

Preparation and Some Applications of Phosphosulfonated Bagasse and Wood Pulp Cation Exchangers

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ABSTRACT: Cation exchangers are prepared by phosphorylation and by sulfonation as well as by incorporating both phosphate and sulfonate functional groups on bagasse and wood pulp. The optimal composition of the acid mixtures used for the preparation of these ion exchanger was determined. Possible applications of these ion exchangers in

columns and for some industrial uses were investigated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 97–104, 2003

Key words: lignocellulosic materials; cation exchangers; phosphorylated; phosphosulfonation

INTRODUCTION

Cellulosic, lignocellulosic, and industrial wastes represent cheap and environmentally safe sources for the preparation of ion exchangers that may be useful for the removal of colors and metal ions from solutions. To ensure good performance, these materials should be structurally stable under mildly acidic or basic aqueous conditions (pH: 2–12).¹ A number of cation exchangers were prepared from some low-value agricultural residues. Phosphate, sulfate, and carboxyl groups were incorporated onto the complex polysaccharide matrix of oat hulls,² bagasse, and rice straw.^{3,4} The magnitude of the incorporated functional groups was taken as a measure of the reactivity of the agricultural residue studied.⁵ Data for the effect of reaction time, cation exchanger concentration, and pH showed that the reaction could be controlled to maximize crosslinking. All products showed high binding.

The produced ion exchangers can be used in columns. The quantity of a sample that can be effectively applied to a given column of a cellulosic ion exchanger depends on the relative concentration and the affinity of the component (or components) of interest under the conditions employed and on the objectives of the particular experiment.

In the present work ion exchangers were prepared by phosphorylation and sulfonation of bagasse and wood pulp. The simultaneous incorporation of both phosphate and sulfonate groups on one and the same material was also investigated. A comparison was

made of the efficiencies of the ion exchangers produced in taking up metal ions. Also, the effect of the metal ion solution's pH on exchanger efficiency was studied. The uptake efficiency of the prepared ion exchangers when applied in columns and their application in the purification of brines and some industrial wastewaters were investigated.

EXPERIMENTAL

Materials

Sugarcane bagasse was provided by Sugar and Integrating Industries Company, Edfo, Egypt. Samples were ground to $\leq 400 \mu\text{m}$. Bleached wood pulp is a waste material remaining from the manufacture of mosquito mats at El Nasr Company for Intermediate Chemicals, Egypt. It was ground to $\leq 400 \mu\text{m}$. Methylene chloride, pyridin, phosphorus oxychloride, and chlorosulfonic acid were purchased from Merck (Darmstadt, Germany) and were used without further purification. Stock standard solutions of $1000 \mu\text{g/mL}$ of the elements Al, Cd, Co, Cr, Cu, Fe, Mn, Pb, P, and S were obtained from Merck (Darmstadt, Germany). Bagasse and wood pulp were oven-dried at 80°C for 4 h before use. Pyridin was dried (moisture free) by KOH pellets.

Methods

Chemical modification of raw materials

Phosphorylation: 5 g of dry raw material was suspended in 50 mL of dry pyridin in a round-bottomed flask. To the cooled and continuously stirred suspension, 5 mL of phosphorus oxychloride in 25 mL of

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methylene chloride was added dropwise over a period of 5 min. The contents were heated under reflux for 2 h at 115°C with continuous stirring. The flask was cooled, and its contents were then poured in ice water; filtered on a sintered glass funnel G2; and successively washed with deionized water, 0.1N HCl, deionized water until neutrality, and methyl alcohol; and then finally air-dried.

Sulfonation: The same procedure as that for phosphorylation was applied, except 5 mL of chlorosulfonic acid in 25 mL methylene chloride was used instead of phosphorus oxychloride.

Phosphosulfonation: For the simultaneous incorporation of phosphate and sulfonate groups on one and the same raw material, the following procedure was followed: Five grams of dry raw material was suspended in 50 mL of dry, cooled pyridin in a round-bottomed flask. A series of solutions of phosphorus oxychloride in methylene chloride and chlorosulfonic acid in methylene chloride were prepared. The series started with 100% phosphorus oxychloride in 25 mL of methylene chloride and ended with 100% sulfonic acid in 25 mL of methylene chloride. Thus, for each member of the series, the total volume of the two acids was 5 mL, whereas the volumes of the chlorosulfonic acid were 0%, 15%, 25%, 33%, 50%, 66%, and 100% and the volume of the methylene chloride was divided between the two acids according to their ratio. Each member of this series was used to prepare one batch of ion exchanger. To the cooled and continuously stirred suspension of raw material in pyridin, the phosphorus oxychloride in methylene chloride was added, followed by the chlorosulfonic acid in methylene chloride, and the mixture was left in ice water for 5 min to cool. The flask containing the mixture was heated under reflux for 2 h at 115°C with continuous stirring. The flask was left to cool, and its contents were poured in ice water; filtered on a sintered glass funnel G2; successively washed with deionized water, 0.1N HCl, deionized water until neutrality, and methyl alcohol; and finally air-dried.

