Differential Adsorption of Heavy Metal Ions by Cotton Stalk Cation-Exchangers Containing Multiple Functional Groups

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ABSTRACT: Esterification of cotton stalks with chlorosulfonic acid, phosphorus oxychloride, and their mixture was carried out with the aim to prepare cation exchangers for the removal of heavy metal ions from industrial waste water. Elemental analysis, Fourier transform infrared (FTIR) analysis, and sodium ions binding capacity were used to prove the occurrence of the esterification. The efficiency of the prepared cation exchangers to remove some heavy metal ions (strontium, arsenic, copper, and nickel) at different metal ion concentration, pH, contact time, and temperature was studied. The results showed that cotton stalks that contain both phosphate and sulfonate groups (phosphosulfonated cotton stalks) showed higher adsorption of the different heavy metal ions than cotton stalks containing sulfonate or phosphate on a separate basis. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4124–4132, 2006

Key words: cotton stalks; sulfonation; phosphosulfonation; phosphorylation; cation-exchangers

INTRODUCTION

During harvesting and processing of some industrial crops, such as cotton stalks, large amount of low-value, residual materials are produced. Until now, cotton stalks have not been effectively utilized in value-added products in spite of the large annual amounts produced; collection and storage of cotton stalks limit converting of these residues as raw material into useful products. Cotton stalks, as wood and agricultural residues, consist of cellulose, lignin, and hemicellulose polymers. These polymers have a weak ability of adsorbing heavy metal ions.[1] Chemical modification is necessary to increase their metal ion removal efficiency. Chemical modification of different agricultural residues such as wheat straw, bagasse, cotton stalks, and saw dust have been studied to prepare cation exchangers.[2–8]

The ongoing research in our laboratories currently focus on utilizing cotton stalks and other under-utilized agricultural residues for preparing ion exchangers for removing industrial waste water pollutants. In a previous paper, cotton stalk constituents, i.e., cellulose, lignin, and unbleached chemical pulp, were isolated from the raw cotton stalks and esterified using phosphorus oxychloride to determine the main reactive component responsible for ion exchange, and the resultant phosphorylated materials were briefly examined to remove Ni, Cu, Hg, and Pb metal ions. Lignin was found to be the most reactive constituent.[4]

In the current work, utilization of the cotton stalks in preparing cation exchangers containing mixture of anionic functional groups (sulfonate and/or phosphate) to increase the selectivity of the prepared cation exchangers was studied. Also, the effects of the different variables (i.e., pH, metal ions concentration, contact time, and temperature) on the adsorption of As, Sr, Cu, and Ni metal ions from their mixture were studied.

EXPERIMENTAL

Materials and reagents

The cotton stalks were ground to pass 1.5-mm screen. It had the following chemical composition: cellulose 43.1%, hemicelluloses 26.9%, lignin 27.3%, ash 1.3%, and ethanol-benzene extractives 5.6%. The chemical composition of cotton stalks was determined according to the standard methods.[9]

Analytical grade phosphorous oxychloride, chlorosulfonic acid, pyridine, and methylene chloride metals chlorides were used.

Sulfonation, phosphorylation, and phophosulfonation of cotton stalks

For the preparation of phosphorylated cotton stalks, the following method was used.[10] Five grams of oven-

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dry material were suspended in 40 mL of pyridine and cooled to 8°C. Twenty milliliters of dichloromethane containing 5 mL of phosphorus oxychloride ($POCl_3$) 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 0.1*N* HCl then with distilled water till neutrality and then air-dried. For sulfonation, the earlier mentioned procedure was followed but chlorosulfonic acid ($ClHSO_3$) was used instead of phosphorus oxychloride. For phosphosulfonation, 5 mL of a mixture containing phosphorus oxychloride and chlorosulfonic acid was used; the molar ratios of phosphorus oxychloride to chlorosulfonic acid were 3 : 1, 1 : 1, or 1 : 3.

Determination of phosphorous and sulfur

0.2 g of phosphorylated, sulfonated, or phosphosulfonated derivatives were digested in 10 mL of concentrated nitric acid. After digestion, the solution was diluted to 100 mL of de-ionized water in a measuring flask. Phosphorous and sulfur were determined using an Induced Coupled Plasma spectrophotometer ICP-AES Jobin Yvon J4 185 spectrometer. Two samples were measured and the results averaged.

