

Synthesis and Analytical Application of a Chelating Resin Based on a Crosslinked Styrene/Maleic Acid Copolymer for the Extraction of Trace-Metal Ions

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ABSTRACT: A new chelating polymer sorbent was synthesized through the copolymerization of styrene and maleic anhydride in the presence of divinyl benzene as the crosslinking agent, followed by hydrolysis. This polymeric resin, bearing O donor groups, had the advantage of being stable in basic and saline media, unlike its linear analogue. This newly developed chelating matrix has a high resin capacity for metal ions such as Cr, Fe, Ni, Cu, and Pb. Various physicochemical parameters, such as the pH, volume, and flow rate, and the interference effect on metal uptake were studied. The sorption capacities of the

crosslinked resin for Cr(III), Fe(III), Ni(II), Cu(II), and Pb(II) were 10.2, 14.3, 14.2, 15.4, and 8.8 mg/g, respectively. A high recovery of 98% was obtained for all the metal ions with 2N HCl as the eluting agent. The chelating resin was characterized by swelling studies, Fourier transform infrared, elemental analysis, X-ray studies, and thermal analysis. The Langmuir and Freundlich adsorption isotherms were used to validate the metal-uptake data. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1771–1779, 2004

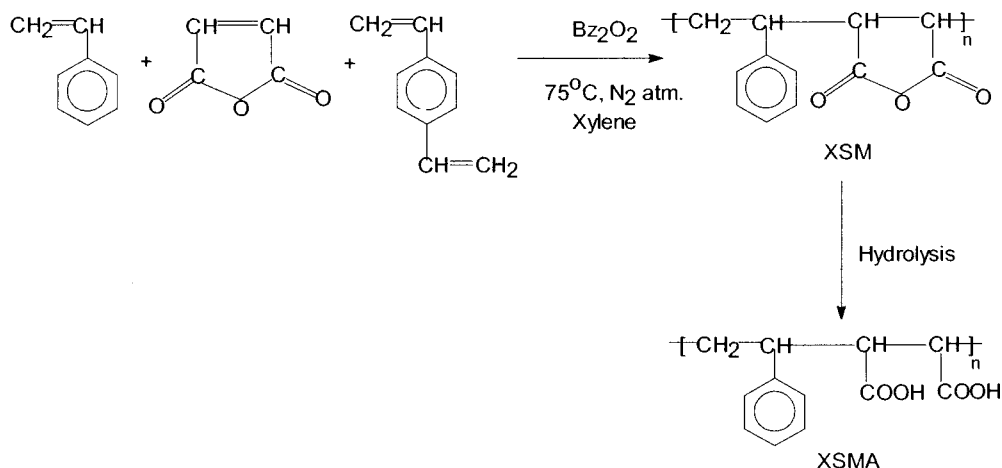
Key words: crosslinking; absorption; resin

INTRODUCTION

The contamination of water resources by industrial effluents has become a serious issue. Metal-ion toxicity has increased substantially because of the use of metal ions as catalysts in industry and as semiconductors in electric and electronic devices. Mineral processing and metal finishing produce large amounts of waste effluents containing harmful metals such as chromium, zinc, cadmium, copper, and nickel. The determination of trace toxic metal ions and their removal with chelating polymers have gained great importance in environmental applications because of their high degree of selectivity, high loading capacity, versatility, durability, and enhanced hydrophilicity.¹ The necessity of reducing the concentration of heavy metals to acceptable levels in wastewater and the need for more highly specific metal-recovery processes in both hydrometallurgical and environmental applications have led to increasing interest in polymer-based adsorbents. The specific and rapid complexation of the metals and the reusability of the chelating polymeric ligands are important criteria for the selection and design of chelating polymers with substantial stability for the selective removal of heavy-metal ions. Chelating ion-exchange