Inductively coupled plasma atomic emission spectrometer

For the determination of the concentrations of the different elements, a sequential inductively coupled plasma atomic emission spectrometer (ICP-AES), Jibin Yvon 38S (France), was used. The monochromator of the spectrometer had a focal length of 1 m and was equipped with a holographic grating of 2400 grooves/mm.

Determination of phosphorus and/or sulfur in prepared ion exchangers

To determine the phosphorus and/or sulfur in the exchangers, the following procedure was followed:

TABLE I
Phosphorus and Sulfur Contents ($\mu\text{mol/g}$) in Phosphosulfonated Bagasse Ion Exchangers Prepared by Different Acid Mixtures

Chlorosulfonic acid (%)	Phosphorus ($\mu\text{mole/g}$)	Sulfur ($\mu\text{mol/g}$)
0	838.7	—
33	545.2	600.0
50	490.3	750.0
66	322.9	1003.1
100	—	1134.4

Brought together in a glass beaker were 0.2 g of the sample and 10 mL of concentrated HNO_3 . The mixture was heated on a hot plate and evaporated to near dryness. Another 5 mL of HNO_3 was added, and the mixture again evaporated until the volume of the acid was about 2 mL. Deionized water was then added to the residue, which readily dissolved to a clear solution. The solution was transferred into a 100-mL measuring flask and the volume made up with deionized water. Phosphorus and/or sulfur was determined in the solution using ICP-AES, and the data were used to calculate their contents in the ion exchanger materials.

Determination of metal ion uptake efficiency

In these experiments 0.2 g of the ion exchanger material was stirred for 30 min with 25 mL of an aqueous solution containing the different elements at a concentration of 20 $\mu\text{g/mL}$. The suspension was then filtered on filter paper (Wattman 41), and the elements were determined in the filtrate using ICP-AES. The elements investigated were Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn.

RESULTS AND DISCUSSION

Effect of functional groups on metal-uptake efficiency

Bagasse

Table I gives the phosphorus and/or sulfur contents of phosphorylated, sulfonated, and phosphosulfonated bagasse. The metal ion uptake efficiencies of the prepared ion exchangers are shown in Figure 1, from which it can be seen that, with the exception of Cr^{3+} , the exchange efficiency of the phosphorylated bagasse was higher than that of the sulfonated bagasse, although the phosphate groups were lower than the sulfonate groups. This can be explained by the phosphorus oxychloride being able to react at a single site of the polymer and the product being able to remain as a dianion, whereas the chlorosulfonic acid reacted with one site of the biopolymer to form one site² as follows:

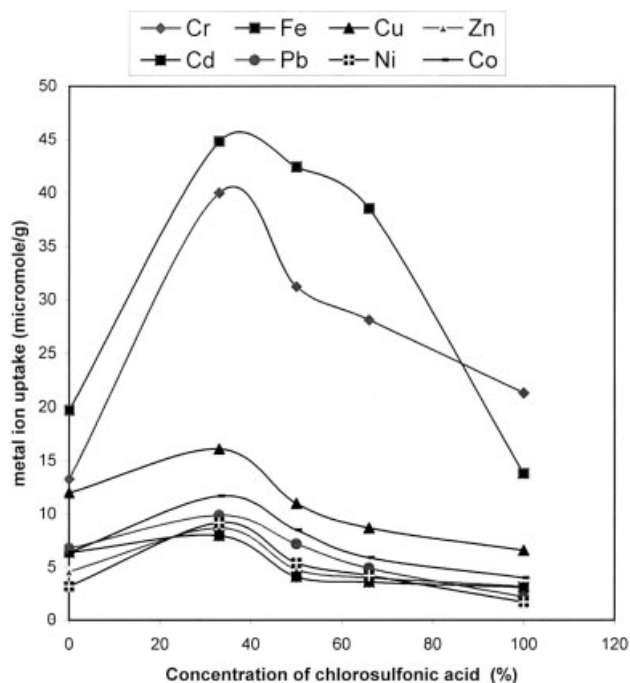


Figure 1 Effect of chlorosulfonic acid in the acid mixture on metal ion uptake of the phosphosulfonated bagasse ion exchanger.