Fourier transform infra red (FTIR) analysis

Infrared spectra of phosphorylated, sulfonated and phosphosulfonated derivatives were obtained by using JASCO FTIR 800 E spectrometer. The samples were measured using KBr disc technique.

Sodium binding capacity

Sodium ions binding capacity of the phosphorylated, sulfonated, and phosphosulfonated were determined as a measure to the extent of the phosphorylation and sulfonation as previously reported.[4]

Adsorption of heavy metals ions

0.2 g of the phosphorylated, sulfonated, and phosphosulfonated ion-exchangers were stirred individually with 25 mL of the aqueous solution of different metal ion mixtures (arsenic, strontium, copper, and nickel) at different concentrations (20, 40, 100, and 200 ppm), temperature (25, 45, and 60°C), pH (1.5, 3.5, 5.5, and 6.5), as well as different contact times (15, 45, and 60 min). The suspension was filtered and the remaining metals ions were determined in the filtrate using ICP-AES Jobin Yvon J4 l85 spectrometer.

RESULTS AND DISCUSSION

Esterification of cotton stalks

Cotton stalks were esterified, after their grinding, with $ClHSO_3$, $POCl_3$, and mixtures of them. Phosphorus oxychloride can react at a single site and the product can remain as a dianion, or it can react with two sites on cotton stalk constituents, crosslink them, and result in only a monoanion. Slow incremental additions of reagents should lead to the formation of monoanion, while addition of the whole amount in a single addition leads to dianion formation[11,12]; chlorosulfonic acid can react at a single site to produce sulfate monoester.

TABLE I
Phosphorus and Sulfur Content of Esterified Cotton Stalks

% of $POCl_3$ and $ClHSO_3$ added	Phosphorus content (mg/g)	Sulfur content (mg/g)
100% $POCl_3$	18.12 (0.517)	–
75% $POCl_3$ and 25% $ClHSO_3$	15.6 (0.445)	5.8 (0.181)
50% $POCl_3$ and 50% $ClHSO_3$	5.6 (0.16)	6.2 (0.193)
25% $POCl_3$ and 75% $ClHSO_3$	0.75 (0.021)	17.3 (0.541)
100% $ClHSO_3$	–	18.4 (0.575)

[a] Values in parentheses are in mmol/g.

Poly—oh + $pocl_3 \rightarrow$ poly—o—po—$(oh)_2$ and/or $(poly—o)_2$—po(oh)

Poly—oh + $clhso_3 \rightarrow$ poly—o—so_2(oh)

The phosphorous and sulfur content of phosphorylated, sulfonated, and phosphosulfonated cotton stalks are shown in Table I. Phosphorylated cotton stalks had phosphorous content of 14.9 mg/g (0.48 mmol/g) and sulfonated cotton stalks had sulfur content of 18.4 mg/g (0.57 mmol/g). The higher extent of reaction in sulfonation of cotton stalks than in its phosphorylation is due to the smaller size of chlorosulfonic acid molecule and thus having higher accessibility to the inner cotton stalk constituents, and also its higher reactivity.[10] The phosphorous and sulfur contents of the different phosphosulfonated samples prepared by adding different ratios of $ClHSO_3$ and $POCl_3$ also showed the higher reactivity of $ClHSO_3$ toward cotton stalk constituents.

FTIR spectra of raw cotton stalks, phosphorylated, sulfonated, and phosphosulfonated cotton stalks are shown in Figure 1. New characteristic peaks appeared at 1250 and 1340 cm^{-1} in case of phosphorylated cotton stalks, and these bands may be assigned to P═O and P—OH vibrations, respectively. In case of sulfonated cotton stalks, characteristic peaks appeared at 1040, 1240, and 1410 cm^{-1}, the first one may be assigned to S═O stretching vibration while the other peaks may be assigned to O—SO_3 stretching vibration. IR Phosphosulfonated cotton stalks showed characteristic peaks that correspond to both sulfonate and phosphate groups.

