Synthesis and Metal Ions Sorption Properties of Styrene-Based Polymers

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ABSTRACT: Atactic polystyrene (PS) was chemically modified with maleic (MAH), succinic (SAH), and phtalic (PhAH) anhydrides. Styrene was copolymerized with acrylic (AA) and methacrylic acids (MA). Amount of carboxyl groups (%) bound to polymers was determined in the range of 6.9–25.9. Different modified polystyrenes (MPS) and styrene copolymers were used in the experiments to study Cu(II) and Zn(II) ions adsorption probability and their comparison. Sorption capacity of the polymers for the metal ions were investigated in aqueous media containing different amounts of these ions (5–40 mg/L) and at different pH values (2.0–6.0). Adsorption behavior of heavy metal ions could be modeled using both the Langmuir and Freundlich isotherms. It was found that the adsorption capacity is highest at pH value of 6, whereas it decreases as the pH value decreases at temperature $25°C \pm 1°C$ for 240 min. The results obtained from the adsorption capacity experiments for Cu(II) and Zn(II) ions were 3.47–5.45 and 5.42–6.85 mg/g, respectively. The affinity order of polymers for both metal ions was observed as follows: SMAC > SAAC > MPS with MAH > MPS with SAH > MPS with PhAH. The maximum adsorption capacities of SMAC were 6.85mg/g for Zn(II) and 5.45 mg/g for Cu(II). © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1192–1198, 2009

Key words: styrene; copolymerization; modification; polystyrene; adsorption

INTRODUCTION

Pollution caused by heavy metals is now a worldwide phenomenon.[1] Among the many heavy metals, lead, cadmium, mercury, arsenic, chromium, zinc, and copper are of most concern; although the last three metals are essential in human and animal nutrition. These metals are widely used in industry, particularly in the production of paint pigments, pottery glazes, inks, rubber, plastics, pesticides, and even in medicines.[2] Most of the heavy metals are toxic because, as ions or in compound forms, they are soluble in water and in humans. These metals, even in small amounts, can cause severe physiological and health effects.[3,4]

In recent years, selective metal ion removal has been widely carried out using specific ligand-modified polymers for the preconcentration of some toxic metal ions.[5–10] Some organic polymer sorbents such as Amberlite XAD, Separon, and Polysorb are well known from the literature.[11] Recently, styrene-divinylbenzene-based insoluble resins (e.g., Lewatit), gelatinous and macroporous copolymers, and crosslinked polymer adsorbents gained vital importance because of their ability to remove high quantities of ions.[12,13] The strong acid resins are the most employed ion exchangers in industrial operations for cation separations from an aqueous stream. The polystyrenic matrix offers a remarkable chemical and physical stability for temperatures of interest in treating aqueous solutions.[14] Plachinda et al.[15] indicated that Fe hydroxide particles are precipitated in a network of polymer chains of sulfonated polystyrene, crosslinked by divinylbenzene. Dithiocarbamate-incorporated monosize polystyrene was used for the selective removal of Hg(II) from aqueous solutions.[16] The chemical modification to change the chemical characteristics of the adsorbent's surface had been examined by several investigators.[17–19] The interaction of divalent metal ions with styrene–maleic acid copolymer (SMA copolymer) has been studied by Kramer and Dunsch. Considering adsorption of the polymer, the studies show that SMA acts as a strong ligand for Cu(II) ions while complexation with Zn(II) is less strong.[20] Kavakli et al.[21] synthesized polymeric microbeads by the suspension polymerization of p-chloromethyl styrene, and then the affinity of the cyclam-modified poly(p-CMS-EGDMA) microbeads for Cu(II), Ni(II), Co(II), and

Figure 1 FTIR spectra of modified PS with (1) PhAH, (2) SAH, and (3) MAH.

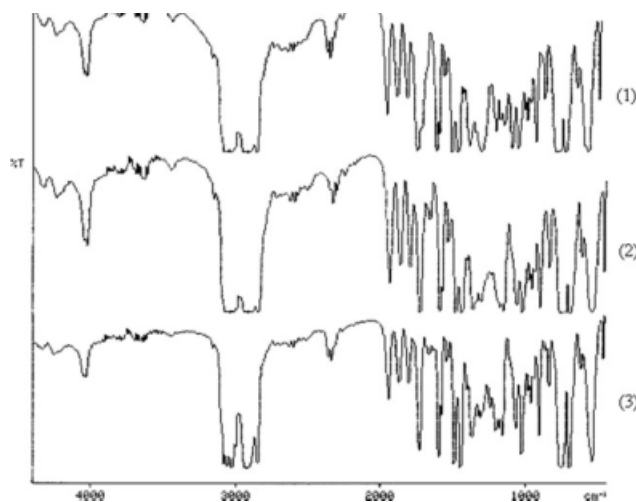**Figure 2** FTIR spectra of (1) SAAC and (2) SMAC.