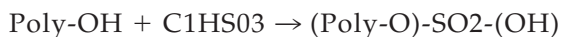
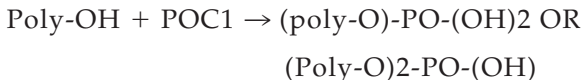


Figure 1 also shows the effect of the percentage of chlorosulfonic acid in the acid mixture on the efficiency of the produced ion exchanger in metal ion uptake. From Figure 1 it is clear that for all metal ions investigated, ion uptake efficiency was maximum when bagasse had reacted with an acid mixture containing 33% chlorosulfonic acid. From Table I it can be seen that the phosphorus and sulfur contents in this ion exchanger were 545.2 and 600 $\mu\text{mol/g}$, respectively. Increasing the concentration of chlorosulfonic acid in the acid mixture greater than 33% affected the decrease in the exchange efficiency of the produced ion exchanger. However, its efficiency was still higher relative to those prepared by phosphorylation or sulfonation. The increase in the percentage of sulfonic acid in the acid mixture also was accompanied by an increase in the sulfur content in the produced ion exchanger, as seen in Table I.

Wood pulp

The above-mentioned investigations were carried out with cellulose. The cellulose material used was bleached wood pulp, a waste product remaining from the production of mosquito mats at El Nasr Company

TABLE II
Phosphorus and Sulfur Contents in Phosphosulfonated Wood Pulp Ion Exchangers Prepared by Different Acid Mixtures

Chlorosulfonic acid (%)	Phosphorus $\mu\text{mol/g}$	Sulfur $\mu\text{mol/g}$
0	1067.7	—
15	712.9	562.5
33	635.5	718.8
50	532.3	909.4
100	—	1110.5

for Intermediate Chemicals (NCIC), Cairo, Egypt. The results are shown in Table II for the phosphorus and sulfur contents in the produced ion exchangers and in Figure 2 for their metal ion uptake efficiencies. From Table II it is clear that the sulfur content in the phosphosulfonated cellulose ion exchanger increased by increasing the percentage of chlorosulfonic acid in the acid mixture used for its preparation. Figure 2 shows that maximum efficiency of metal ion uptake was achieved with an acid mixture containing 15% chlorosulfonic acid. On the other hand, a comparison of Tables I and II shows that the sulfur content of the sulfonated cellulose was lower than that of the phosphorylated bagasse, whereas the total functional groups in the cellulose ion exchanger were always higher than those in the bagasse ion exchanger. This is because of the relatively higher reactivity of the bleached wood pulp as a result of the absence of lignin. The latter, when present, formed a bond with cellulose and hemicellulose, blocking the hydroxyl groups of the cellulose, lignin, and hemicellulose and consequently decreasing the number of free OH

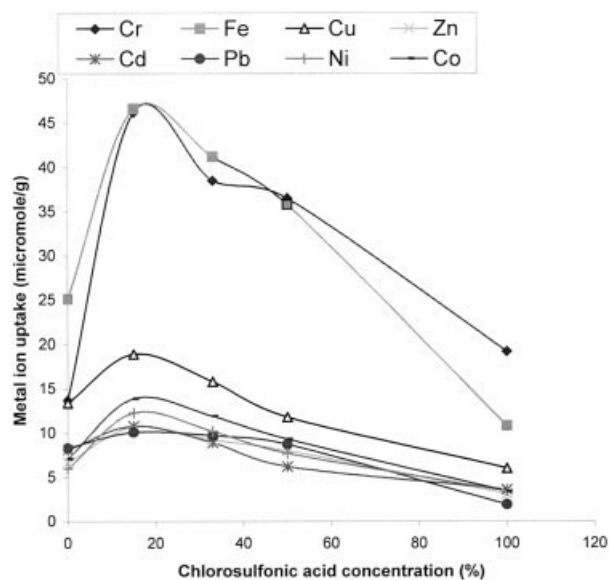


Figure 2 Effect of chlorosulfonic acid concentration in the acid mixture on the efficiency of phosphosulfonated wood pulp in metal ion uptake.