Sodium ions binding capacity of cotton stalks derivatives

Table II shows sodium ion binding capacity of the different cotton stalks ion-exchangers as a measure of

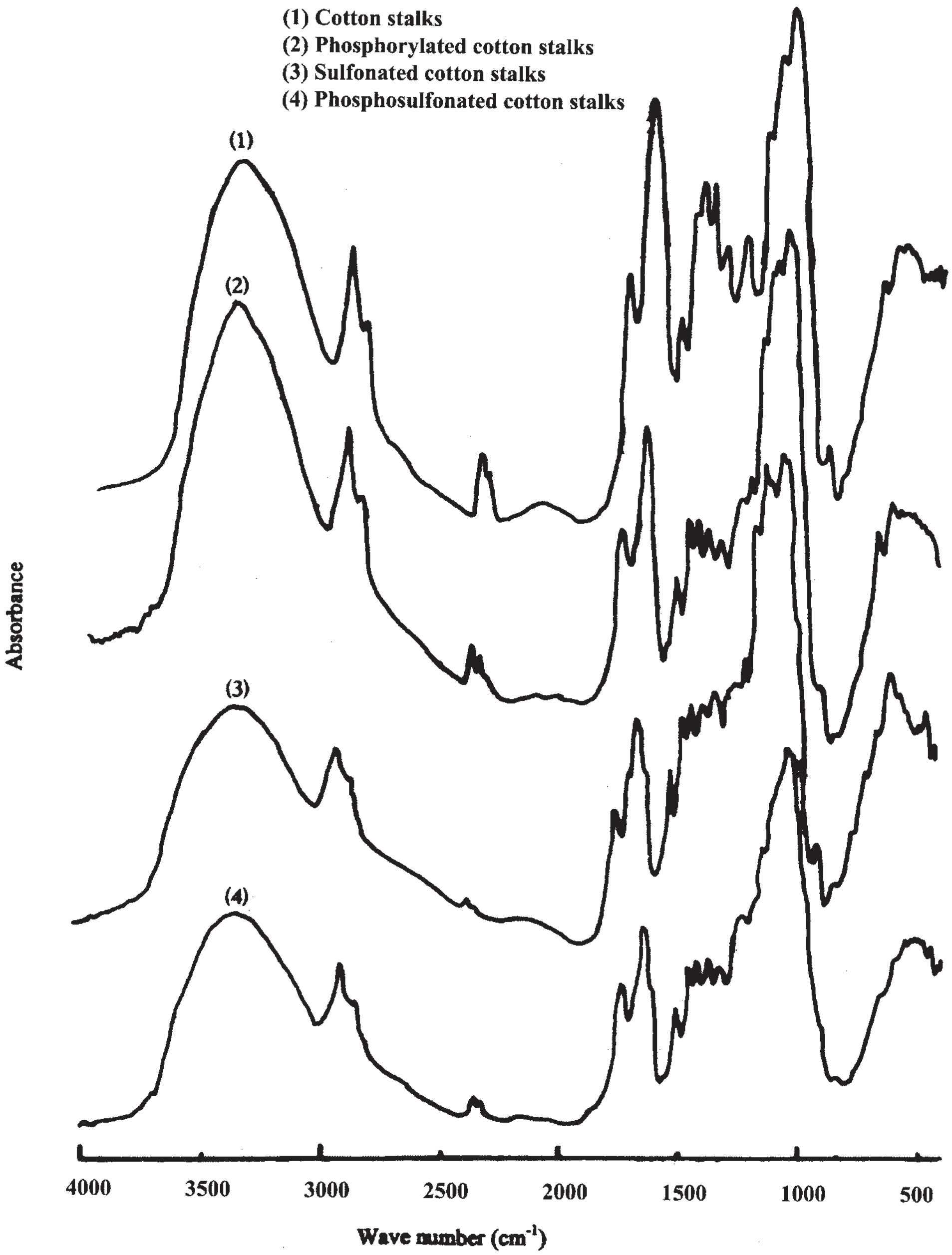

Figure 1 FTIR spectra of the different esterified cotton stalk derivatives.

the extent of the esterification. As shown, sodium binding capacity of phosphorylated, phosphosulfonated, and sulfonated cotton stalks are higher than raw cotton stalks. The sodium binding capacity of sulfonated cotton stalks is higher than that of the phosphorylated stalks because of the higher number of sulfonate groups than phosphate groups, as shown from the elemental analysis of sulfur, and also because of the higher acidity of the sulfonate group. The sodium binding capacities of all phosphosulfonated cotton stalks were higher than both sulfonated and phosphorylated cotton stalks. The higher adsorption capacity of the phosphosulfonated derivatives than that of both phosphorylated and sulfonated derivatives may be due to the synergetic effect of phosphate and sulfonate groups. The presence of different functional groups on the same matrix (cotton stalks) may lead to increase of the selectivity of the adsorption because of the presence of polydentate bonding.[10]