Zn(II) metal ions was examined. The selectivity of metal ions was found in the order of Cu (II) $\gg$ Ni(II) > Zn(II) > Co(II). Tseng et al.[22] studied the synthesis and application of polymer adsorbent (MPA) coupling with metal-chelating ligands of iminodiacetic acid (IDA) for the removal of Cu(II) ion. It was found that the adsorption capacity of Cu(II) ion is highest at pH value of 4.5 while it decreases as the pH value decreases. The effects of the structure of sulfonated polystyrenic resins of type gel, macroporous, and macronet (hyper-crosslinked) on Cu^{2+}, Zn^{2+}, and Cd^{2+} binary ion exchange equilibria were investigated by Oancea et al.[23] It was found that the affinity of the macronet strong acid polystyrenic resin is higher than the affinity of the gel strong acid polystyrenic resin, for each investigated ion.

All these literature findings indicated that polymeric synthetic resins are available and efficient for adsorption and ion exchange process. Therefore, this investigation was undertaken to evaluate the sorption performance of styrene-based polymers synthesized by us in the presence of copper and zinc ions
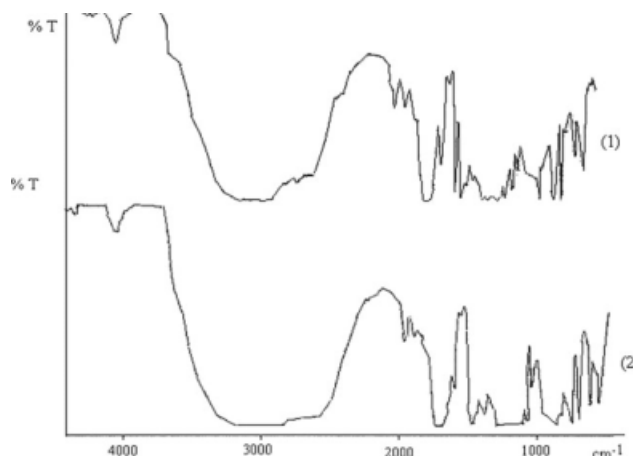
solution. Polymer (0.1 g) was added to each metal solutions containing 20 mg/L Cu(II) or Zn(II) ions, and then the mixture was shaken for 4 h.

EXPERIMENTAL

Materials

PS ($M_n = 350 \times 10^3$), styrene, MAH, SAH, PhAH, chloroform as solvent, and cationic catalyst $BF_3 \cdot O(C_2H_5)_2$ were purchased from Merck (Darmstadt, Germany). Copper(II) chloride ($CuCl_2 \cdot 2H_2O$), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), potassium hydroxide, and hydrochloric acid were purchased from Fluka (Buchs, Switzerland).