TABLE III
Metal Ion Uptake Efficiency of Phosphorylated, Sulfonated, and Phosphosulfonated Bagasse and Wood Pulp Ion Exchangers

Ion	Incorporated group(s)	Efficiency ($\mu\text{mol/g}$)	
		Bagasse	Wood pulp
Cr^{3+}	P	13.3	13.7
	S	21.3	19.2
	PS	40.0	46.2
Fe^{3+}	P	19.7	25.1
	S	13.8	10.8
	PS	44.8	46.8
Cu^{2+}	P	12.0	13.4
	S	6.6	6.0
	PS	16.1	18.9
Zn^{2+}	P	4.0	6.7
	S	3.2	3.1
	PS	8.7	10.7
Cd^{2+}	P	6.4	8.1
	S	3.1	3.6
	PS	8.0	10.8
Pb^{2+}	P	6.8	8.3
	S	2.2	1.9
	PS	9.9	10.1
Ni^{2+}	P	3.2	6.0
	S	1.7	3.4
	PS	9.2	12.3
Co^{2+}	P	6.4	7.1
	S	4.0	3.4
	PS	11.7	13.9

groups. In Table III is a comparison of the efficiencies of phosphorylated, sulfonated, and phosphosulfonated bagasse and wood pulp. The efficiency values of phosphosulfonated ion exchangers given in Table III are the values obtained under optimal preparation conditions for each material that showed maximum efficiency for the individual material. Comparing the results obtained with bleached wood pulp with those obtained with bagasse, it can be seen that ion exchange efficiency of phosphorylated cellulose was higher than that of phosphorylated bagasse. This can be attributed to the increased number of phosphate groups incorporated into the cellulose compared to those incorporated into the bagasse, as indicated in Table II. On the other hand, for most ions investigated, sulfonated cellulose was less efficient in taking up metal ions than was sulfonated bagasse. This was also clear from the lower substitution of the sulfate groups incorporated into the cellulose relative to those incorporated into the bagasse. This can be explained by the mechanisms of reactions that can take place between chlorosulfonic acid and wood pulp. Part of the chlorosulfonic acid reacts with the OH of the cellulose, forming sulfate ester, whereas the other part causes a partial degradation of the cellulose, with the consequence of lower reactivity of the produced sulfated cellulose. Comparing Figures 1 and 2 and given the results shown in Table III, it can be seen that, in

general, metal ion uptake efficiencies of the prepared cellulose ion exchangers were higher than those of bagasse.

Effect of pH on ion exchange efficiency

Normally, metal ion absorbents exhibit a drastic decrease in metal ion uptake in low pH conditions because of the competition with hydronium ions.⁶ On the other hand, an increase in pH 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 the metal ions in the form of hydroxide starts to take place and will be adsorbed on the surface of the ion exchanger. The effect of the metal ion solution's pH when in the 1–7 range on the ion exchange efficiencies of the prepared phosphorylated, sulfonated, and phosphosulfonated bagasse was investigated. The obtained results are shown in Figure 3, from which it