Adsorption of heavy metals ions by the sulfonated, phosphosulfonated, and phosphorylated cotton stalks ion exchangers

Industrial wastewaters effluent may contain a mixture of heavy metals ions, and therefore testing of an ion exchanger is recommended to be carried out using a mixture of the expected heavy metal ions in the waste-

TABLE II
Sodium Binding Capacity of Esterified Cotton Stalks Exchangers

% of $POCl_3$ and $ClHSO_3$ added	Sodium binding capacity (meq./g)	Phosphorus content (mg/g)	Sulfur content (mg/g)
None	418	–	–
100% $POCl_3$	445	18.12 (0.517)[a]	–
75% $POCl_3$ and 25% $ClHSO_3$	492	15.6 (0.445)	5.8 (0.181)[a]
50% $POCl_3$ and 50% $ClHSO_3$	495	5.6 (0.16)	6.2 (0.193)
25% $POCl_3$ and 75% $ClHSO_3$	500	0.75 (0.021)	17.3 (0.541)
100% $ClHSO_3$	468	–	18.4 (0.575)

[a] Values in parentheses are in mmol/g.

water effluents. The ions exchange adsorption affinities are determined chiefly by the magnitude of the charge and the hydrated radius of the ions in solution.[13] In this study, adsorption of strontium, arsenic, copper, and nickel metal ions from a mixture of them by the prepared cotton stalks ion-exchangers at different metal ions concentration, temperature, pH and times was studied.

Effect of pH

A large number of industrial systems employing metal ion solutions are characterized by slightly low pH since at this condition, metals exist in the soluble ionic form. Hence, for the treatment of waste stream, it would be an advantage if the exchanger to be used exhibits sufficient metal affinity even in low pH conditions.[14] The adsorption of the metal ions by the prepared ion-exchanger at pH 1.5, 3.5, 5.5, and 6.5, at 25°C, for 30 min and 100 ppm metals ions concentration is illustrated in Figure 2 Normally, metal ions adsorption exhibits a drastic decrease at low pH condition because of the competition with hydronium ions.[15] The increase in pH causes a decrease in hydronium ions concentration up to a certain pH value, above which precipitation of metal ions in the form of hydroxide starts to take place.

Figure 2 shows the effect of the pH of the metal ion solutions on the amount of metal ions adsorbed at room temperature and 100 ppm metal ions concentration. Generally, maximum adsorption by the different cotton stalks cation exchangers was observed at pH value of 3.5. At higher pH values, the replaceable hydrogen atoms of the phosphate and sulfonate groups are replaced by the hydroxide metal ions and become no longer capable of adsorbing the heavy metal ions. While at the lower pH value (pH 1.5), the strong acidity may result in replacing the adsorbed metal ions by the hydrogen ions.

The phosphosulfonated cation exchanger, which contains a mixture of phosphate groups and sulfate groups, had higher adsorption capacity than that of the phosphorylated and sulfonated cotton stalks. Phosphorylated cotton stalks showed higher metal ion uptake than sulfonated cotton stalks. As mentioned earlier, phosphorylated cotton stalks may contain both dianion and monoanion phosphate groups while sulfonated cotton stalks contain only monoanion sulfonate groups. At the optimum pH (pH 3.5), the phosphosulfonated cotton stalks that has higher phosphate groups than sulfonate groups (prepared using 3:1 mixture of $POCl_3$:$ClHSO_3$) showed higher metal uptake than that containing higher sulfonate groups or phosphate groups; the adsorption of the metal ions by different cation exchangers was in the order Cu > Sr > Ni > > As. 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 of materials is determined by their surface areas, which can be observed by the effect of different sizes of adsorbents on the adsorption.

Effect of metals ions concentration

Figure 3 shows the adsorption of the different heavy metals ions by different cotton stalk derivatives at pH 3.5, at 25°C room temperature, for 30 min, and at metal ions concentration up to 200 ppm. As shown, the adsorption of the different metal ions increased with increase in the concentration. The phosphosulfonated cotton stalks showed higher adsorption capacity than both sulfonated and phosphorylated cotton stalks. Sulfonated cotton stalks showed higher affinity toward Sr and As metal ions than that of phosphorylated cotton stalks while the later showed higher affinity toward Cu and Ni metal ions. At the maximum adsorption (at 200 ppm) the order of the adsorption of the metal ions was Cu > Ni > Sr > As. The adsorption of As metal ions was very weak when compared with that of the other metal ions.