Synthesis of modified polystyrene

A reactor consisting of a mixer, cooler, and thermometer was used in the experiment. 5.2 g modifier (20% of the polymer amount) was added to the solution of 26 g PS in 200 mL chloroform by mixing. After anhydride was dissolved completely, 7.54 g (6.7 mL) $BF_3 \cdot O(C_2H_5)_2$ was added drop by drop and was
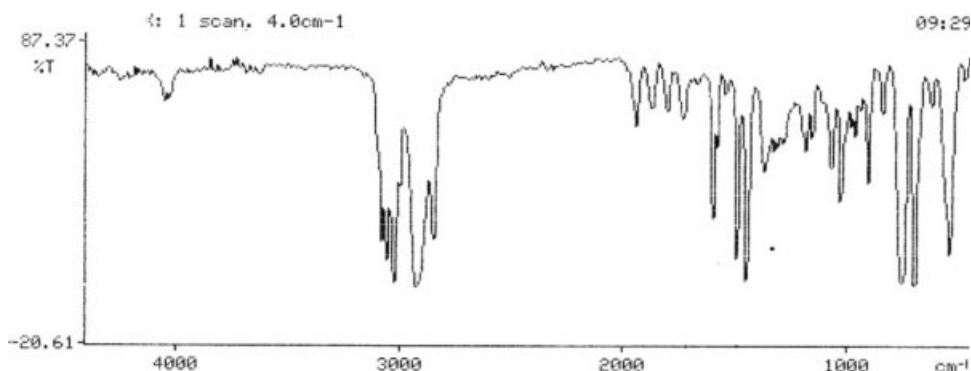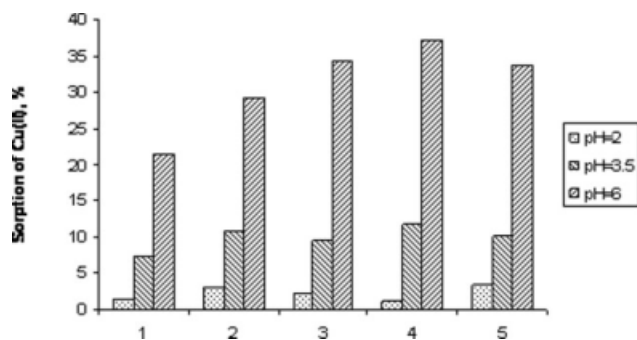

Figure 3 FTIR spectrum of unmodified PS.

Figure 4 Effect of initial pH on Cu(II) sorption (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 180 rpm; initial metal concentration 20 mg/L; time 240 min).

stirred for 3 h at 25°C to end the reaction. The mixture was poured into a beaker, and the modified polystyrene (MPS) was precipitated with ethanol, dried in a vacuum oven at 50–60°C for 4 h, weighed, and analyzed.

Synthesis of styrene copolymers (SMAC AND SAAC)

A 150-mL flask, equipped with a magnetic stirrer, condenser, and thermometer, was charged with St : MA (or AA) in different ratios from 9 : 1 to 5 : 5. Then, toluene and benzoil peroxide (0.5 wt %) was added to the mixture. The mixture was heated to 70°C with stirring for 4 h. After completion of the reaction, the copolymers were filtered, and then dried under vacuum at 40°C.

Characterization of polymers

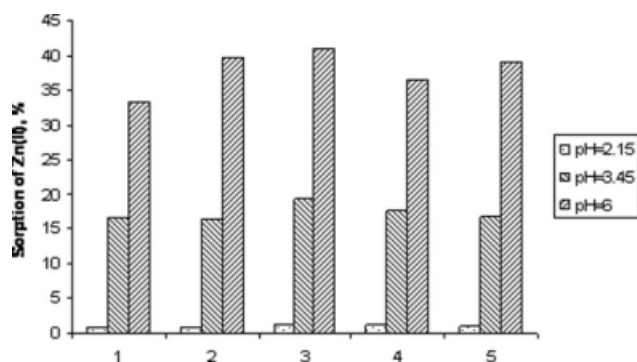The FTIR spectra of polymers were recorded on a Perkin-Elmer 1605 FTIR spectrometer.

Figure 5 Effect of initial pH on Zn(II) sorption (amount of resin 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 180 rpm; initial metal concentration 20 mg/L; time 240 min).

Figure 6 Effect of initial Cu(II) concentration on sorption (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 180 rpm; initial pH 6).

Determination of acid number of MPS

Quantitative analysis corresponding to the amount of pendant carboxyl groups incorporated onto PS was done by titration method with KOH.[8]

Apparatus

Atomic absorption spectrometric measurements were investigated by an atomic absorption spectrometer model Unicam 929 using an air–acetylene flame (air and acetylene flow rates of 7 and 2 dm^3/min, respectively). The pH measurements were made on JENWAY model pH meter, 3305-digital. A mechanical shaker having speed control facility was used for batch equilibration NUVE SL 350.