resins with specific chelating groups attached to polymers have found extensive use in the separation and preconcentration of metal ions.^{2–7} Chelate-forming polymeric resins are capable of coordinating to different metal ions through reactive functional groups containing O, N, S, and P as donor atoms.^{8,9} These resins show preferential selectivity toward certain metal ions, which facilitates their use for the preconcentration and separation of trace metal ions from saline and nonsaline water. Chelating resins containing Schiff bases with multidentate coordination sites have been studied for their affinity and selectivity toward metal ions at appropriate pH.^{10,11} Although several chelating supports have been synthesized,^{4,8,12–15} styrene divinyl benzene resins have found practical applications because they can be easily loaded with a variety of organic ligands with various functional groups.^{1,4,16} A number of chelating resins containing carboxylic acid groups, such as ethylenediamine tetraacetic acid,¹⁷ propylene diamine tetraacetic acid,¹⁸ bicine,¹⁹ imino diacetic acid,²⁰ methacrylic acid,²¹ maleic acid functionalized XAD,²² and N-substituted diamides of malonic acid,²³ have been prepared and studied for their analytical properties. Bis-type resins exhibit significantly higher uptakes of metals than analogous monoresins for N-substituted amides of carboxylic acids. Recently, poly(styrene-*alt*-maleic acid)²⁴ and poly(maleic acid)²⁵ were synthesized and shown to coordinate with metals through two carboxylic groups

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Scheme 1 Reaction sequence.

pertaining to two different polymer chains; indicating intermolecular complexation.

However, linear polymers containing dicarboxylic acidic groups suffer from the disadvantage of being soluble in bases, and this restricts their use as sorbents to acidic aqueous media. As a continuation of our previous work in the development of chelating polymers,²⁶ here we report the synthesis and analytical characterization of a crosslinked styrene/maleic acid copolymer stable in acidic and basic media, the stability greatly enhancing its applicability. Both column and batch studies were performed for metal ions. The sorption capacity was found to be independent of the degree of crosslinking at lower percentages. The resin could be used several times without its efficiency being affected.

EXPERIMENTAL

Materials

All the chemicals used in this work were analytical-reagent-grade and were acquired from E. Merck (Mumbai, India) or Qualigens (Glaxo, Mumbai, India). Commercial maleic anhydride, dissolved in chloroform and filtered, was recrystallized to eliminate maleic acid. Styrene and divinylbenzene was washed with 10% aqueous sodium hydroxide to remove the inhibitor, and this was followed by washing with water until it was neutral. It was dried over anhydrous sodium sulfate and was further purified by vacuum distillation at 60°C. Standard stock solutions with 1000 ppm chromium(III), iron(III), nickel(II), copper(II), and lead(II) were prepared separately through the dissolution of requisite amounts of chromium nitrate, iron nitrate, nickel nitrate, copper sulfate, and lead nitrate in 0.1M of the corresponding acid.²⁷ Milli Q (Bedford, USA) ultrapure water was used throughout this work.

Preparation of the crosslinked styrene/maleic acid copolymers

The copolymers were prepared with styrene and maleic anhydride in a molar ratio of 1:1 and with xylene as a solvent, and the polymerization was carried out at 75°C with benzoyl peroxide (0.01%) as an initiator and divinyl benzene (5 and 10%) as a crosslinking agent²⁸⁻³⁰ (Scheme 1). The mixtures were heated at 75 ± 1°C under an inert atmosphere for approximately 6 h, and the polymer precipitates were separated by filtration. They are called XSMA5 and XSMA10. The resins were washed repeatedly with xylene to remove the unreacted monomers and were further purified by Soxhlet extraction with diethyl ether (~3 days) and then dried in a vacuum oven at 60°C to a constant weight. The copolymers were then hydrolyzed to convert the anhydride to an acid moiety by the treatment of the powdered polymers with 1N NaOH for 30 min. The linear copolymers were prepared similarly without the addition of a crosslinking agent and are called SMA in the following text.