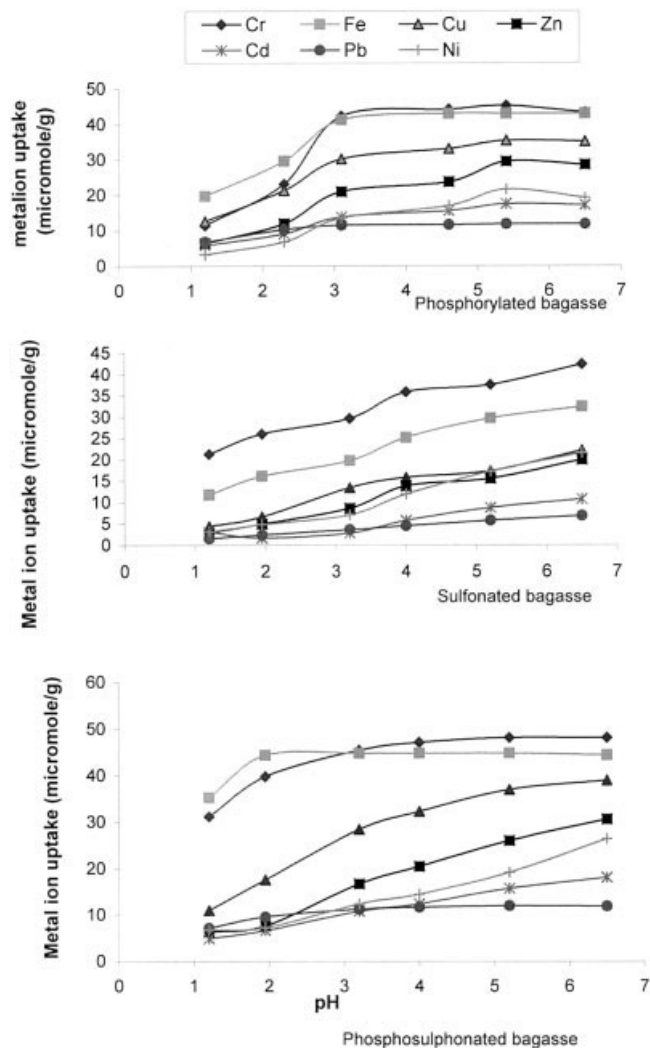


Figure 3 Effect of pH of metal ion solution on the efficiency of the bagasse ion exchanger in metal ion uptake.

is clear that the metal ion uptake of the phosphorylated bagasse was significantly increased for all metal ions by increasing the pH to 3. At higher pH values a slight increase in efficiency was observed with Pb, Fe, Cr, and Cu, whereas for the other ions no further increase in uptake efficiency was detected. Similar results were obtained with phosphosulfonated bagasse but with higher uptake values. On the other hand, for sulfonated bagasse, a gradual increase in the uptake efficiency with an increase in pH, however, with a lower rate, took place up to pH 7. The obtained results show that the bagasse cation exchanger containing the two functional groups, namely phosphate and sulfate, had a higher affinity for metal ion uptake and reached a maximum value at pH 3. The same finding was obtained with phosphosulfonated wood pulp prepared with an acid mixture containing 15% chlorosulfonic acid.

Application of the produced ion-exchangers in column

Phosphosulfonated bagasse ion exchanger

For this experiment two glass columns each having an internal diameter of 10 mm were prepared. Each column was packed with 1 g of phosphosulfonated bagasse. The two columns were thoroughly washed with deionized water. One of the columns was activated with 100 mL of 1N HCl and then thoroughly washed with deionized water until neutrality. Through the two columns 200 mL of a solution containing a mixture of metal ions each at a concentration of 20 $\mu\text{g}/\text{mL}$ was passed at a flow rate of 10 mL/min. The concentrations of the metal ions passing the columns were determined. The results of the metal ion uptake are shown in Figure 4, from which it can be seen that the activation of the phosphosulfonated bagasse ion exchanger increased its exchange efficiency. Thorough washing of the bagasse ion exchanger removed any contamination that may have been produced during its preparation. It also brought the ion exchange material into hydrated conditions that provided adequate accessibility to ionized sites of the molecules for the metal ions to be absorbed. The wet adsorbent ion exchanger should also be washed once more with several volumes of 1N HCl and rinsed free from acid before passing the metal ion solution through the column. Moreover, washing helps and permits coarse particles of resin to orient themselves as they come to rest on the rising surface of the packed material.

From the obtained results it is clear that for both inactivated and activated columns, the highest uptake was achieved for the Fe and Cr ions, moderate uptake was observed for Pb and Cu, and uptake of much smaller amounts was observed for the Ni, Co, Cd, and Zn ions. Accordingly, the tendency of a phosphory-

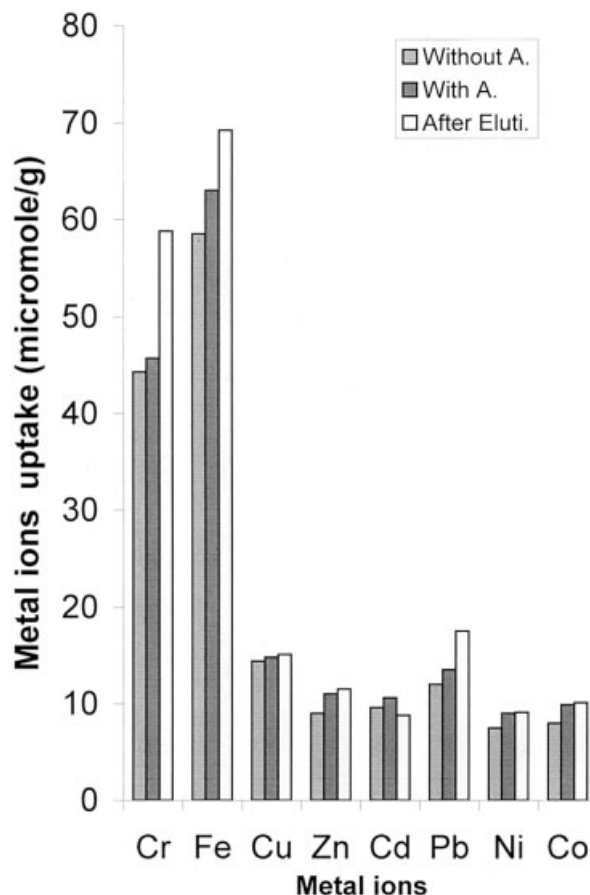


Figure 4 Comparison between the ion exchange efficiencies of inactivated, activated, and eluted phosphosulfonated bagasse columns.