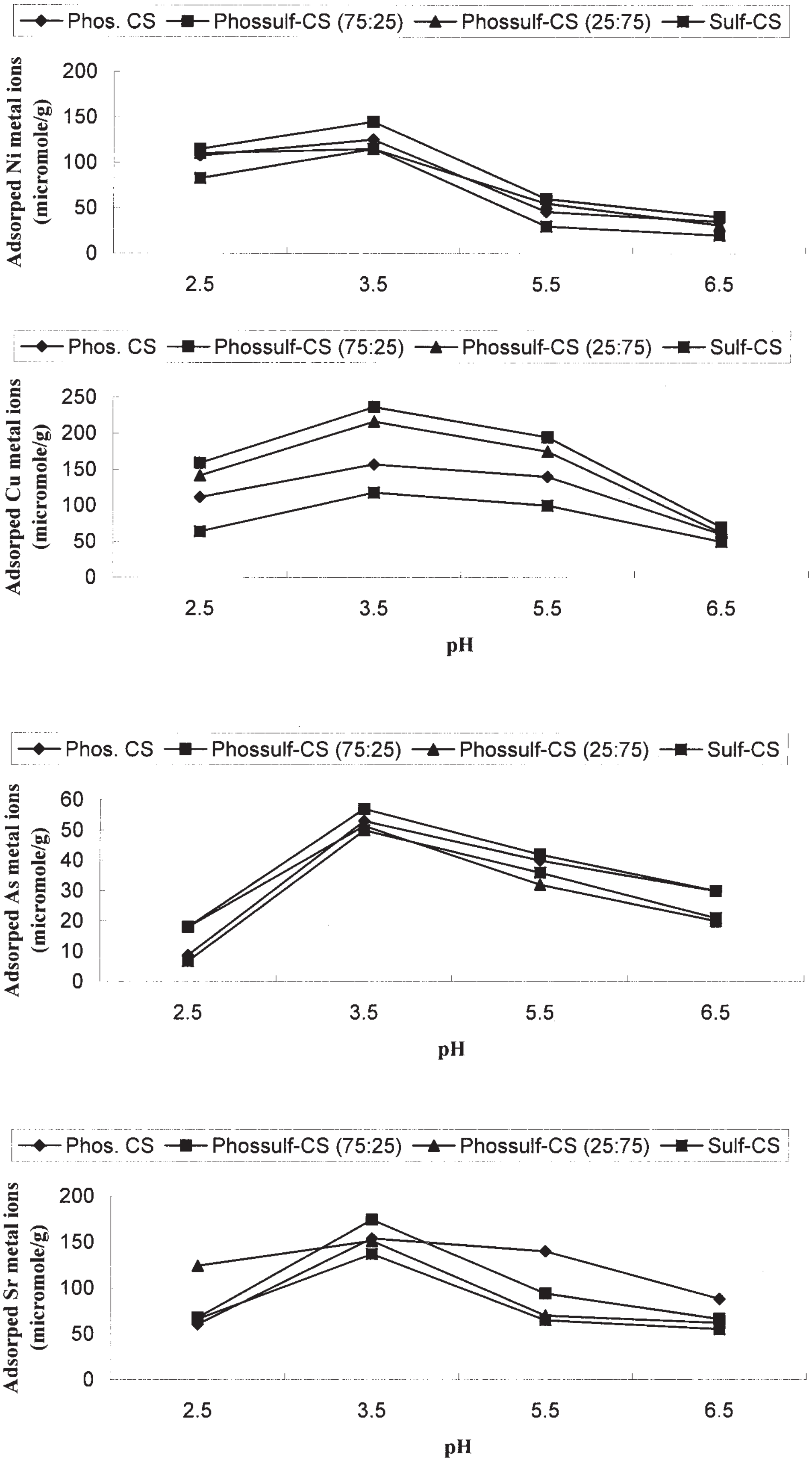

Figure 2 Effect of pH on the quantity of adsorbed metal ions.