Structural characterization

The IR spectra of the polymers were recorded from 400 to 4000 cm⁻¹ on a PerkinElmer 3100 IR spectrophotometer-3100 (Norwalk, USA). The surface area was determined with a surface area analyzer (Micromeritics, ASAP-2010, Norcross, Georgia). The X-ray diffraction patterns of the copolymers were recorded on an X-ray diffractometer (PW3020, Philips, Almelo, Netherlands (Cu K α radiation, 40kV voltage, and 20mA current). The range of diffraction angles (2 θ) was 10–40°, and the scanning speed was 0.05° (2 θ /s). The C and H contents were determined with an elemental analyzer (Elementar, Vario EL, Hanau, Germany). The carboxyl content in the copolymers was determined chemically by the titration of the carboxyl

groups against a standard base. For this purpose, a known amount (~1 g) of each dry polymer was hydrolyzed and swelled in acetone. Thereafter, the solution was titrated against previously standardized methanolic NaOH with phenolphthalein as an indicator. The carboxyl content was then calculated with the following equation:

$$\text{Carboxyl content} = \frac{(V_1 - V_2) \times N_1}{W \times 1000}$$

where V_1 and V_2 are the volume (mL) of NaOH consumed by the polymer and blank, respectively; N_1 is the normality of methanolic NaOH; and W is the weight (g) of the polymer used.

Swelling index

A known weight (~2 g) of fully dried XSMA was immersed in different solvents. After 24 h, the polymer was filtered and blotted dry. The swollen polymer was weighed. The swelling index was determined by the ratio of the weight of the swollen polymer to the initial weight of the resin.³¹

Thermal characterization

The thermal characterization was done using a DuPont 2100 thermal analyzer (Newcastle, USA) with a 910 differential scanning calorimetry (DSC) module under a static air atmosphere, and a 951 thermogravimetry module (TG) was used for recording traces in nitrogen atmosphere.

Analytical characterization

The concentration of metal ions such as Cr(III), Fe(III), Ni(II), Cu(II), and Pb(II) in solution both before and after chelation was determined using Flame Atomic Absorption Spectroscopy (FAAS) (GBC model 932AA, Victoria, Australia). The pH measurements were made with a Labindia (Toshniwal, India) pH analyzer with a glass electrode calibrated with Titrisol buffers

Analytical procedure

A batch equilibration technique was used to determine the optimum sorption conditions, such as the pH, adsorption time, and capacity of the sorbent. The chelating resin was equilibrated with suitable concentrations of metal ions. The resin was filtered, and the metal concentration in the filtrate was determined by atomic absorption spectroscopy (AAS). The concentrations of metal ions adsorbed by the solid phase was determined as follows:

$$N_f = \frac{(X - Y)}{Z}$$

where X is the initial amount of the metal ion, Y is the amount of the metal ion in the supernatant, N_f is the amount of the adsorbed metal ion, and Z is the amount of the chelating resin. Elution was carried out with 1N HCl/HNO₃, and the metal concentration in the eluent was determined by AAS. All adsorption experiments were carried out in triplicate to determine the precision of the method.

Optimum pH of the metal-ion uptake

The optimum pH of the metal-ion uptake was determined with a batch equilibration technique. Excess metal ions (50 mL, 30 μg/mL) were shaken with 100 mg of the resin for 2 h. The pH of the metal-ion solution was adjusted before equilibration over a range of 2–8 with a buffer solution. The resin was filtered off, and the concentration of the metal ion remaining in the filtrate was determined with AAS. Adsorption experiments were carried out in triplicate to determine the precision of the method.

Adsorption isotherms

The adsorption isotherm studies were carried out by 100 mg of XSMA5 being shaken with different concentrations of metal-ion solutions of Fe, Ni, Cu, and Pb at 30°C for 24 h. The solutions were then filtered, and the concentrations of the metals in the filtrates was determined by AAS.

Total sorption capacity

The total sorption capacity of the resin was determined by an excess of the metal-ion solution (100 mL, 50 μg/mL) being shaken with 100 mg of the resin for 24 h at the optimum adsorption pH at 30°C in a mechanical shaker to ensure complete equilibrium. The resin was filtered off, and the concentration of the metal ion in the filtrate was determined with AAS.