lated wood pulp ion exchange column to take up metal ions can be arranged in descending order as: Fe > Cr > Cu > Pb > Zn > Co > Cd > Ni. This can be attributed to the steric and electronic effects of the metal ions. The binding ability of the metal ions to the ion exchanger was also affected by the semihard acid.⁷

Elution of phosphosulfonated bagasse column

Two columns packed with activated phosphosulfonated bagasse were prepared, and 200 mL of the metal ion solution was passed through each. The two columns were eluted with HCl, the first in three steps—100 mL of 1N HCl followed by 50 mL of 2N HCl and finally 50 mL of 3N HCl—and the second with 100 mL of 3N HCl. The concentrations of the eluted metals were determined in solutions that passed through the columns, from which the amounts of the elements were calculated and compared with those picked up by the columns. The obtained results are given in Table IV, from which it can be seen that all metal ions picked up by the column except Fe³⁺ were nearly eluted from the ion exchanger using 1N HCl. From the 58.5 $\mu\text{mol}/\text{g}$ Fe that was picked up by the column,

TABLE IV
Results of Loading and Eluting Columns Packed with Phosphosulfonated Bagasse ($\mu\text{mol/g}$)

Process	Cr	Fe	Cu	Zn	Cd	Pb	Ni	Co
Total uptake ($\mu\text{mol/g}$)—unactivated	44.3	58.5	14.4	9.04	9.6	12.0	7.5	8.0
Total uptake ($\mu\text{mol/g}$)—activated	45.7	63.0	14.8	11.0	10.6	13.6	9.02	9.9
ELUTION								
1N 100 mL	44.9	30.8	10.90	7.00	5.30	11.30	6.3	4.74
2N 50 mL	0.04	6.8	0.16	0.14	0.16	0.08	0.39	0.03
3N 50 mL	0.04	17.9	0.13	0.17	0.14	0.05	0.34	0.03
Total	44.98	55.5	11.19	7.31	5.60	11.43	7.03	4.80
Uptake ($\mu\text{mol/g}$) of reused ion exchanger	58.8	69.2	15.1	11.5	8.8	17.5	8.44	9.6
Elution of activated ion exchanger with 100 mL 3N HCl	48.5	53.8	8.2	5.2	3.3	13.3	4.8	2.3

only $30.4 \mu\text{mol/g}$ was eluted by 1N HCl, $6.8 \mu\text{mol/g}$ by 2N HCl, and $17.9 \mu\text{mol/g}$ by 3N HCl. So, from all elements investigated, Fe was the only element that required 3N HCl for its elution. From the results obtained for the elution of the second column, it can be seen that an almost complete elution of the column can be achieved in one step by using 3N HCl.

Reuse of the eluted column

After elution of the column containing the phosphosulfonated bagasse, it was further washed with 100 mL of 3N HCl, then thoroughly rinsed with deionized water until neutrality, and then another 200 mL of the metal ion solution was passed through the column. The solution passing the column was analyzed, and the amounts of the elements picked up were determined. For the sake of comparison, these results are shown in Figure 4, from which it can be seen that for most of the metal ions investigated, the reused eluted ion exchanger was more efficient in taking up metal ions than were the fresh ones. This may be attributed to the increased removal of contamination as well as the increased porosity of the ion exchanger.

The column was then eluted using 100 mL of 3N HCl. The solutions passing the column in the elution process were analyzed, and the amounts of elements eluted were determined. The obtained results are given in Table IV, from which it can be seen that the amounts of eluted elements also were higher than those eluted from the freshly used columns.