Preparation of metal ion solution

Stock solutions (1000 mg/L) of copper and zinc were prepared by dissolving appropriate amounts of analytical reagent-grade copper(II) chloride and zinc

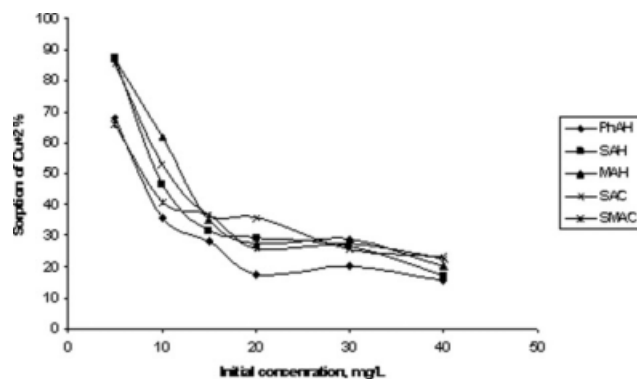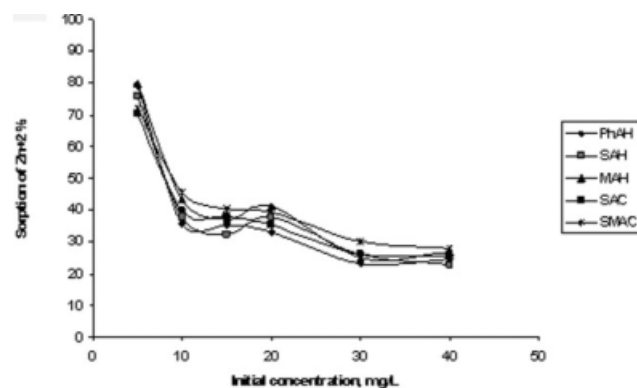**Figure 7** Effect of initial Zn(II) concentration on sorption (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 180 rpm; initial pH 6).
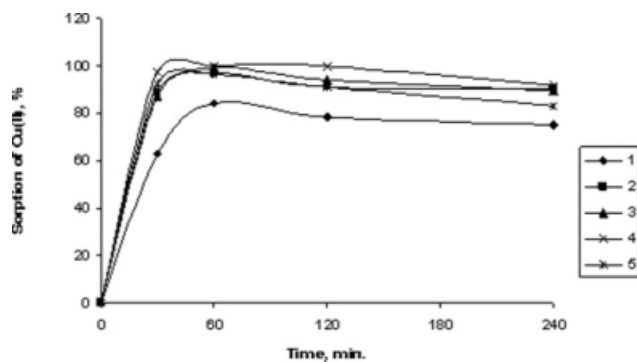
Figure 8 Effect of shaking time on Cu(II) sorption (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 180 rpm; initial pH 6; initial metal concentration 5 mg/L).

nitrate, respectively, in doubly distilled water. pH adjustments were made with HCl acid.[24–27]

Adsorption study

Heavy metal ions adsorption from the single metal aqueous solution was investigated by batch adsorption–equilibrium experiments. Effects of the initial concentration of metal ions (in the range of 5–40 mg/L), time (in the range of 30–240 min), and pH (in the range of 2.0–6.0, adjusted with HCl) on the adsorption capacity were studied at room temperature, in the flasks stirred magnetically at 180 rpm. The amount of polymer used in this study was 0.1 g per 50 mL of metal ion solution. After the equilibration, the polymers were separated from the adsorption medium, and then the concentration of the metal ions in the aqueous phase was determined.

The metal binding could be quantitatively determined experimentally under varying conditions. The effect of pH, metal concentration, and time has been studied in batch systems. The degree or percentage of metal sorption was calculated by measuring the
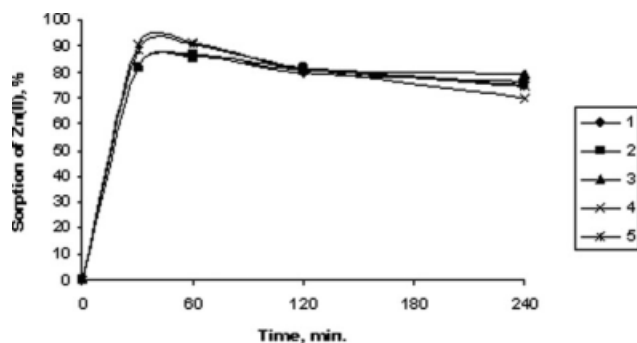

Figure 10 Adsorption isotherms of Cu(II) ions onto MPSs with various anhydrides (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 220 rpm; initial pH 6).

metal content before and after the adsorption. The ion adsorption isotherms were plotted as a function of the amount of metal ion adsorbed per gram of resin (mg/g) against the amount of metal ions left in equilibrium solution, C_e, mg/L.