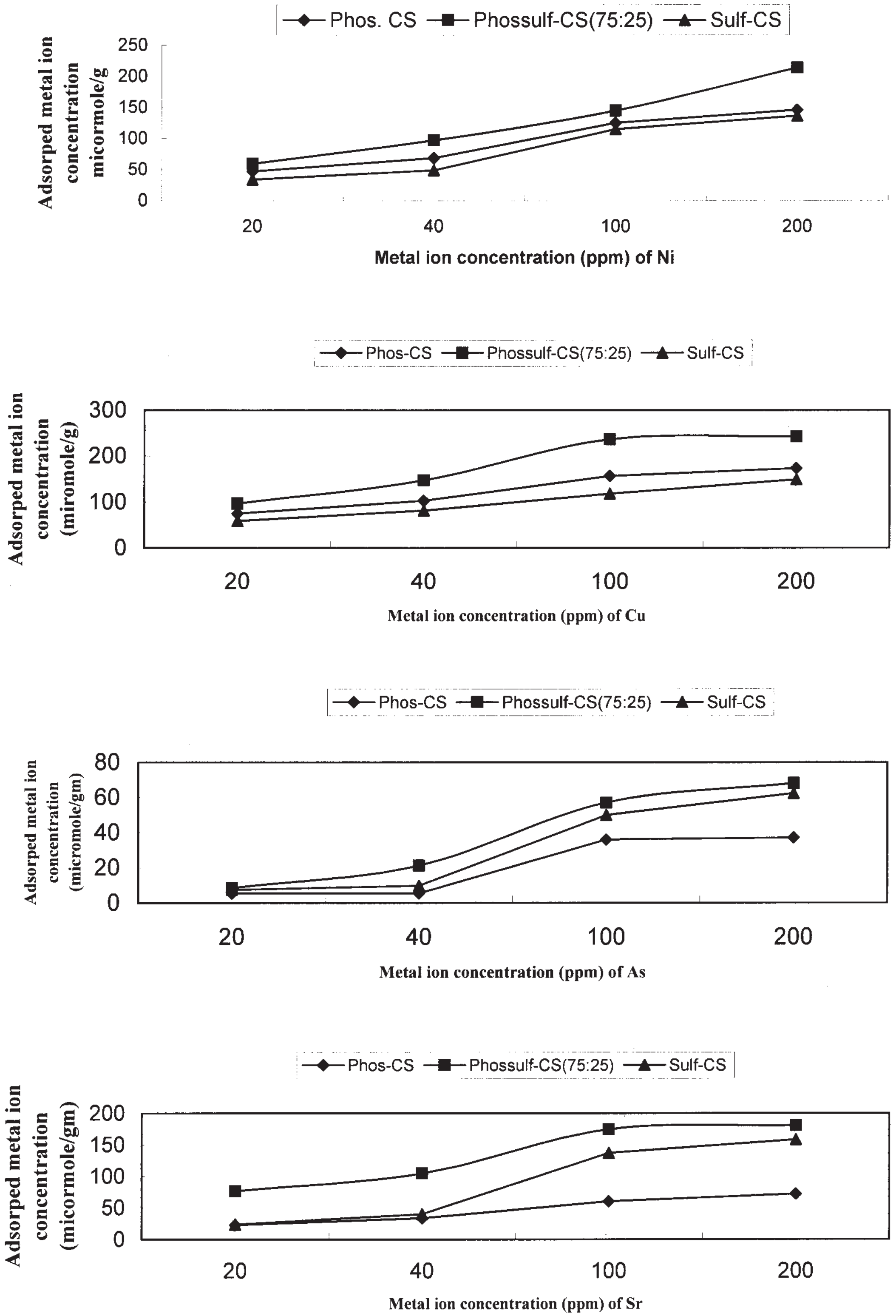

Figure 3 Effect of metal ion concentration on the adsorption of the different cotton stalk derivatives.

Effect of contact time

Figure 4 shows the adsorption of different heavy metal ions by the different ion-exchangers at different time intervals (15–60 min), pH 3.5, at 25°C, and 100 ppm metal ion concentration. The majority of the adsorption of the heavy metal ions approximately took place in the first 30 min and reached equilibrium after about 45 min.