Phosphosulfonated wood pulp

From the previously mentioned results it was found that, in general, the metal ion uptake efficiencies of the prepared wood pulp ion exchangers are higher than those of bagasse. Also, maximum efficiency in metal ion uptake is achieved by reacting the wood pulp with a phosphorus oxychloride/chlorosulfonic acid mixture containing 15% chlorosulfonic acid. For this rea-

son phosphosulfonated wood pulp was applied in column and the metal ion uptake was determined. The obtained results are shown in Figure 5 together with those obtained with phosphosulfonated bagasse. As can be seen from Figure 5, the affinity of phosphosulfonated wood pulp for absorbing metal ions was higher than that of phosphosulfonated bagasse. This could be because of the lower crystallinity and higher porosity of wood pulp compared to bagasse. Moreover, the bleached wood pulp contained more free OH

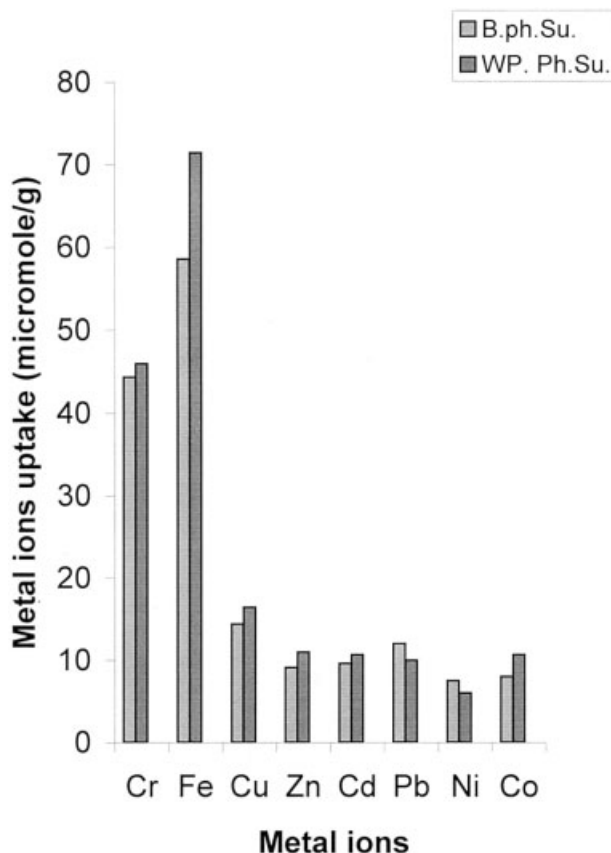


Figure 5 Metal ion uptake by phosphosulfonated bagasse and phosphosulfonated wood pulp ion exchangers.

TABLE V
Concentration ($\mu\text{g/mL}$) of Impurity Elements in Brine Solutions Passing Different Ion-Exchange Columns

Ion-exchanger	Mg		Ca		Sr		Ba	
	1 g	2 g	1 g	2 g	1 g	2 g	1 g	2 g
Phosphorylated wood pulp	77	53	150	102	401	202	15.7	12.2
Phosphosulfonated wood pulp	84	56	95	43	503	350	16.4	14.3
Activated phosphorylated w.p.	60	42	120	83	320	190	14.0	10.2
Phosphosulfonated bagasse	600	500	353	325	950	840	20.0	19.1
Phosphorylated bagasse	560	459	NM	NM	NM	NM	NM	NM

NM: not measurable

groups that could easily react with chemicals, with the consequence of the formation of more functional groups.

Some applications of the prepared ion exchangers

Purification of brine

In the chlor-alkali membrane electrolyzer cells the impurity of the feed brine (NaCl concentration of 300 g/L) is of the utmost importance for the performance efficiency as well as for the lifetime of the membrane.⁸ The most harmful impurities are the alkaline earth elements: Ca, Mg, Sr, and Ba. In the chlor-alkali industry purification of the brine usually takes place in two main steps. The first, or primary, treatment step comprises a chemical treatment process in which impurities are precipitated, followed by filtration. In the secondary treatment step, the use of ion-exchange resins have proven to be the most effective way of producing ultrapure brine that is suitable for introduction into the membrane cell.

For this reason it was of interest to investigate the application possibilities of the prepared ion exchangers for purification of the brine used in the chlor-alkali plant of the El Nasr Company for Intermediate Chemicals, Cairo, Egypt. For this purpose, different columns, each with an internal diameter of 10 mm, were prepared. The columns were packed with, respectively, phosphorylated wood pulp, phosphosulfonated wood pulp, activated phosphosulfonated wood pulp, phosphosulfonated bagasse, and phosphorylated bagasse. For each kind of ion exchanger, two columns were prepared—one packed with 1 g and the second with 2 g of the respective ion exchanger. The brine samples used in this work represent pure brine produced from the primary treatment step. The concentrations of Ca, Mg, Sr, and Ba in this brine were 732, 369, 1668, and 20.6 g/mL, respectively. Through each column 100 mL of brine was passed, and the metal ion concentrations in the solutions passing each