RESULTS AND DISCUSSION

The FTIR spectra of MPSs and copolymers are shown in Figures 1 and 2. Both MPSs showed medium to weak peaks of aromatic C—C multiple bonds stretching at 1598 and 1445 cm^{-1}. In the spectra of MPSs, the bands at 756 cm^{-1} ascribed to the out-of-plane bending vibrations of aromatic =C—H and C=C groups of polystyrene. In the spectrum of MPSs, a broad and intense absorption band at 1733 and 1724 cm^{-1} (Fig. 1) and a weak absorption band at 1800 cm^{-1}, which were not observed in the spectrum of unmodified PS (Fig. 3), are found. These absorption bands that can be assigned to grafted anhydrides confirmed the presence of carbonyl groups in the MPSs. The absorption band at 1370 cm^{-1} is attributed to acid C—O bond of grafted anhydrides end groups. All MPSs showed wide characteristic peaks in the wave number region 3041–2332 cm^{-1}, which correspond to —OH of

Figure 9 Effect of shaking time on Zn(II) sorption (amount of resin 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 180 rpm; initial pH 6; initial metal concentration 5 mg/L).

Figure 11 Adsorption isotherms of Cu(II) ions onto styrene copolymers (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 220 rpm; initial pH 6).
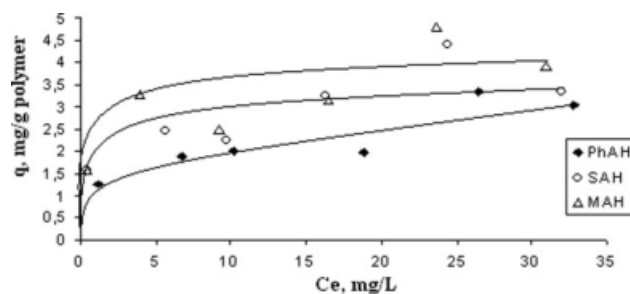
Figure 12 Adsorption isotherms of Zn(II) ions onto MPSs with various anhydrides (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25 ± 1°C; stirring rate 180 rpm; initial pH 6).
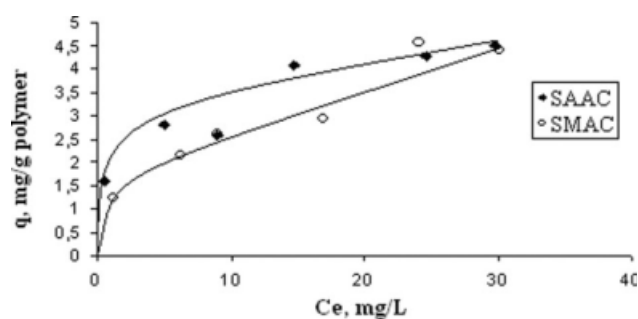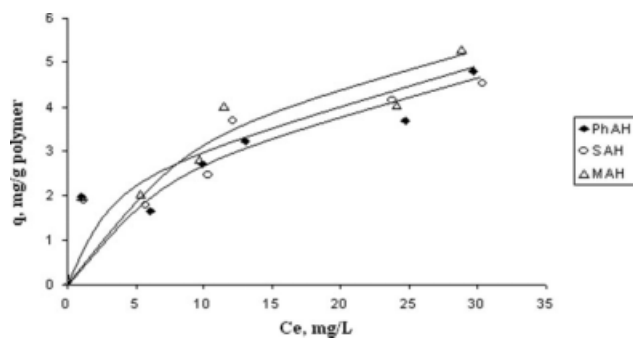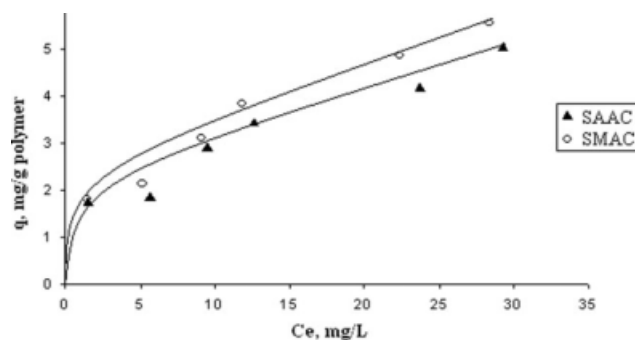

Figure 13 Adsorption isotherms of Zn(II) ions on styrene copolymers (amount of polymer 0.1 g; volume of sorption medium 50 mL; temperature 25°C ± 1°C; stirring rate 180 rpm; initial pH 6).

carboxyl group. The absorption bands at 750, 1024, 1057, and 1066 cm^{-1} observed in MPSs indicate monosubstitution of anhydries to the aromatic ring of PS (Fig. 1).