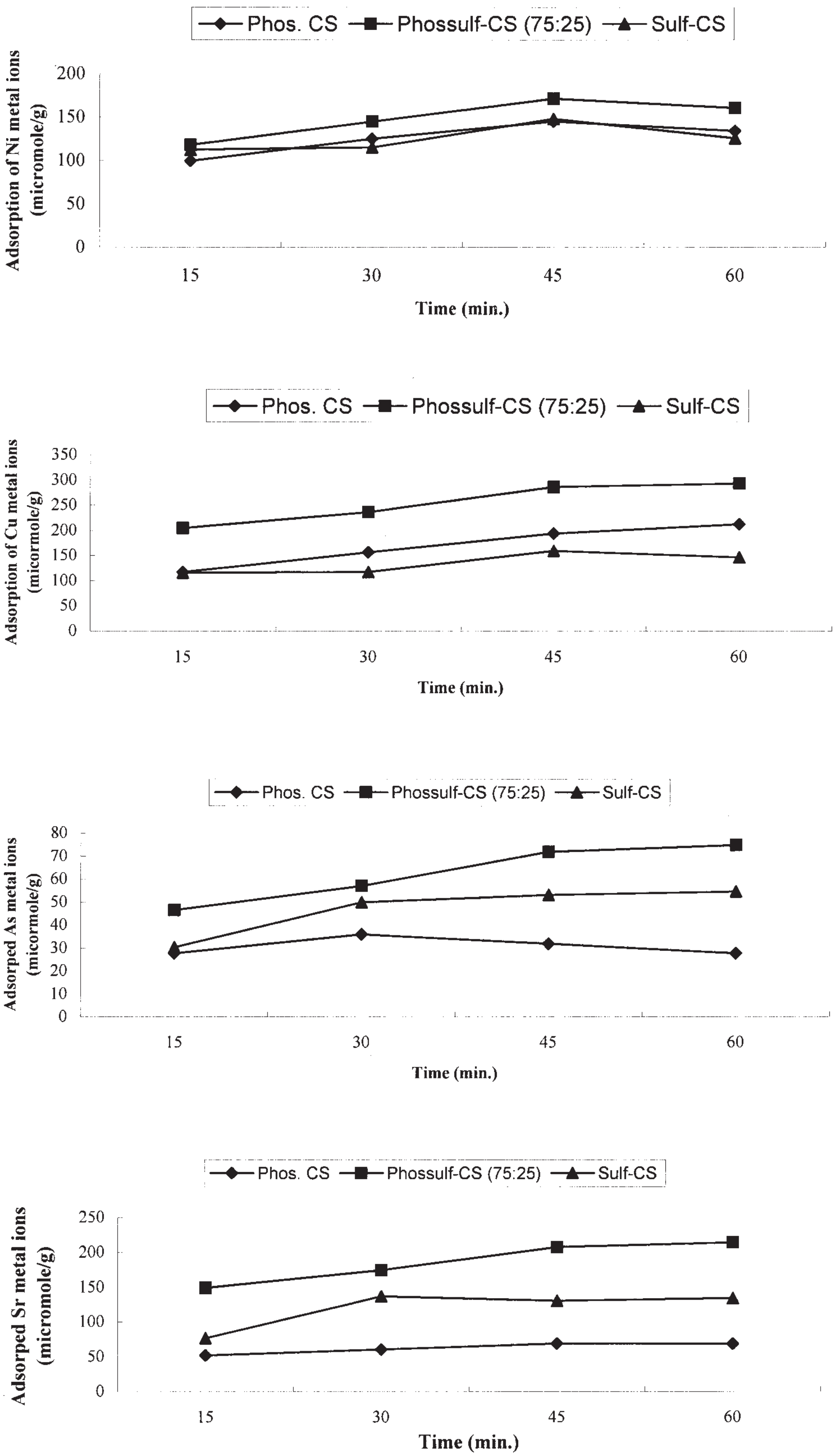

Figure 4 Effect of contact time on quantity of adsorped metal ions.

