychloride is shown in Figure 6. For all elements investigated, the relation shows a maximum at about 7 mL phosphorus oxychloride, above which the ion-exchange efficiency decreases. This decrease can be due to the possible dissolution of lignin and hemicellulose as well as

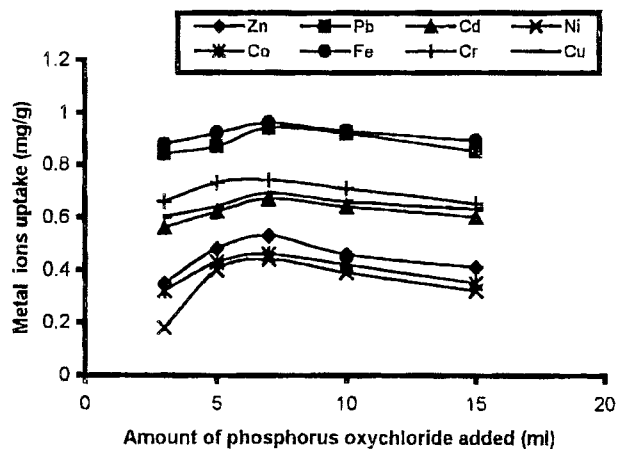


Figure 6 Effect of phosphorus oxychloride on metal ion uptake.

the degradation of cellulose and the consequent decrease in the incorporated phosphate groups.

Effect of Reaction Time

Figure 7 shows the effect of the reaction time on the ion-exchange efficiency of the phosphated bagasse. This series of experiments was carried out at a temperature of 115°C and using a ratio of phosphorus oxychloride to raw material of 1 mL/g. From the figure, it can be seen that increasing the reaction time from 0.5 to 3.0 h causes an increase in the ion-exchange efficiency for most of the elements investigated. This can be attributed to the fact that the increase of the reaction time increases the contact time of the chemicals and bagasse and, hence, increases the number of incorporated phosphate groups. The increase is more profound in case of Pb and Zn. From this experiment, a time of 3 h can be considered as the optimum reaction time for the phosphorylation process.

Effect of Temperature

Figure 8 shows the results obtained for the effect of the temperature of the phosphorylation reaction on the cation-exchange efficiency of the produced phosphated bagasse. From the results, it can be seen that the increase of the reaction temperature from 100 to 135°C has no significant effect on the metal uptake of the produced cation exchanger except in case of Cu and Fe. For these two elements, the relation shows a maximum at 115°C. This temperature was considered as optimum for the phosphorylation reaction.

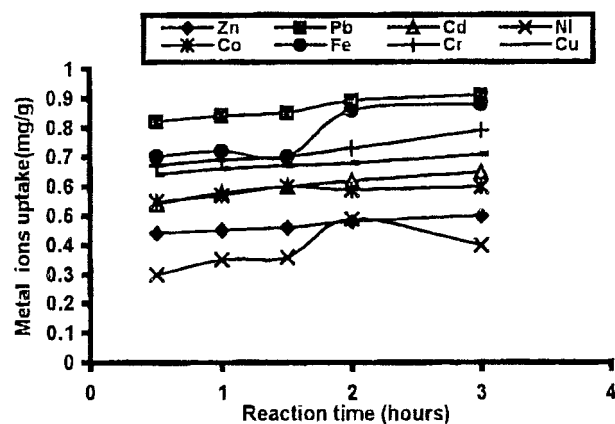


Figure 7 Effect of phosphorylation time (hours) on metal ion uptake.

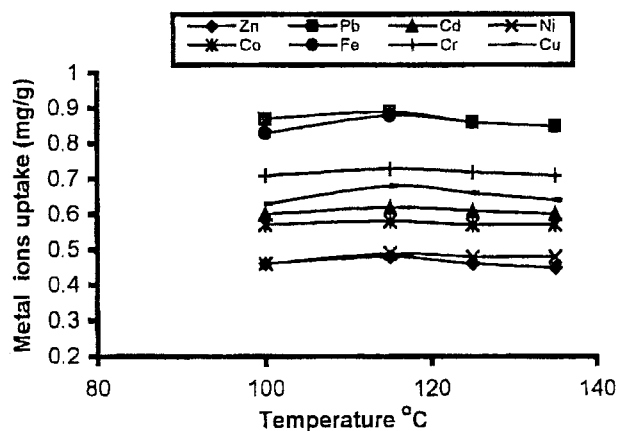


Figure 8 Effect of phosphorylation temperature on metal ion uptake.

CONCLUSIONS

From the results obtained in the present work, it can be seen that the phosphorylation of the investigated agricultural residues, namely, rice straw, cotton stalks, and bagasse, produces efficient cation exchangers. The efficiency of phosphorylation of these materials follows the sequence bagasse > cotton stalks > rice straw. Both the particle size and chemical constitution of the raw lignocellulosic material play important roles in the phosphorylation process. Also, the phosphorylation of both cellulose and lignin is higher than that of the original raw material. Besides, the phosphorylation reaction depends on the reaction time, the reaction temperature, and the amount of phosphorus oxychloride which could be optimized. The cation-exchange efficiency of the produced ion exchanger toward different elements follows the same above-mentioned sequence. However, Pb and Fe showed the highest binding affinity.

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