In the FTIR spectra of copolymers, characteristic bands appeared in the regions of 1700, 1580, and 2000 cm^{-1} for acid C=O group, aromatic C=C, and aromatic C—H, respectively (Fig. 2).

The effect of pH on recovery of the metals

The adsorption of heavy metal ions by resins is strongly dependent on pH.[16] As discussed in the literature, precipitation of Zn(II) and Cu(II) ions occurs at pH 6.43 and 5.34, and these ions complete precipitate at pH 8.43 and 7.34, recpectively.[28] Therefore, the influences of pH on the recoveries of analyte ions on styrene-based polymers were investigated in the pH range 2–6. The change of recovery of metals with pH is shown in Figures 4 and 5. In all of the cases, the adsorption increases with increasing pH. At low pH value, i.e., pH 2, the adsorption capacities are lower for both metal ions. The most suitable pH values for the maximum uptake of all metal ions were found to be 6.0. The maximum recovery for both metal ions was about 40%.

The effect of initial concentration on adsorption

Figures 6 and 7 show the effects of initial concentration (5, 10, 20, 30, and 40 mg/L solutions) of the metal ions uptake onto the polymers. The results indicated that the most suitable metal concentration for maximum recovery of both metal ions was 5 mg/L. As presented in Figures 6 and 7, with increasing initial metal ion concentrations in the solution, the uptake of the metal ions by the polymers decreases almost exponentially up to 20 mg/L for Cu(II) and 30 mg/L for Zn(II), and then approaches a plateau region.

Metal sorption as a function of time

Figures 8 and 9 illustrate the percentage removal of Cu(II) and Zn(II) ions in 5 mg/L concentration by polymers at room temperature for 30, 60, 120, and 240 min, respectively. As seen here, the % metal sorption increases with the time, and the required time for maximum percentage removal of both metal ions was below 60 min. After 60 min, the % sorption of both metal ions decreased, probably, because of the desorption, and then it reached the plateau value at 120 min.

Adsorption isotherms

The ion adsorption isotherms were plotted as a function of the amount of metal ion adsorbed per gram of resin (mg/g) against the amount of metal ions left in equilibrium solution, C_e, mg/L. The results for copper and zinc ions were determined at room temperature by using styrene-based polymers as shown in Figures 10–13. These results show that the adsorption of Zn(II) was higher than that of the Cu(II) ions for all polymers. The variation of the selectivity on polymers is in good agreement with the variation of the polarizability of the selected divalent ions, which decreases with the decrease of the ionic radius and depends on electronic structure of the ion.[29] The adsorption capability of the SMAC was compared with the other polymers. The adsorption studies done by all polymers showed that recovery of both

TABLE I
Amount of Carboxyl Groups Bound to Polymers

	Polymers				
Carboxyl group (%)	MPS with PhAH	MPS with SAH	MPS with MAH	SAAC	SMAC
	6.9	6.12	7.6	21	25.9

TABLE II
Parameters of Langmuir and Freundlich Isotherms for Sorption of Cu(II) onto Polymers with pH 6 at 25°C

Polymers	Langmuir			Freundlich		
	q_0	b	r^2	k_F	n_F	r^2
MPS with PhAH	3.47	0.169	0.8705	1.116	3.692	0.8323
MPS with SAH	3.949	0.334	0.9189	1.771	4.786	0.7989
MPS with MAH	4.39	0.343	0.9182	1.94	4.629	0.7685
SAAC	4.93	0.263	0.96	1.793	3.79	0.9281
SMAC	5.45	0.119	0.8969	1.061	2.427	0.9614

metal ions by SMAC were higher than other polymers studied because of more carboxyl groups were in the structure (Table I).