column were determined. The obtained results are tabulated in Table V. It was observed that the passage of high concentrated brine through both phosphosulfonated and phosphorylated bagasse columns deteriorated the ion exchangers, which may be a result of the dissolution of the lignin and hemicellulose of the bagasse ion exchanger by the concentrated brine solution. More deterioration occurred for the phosphorylated bagasse. The solution passing the columns turned yellow in color. On the other hand, the wood pulp ion exchanger showed a remarkable affinity for the removal of the impurity metals from the saturated brine that passed the columns. A glance at Table V shows that the activated phosphorylated wood pulp column had the highest efficiency in removing impurity elements from the brine. The increase in the weight of the ion exchanger increased the amount of elements removed. Accordingly, activated phosphorylated wood pulp can be recommended for this purpose.

Removal of chromium from tannery effluents

Tannery wastewater contains unusually high concentrations of chromium, which is usually drained into the environment. Even if the chromium content of this wastewater is mostly trivalent, its presence in the environment may cause its transformation to the highly toxic hexavalent chromium.

An investigation was done of the application of the prepared phosphosulfonated bagasse and phosphosulfonated wood pulp for the removal of chromium from the wastewater of a local tannery containing a Cr^{3+} ion concentration of 370 $\mu\text{g/mL}$. The investigation was first carried out by steeping 0.2 g of each ion exchanger in 25 mL of the waste solution for 30 min. The obtained results revealed that the bagasse and wood pulp ion exchangers picked up 171.2 and 232.7 $\mu\text{mol/g}$, respectively. In a further experiment, four columns were prepared for each ion exchanger, and

TABLE VI
Chromium Concentration ($\mu\text{g/mL}$) in Solutions Passing
Different Ion-Exchange Columns

Ion exchanger	Chromium concentration ($\mu\text{g/ml}$)			
	10 mL/min	5 mL/min	3.33 mL/min	2.5 mL/min
Phosphosulfonated wood pulp	220	170	120	105
Phosphosulfonated bagasse	260	230	172	150

each was packed with 1 g of the respective ion exchanger. Through each column 100 mL of the waste solution was passed. However, for each ion exchanger the flow rate of the solution was varied from 10 to 2.5 mL/min, and the chromium concentrations in the solutions passing the columns were determined. The obtained results are given in Table VI. From the results it can again be seen that the efficiency of the phosphosulfonated wood pulp in Cr^{3+} ion uptake was higher than that of the phosphosulfonated bagasse. Also, for both ion exchangers the uptake efficiency increased by decreasing the flow rate through the column. This can be attributed to the increase of the contact time of the metal ion solution and the resin. A flow rate of 3.33 mL/min can be considered optimal for these column conditions. At this flow rate the Cr^{3+} uptake was 480 $\mu\text{mol/g}$ for phosphosulfonated wood pulp and 327 $\mu\text{mol/g}$ for phosphosulfonated bagasse.

In a further experiment two columns were prepared; the first was packed with 1 g of phosphosulfonated bagasse and the second with 1 g of phosphosulfonated wood pulp. The two columns were each activated with 100 mL of 1N HCl, then rinsed thoroughly with deionized water before passing 100 mL of the tannery wastewater solution through each at a flow rate of 3.33 mL/min. The amount of Cr^{3+} picked up was found to be 567 $\mu\text{mol/g}$ for the phosphosul-

fonated wood pulp and 480 $\mu\text{mol/g}$ for the phosphosulfonated bagasse, which are higher values than those obtained without activation of the columns.

CONCLUSION

From the results obtained in the present work, it can be concluded that ion exchangers produced by reacting cellulosic and lignocellulosic materials with mixtures of chlorosulfonic acid and phosphorus oxychloride have higher ion-exchange efficiency compared to those prepared using only one of these acids. The optimal composition of the acid mixture depends on the kind of raw material. Phosphosulfonated bagasse is best prepared using an acid mixture containing 33% chlorosulfonic acid, whereas wood pulp requires a mixture containing only 15% chlorosulfonic acid. The results revealed that phosphosulfonated wood pulp had a higher efficiency for metal ion uptake than did phosphosulfonated bagasse. Also, the activation of the ion exchanger with HCl beforehand had the effect of increasing its efficiency. Phosphosulfonated wood pulp proved its efficiency in the purification of brine and removal of chromium from tannery effluents; meanwhile, brine deteriorated the phosphosulfonated bagasse.

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