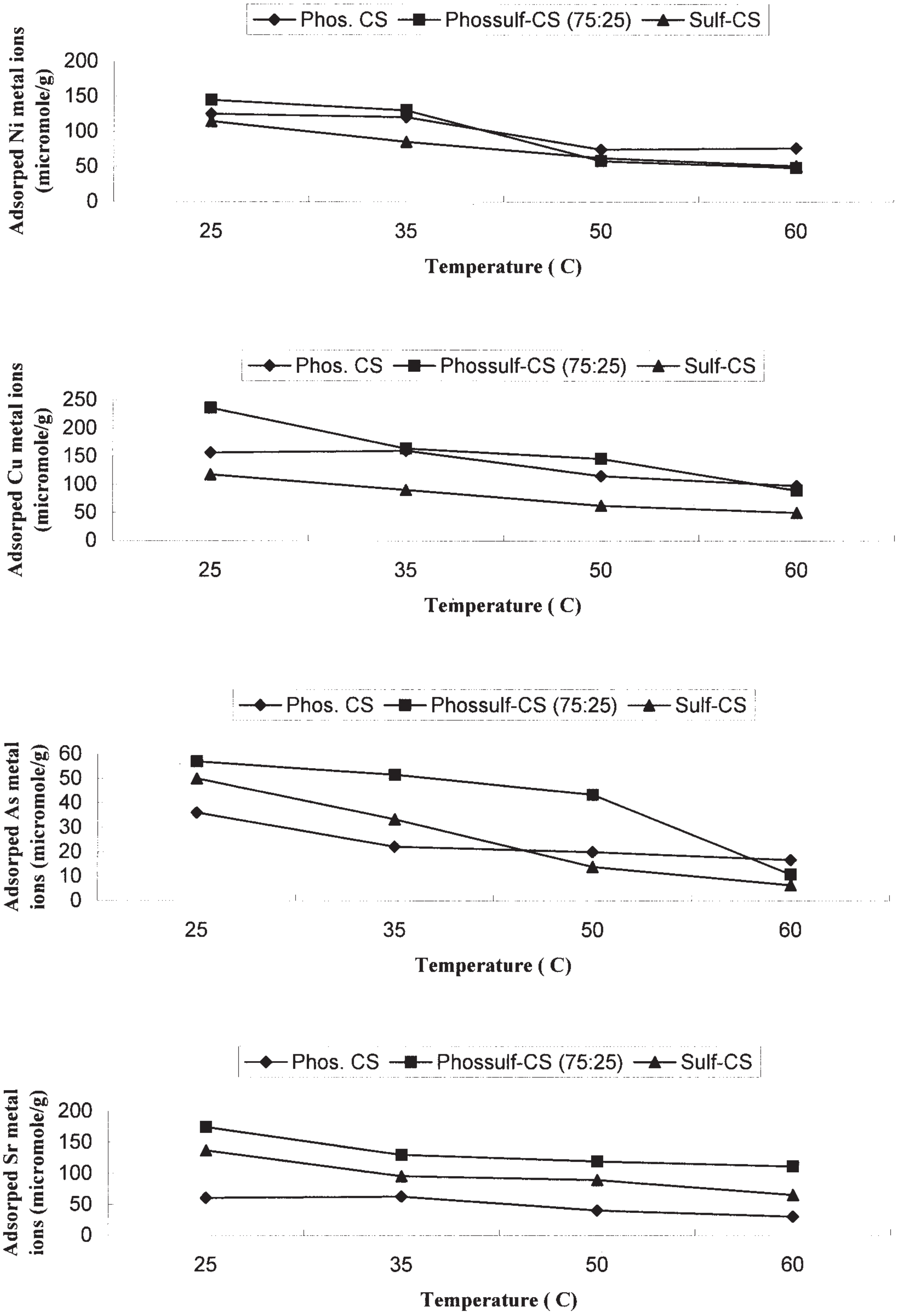

Figure 5 Effect of temperature on the adsorption of the different cotton stalk derivaties.

Effect of temperature

Since the effluents of industrial wastewater may have different temperatures, it is reasonable to test the ion exchange capacity at a temperature range when comparable with the real conditions. Figure 5 shows the effect of temperature on the adsorption of the different heavy metal ions by the different cation exchangers at constant pH 3.5, for 30 min and 100 ppm metal ions concentration. Changing the temperature affected the reaction of the sulfonate and phosphate groups of the different cation exchangers with the different metal ions. Generally, increasing the temperature resulted in a decrease in the adsorption of the different metal ions; this means that the increasing the temperature shifted the reaction between the metal ion and the free acid form to the backward direction. The extent of this decrease was dependant on the kind of metal ions. For As metal ions, the highest decrease of adsorption is due to increase in temperature while for Sr, the lowest decrease of adsorption is due to increase in temperature.

CONCLUSIONS

Cotton stalks could be used for the preparation of cation exchanger for the removal of heavy metal ions. Introduction of a mixture of the anionic functional groups (phosphate and sulfonate groups) into cotton stalk constituents increase the adsorption capacity of the cationic exchangers when compared with that of the cationic exchangers containing sulfonate or phosphate functional groups on a separate basis. Phosphosulfonated cotton stalks that contain higher amount of phosphate groups than sulfonate groups showed the highest metal ion adsorption capacity among the different cation exchangers prepared.

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