Adsorption capacity of the polymers

The amount of metal ions adsorbed is determined as a function of the concentration at a constant temperature that could be explained in adsorption isotherms. Different adsorption isotherms (Freundlich and Langmuir) were fitted to experimental data. Langmuir adsorption isotherm is one of the most well-known and applied adsorption isotherms and described by the equation later:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium, and q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.[30]

The Freundlich adsorption isotherm is expressed as follows:

$$q_e = \frac{n_A}{m_s} = k_F C_e^{1/n_F}$$

The logarithmic form of the equation becomes:

$$\log q_e = \log k_F + \frac{1}{n_F} \log C_e$$

The Freundlich adsorption isotherm represents the equilibrium relationship between the amount of metal ion (n_A, mmol) adsorbed per unit mass of ad-

sorbent (m_s, g) ($q_e = n_A/m_s$), and the concentration of metal ion (C_e, mg/L). k_F and n_F are constants representing the adsorption capacity and intensity of adsorption, respectively.[31]

Parameters of Freundlich and Langmuir adsorption isotherms at pH 6 for Cu(II) and Zn(II) are listed in Tables II and III, respectively. The results show that the Langmuir isotherm is a good approximation for Cu(II) and Zn(II) adsorption, supporting the existence of chemical interactions between ions and styrene-based polymer's carboxyl groups. Thus, the Langmuir equation was applicable for the case at pH 6 for the adsorption of Cu(II) and Zn(II) ions on all polymers in this study. The values of n_F lie in the Freundlich equation between 1 and 10 indicating favorable adsorption. The correlation coefficient for the Freundlich plot for SMAC and SAAC were found to be 0.9, indicating a good fit of the experimental data when compared with Langmuir plot.

The amounts of maximum metal (q_0) adsorbed on 0.1 g of polymers were calculated as mg/g from the plots obtained for each metal and polymer. The results obtained from the adsorption capacity experiments for Cu(II) and Zn(II) ions were 3.47–5.45 and 5.42–6.85 mg/g, respectively (Tables I and II). From the Langmuir sorption constants, the affinity order of polymers for both metal ions was observed as follows: SMAC > SAAC > MPS with MAH > MPS with SAH > MPS with PhAH.

Comparison with other styrene-based polymers

The sorption capacities of these polymers are varied in the range of 3.47–5.45 and 5.42–6.85 mg/g for Cu(II) and Zn(II) ions, respectively. The synthesized

TABLE III
Parameters of Langmuir and Freundlich Isotherms for Sorption of Zn(II) onto Polymers with pH 6 at 25°C

Polymers	Langmuir			Freundlich		
	q_0	b	r^2	k_F	n_F	r^2
MPS with PhAH	5.42	0.121	0.8537	1.602	3.895	0.6369
MPS with SAH	5.49	0.129	0.8845	1.488	3.36	0.7213
MPS with MAH	5.75	0.154	0.8889	1.692	3.47	0.762
SAAC	6.11	0.111	0.91	1.295	2.699	0.8753
SMAC	6.85	0.117	0.9328	1.392	2.55	0.928

polymers exhibit better capacity values in comparison with most of the other styrene-based polymer adsorbents, such as Amberlite XAD-2 functionalized with *o*-aminophenol,[32] Amberlite XAD-2-*o*-vanilline thiosemicarbazone,[33] pyrocatechol violet-immobilized Amberlite XAD-2,[34] salicylic acid-functionalized Amberlite XAD-2,[35] alizarin red-S-loaded Amberlite XAD-2,[36] aminophosphonic and dithiocarbamate group containing polyacrylonitrile,[10] and Amberlite XAD-2 loaded 1-(2-pyridylazo)-2-naphthol.[37] Thus, the synthesized polymers in this work may be applied to the preconcentration and separation of copper and zinc ions from natural or drinking water, containing trace amount of metals.

CONCLUSIONS

The affinity order of polymers for both metal ions was observed as follows: SMAC > SAAC > MPS with MAH > MPS with SAH > MPS with PhAH. The maximum adsorption capacities of SMAC were 6.85 mg/g for Zn(II) and 5.45 mg/g for Cu(II). The results indicate that synthesized polymers having carboxyl groups remove the metal ions copper and zinc from solution better than most of the styrene-based polymers. Thus, these polymers would be useful as metal ion adsorbents for the preconcentration of water containing trace amounts of metal ions.

References

1. Friberg, L.; Nordberg, G. F.; Vouk, B., Eds. Handbook on the Toxicology of Metals; Elsevier, North-Holland, Biomedical Press: Amsterdam, 1979.
2. Stokinger, H. E. In Patty's Industrial Hygiene and Toxicology; Clayton, G. D.; Clayton, F. E., Eds.; Wiley: New York, 1981.
3. Dunnick, J. K.; Fowler, B. A. Handbook of Toxicity of Inorganic Compounds; Marcel Dekker: New York, 1988.
4. Cullen, M. R.; Jobinds, J. M.; Eskenazi, B. Medicine 1983, 62, 221.
5. Kimaru, E.; Kurogi, Y.; Takahashi, T. Inorg Chem 1991, 30, 4117.
6. Sirivastava, S. K.; Gupta, V. K.; Jain, S. Analyst 1995, 120, 495.
7. Soylak, M.; Elci, L.; Dogan, M. Anal Lett 2000, 33, 513.
8. Benyahya, I.; Garnier, J. M. Environ Sci Technol 1999, 33, 1398.
9. Kabay, N.; Demircioglu, M.; Yayli, S.; Yuksel, M.; Saglam, M.; Levison, P. R. Sep Sci Technol 1999, 34, 41.
10. Wen, B.; Shan, X. Q.; Liu, R. X.; Tang, H. X. Fresenius J Anal Chem 1999, 363, 251.
11. Hackman, E. Toxic Organic Chemicals: Destruction and Waste Treatment; Noyes Data Corporation: New Jersey, 1978.
12. de Farias, R. F.; de Souza, A. G.; Nunes, L. M.; de A. Cardoso, V. Colloids Surf A 2002, 211, 295.
13. Ahmetli, G.; Tarlan, E. J Appl Polym Sci 2007, 104, 2696.
14. Dyer, A. In Encyclopedia of Separation Science; Wilson, I.; Poole, C.; Cooke, M., Eds.; Academic Press: New York, 2000.
15. Plachinda, A. S.; Sedov, V. E.; Khromov, V. I.; Suzdalev, I. P.; Goldanskii, V. I.; Nienhaus, G. U.; Parak, F. Phys Rev B 1992, 45, 7716.
16. Denizli, A.; Kesenci, K.; Arica, Y.; Pişkin, E. React Funct Polym 2000, 44, 235.
17. Wang, C. C.; Chen, C. Y.; Chang, C. Y. J Appl Polym Sci 2002, 84, 1353.
18. Tsai, H. A.; Chen, C. H.; Lee, W. C. J Colloid Interface Sci 2001, 240, 379.
19. Chen, C. Y.; Chen, C. Y. J Appl Polym Sci 2002, 86, 1986.
20. Kramer, C.; Dunsch, L. Electrochim Acta 1998, 44, 819.
21. Kavakli, C.; Tuncel, S. A.; Salih, B. Sep Purif Technol 2005, 45, 32.
22. Tseng, J.-Y.; Chang, C.-Y.; Chen, Y.-H.; Chang, C.-F.; Chiang, P.-C. Colloids Surf A 2007, 295, 209.
23. Oancea, A. M. S.; Drinkal, C.; Höll, W. H. React Funct Polym 2008, 68, 492.
24. Fiol, N.; Villaescusa, I.; Martinez, M.; Miralles, N.; Poch, J.; Serarols, J. Sep Purif Technol 2006, 50, 132.
25. Chen, H.; Zhao, Y.; Wang, A. J Hazard Mater 2007, 149, 346.
26. Madhava Rao, M.; Chandra Rao, G. P.; Seshaiah, K.; Choudary, N. V.; Wang, M. C. Waste Manage 2008, 28, 849.
27. Escudero, C.; Gabaldon, C.; Marzal, P.; Villaescusa, I. J Hazard Mater 2008, 152, 476.
28. Alekseev, V. N. Course of Qualitative Chemical Half-Micro-analysis Chemistry: Moscow, 1973.
29. Akhmetov, N. S. General and Inorganic Chemistry, Higher School: Moscow, 1998.
30. Langmuir, I. J Am Chem Soc 1918, 40, 1361.
31. Freundlich, H. Z. Phys Chem 1906, 57, 384.
32. Kumar, M.; Rathore, D. P. S.; Singh, A. K. Talanta 2000, 51, 1187.
33. Jain, V. K.; Sait, S. S.; Shrivastav, P.; Agrawal, Y. K. Talanta 1997, 45, 39.
34. Saxena, R.; Singh, A. K. Anal Chim Acta 1997, 340, 285.
35. Saxena, R.; Singh, A. K.; Rathore, D. P. S. Analyst 1995, 120, 403.
36. Saxena, R.; Singh, A. K.; Sambi, S. S. Anal Chim Acta 1994, 295, 199.
37. Ferreira, S. L. C.; Brito, C. F.; Dantas, A. F.; Araujo, N. M. L.; Costa, A. C. S. Talanta 1999, 48, 1173.