Resin stability test

The following conditions were used for the resin stability study: 100 mg of the resin was stirred with 100

TABLE I
Elemental Analysis

Sample name	Found (%)			Calcd (%)		
	C	H	O	C	H	O
SMA · 2H ₂ O	56.4	6.6	37.0	56.2	6.2	37.5
XSMA5 · 1H ₂ O	59.6	6.4	33.9	60.5	5.9	33.6

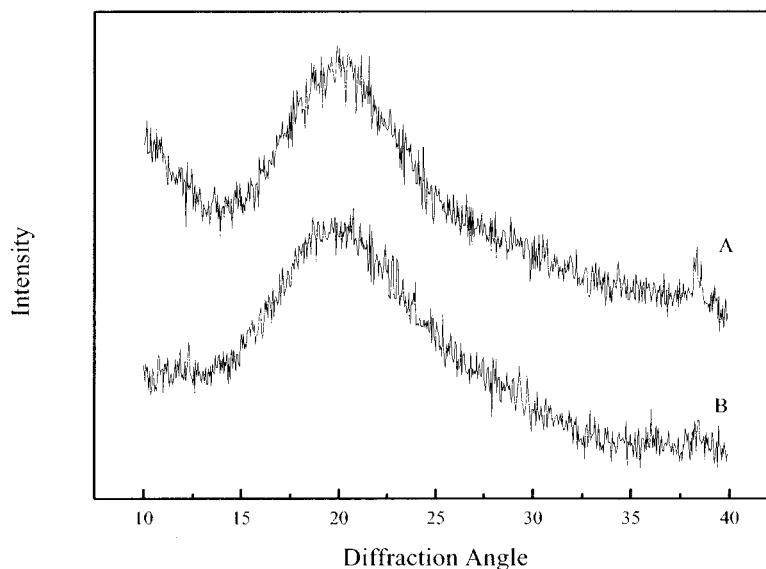


Figure 1 X-ray diffraction patterns of the copolymers: (A) SMA and (B) XSMA5.

mL of a 50 ppm solution for 6 h at 30°C. The elution operation was carried out by the resin being shaken with 20 mL of the eluent for 4 h to ensure complete equilibration. The metal content in the eluent was determined by AAS.

Column experimentation

The preconcentration test, resin stability test, and effect of the flow rate were determined in a glass column 5 mm in diameter. The column was packed with 100 mg of the chelating resin. A suitable aliquot (20 mL of 10 ppm) of a desired metal solution was passed through the resin at various flow rates to evaluate the effect of the flow rate and at 3 mL/min for the resin stability test and preconcentration test. The stripping of the metal was carried out with suitable eluting agents such as 2N HCl/HNO₃.

RESULTS AND DISCUSSION

Structural characterization

The data obtained from CH elemental analysis of SMA and XSMA5 are presented in Table I. The results are comparable to the theoretical values, indicating differ-

ent waters of hydration upon crosslinking. The X-ray diffraction patterns of the copolymers are shown in Figure 1. The polymers were amorphous, and there is no obvious difference in the diffraction patterns of the copolymers due to crosslinking. The surface areas of SMA and XSMA were 8.5 and 8.3 m²/g, respectively. The Fourier transform infrared spectrum of the copolymer after hydrolysis showed the characteristic absorption bands of the carboxylic groups at 1722 (C=O) and 1409 cm⁻¹ (C—O). Two additional bands at 1642 and 1448 cm⁻¹, assigned to an aromatic group, were also present, which indicated the presence of styrene groups. The carboxyl content of SMA, as determined by titration, was 0.011 equiv/g, lower than the value of 0.019 equiv/g, which was expected from the alternating structure. The carboxyl content was not affected by crosslinking. Similar results have already been reported for styrene/maleic acid copolymers by potentiometric and pH metric titration.³² Titration with a base such as NaOH or KOH resulted in titration of only half of the carboxylic acid groups; that is, the titration showed only one inflexion point. This was attributed to intermolecular hydrogen bonding or steric hindrance to neutralization of both carboxylic groups.³³

TABLE II
Swelling Index

Crosslinking (%)	Water	Toluene	Acetone	Tetrahydrofuran	Dimethylformamide
0	2.7	4.0	Soluble	Soluble	4.0
5	2.5	2.7	2.3	3.6	3.9
10	1	2.5	2.1	2.5	3.3

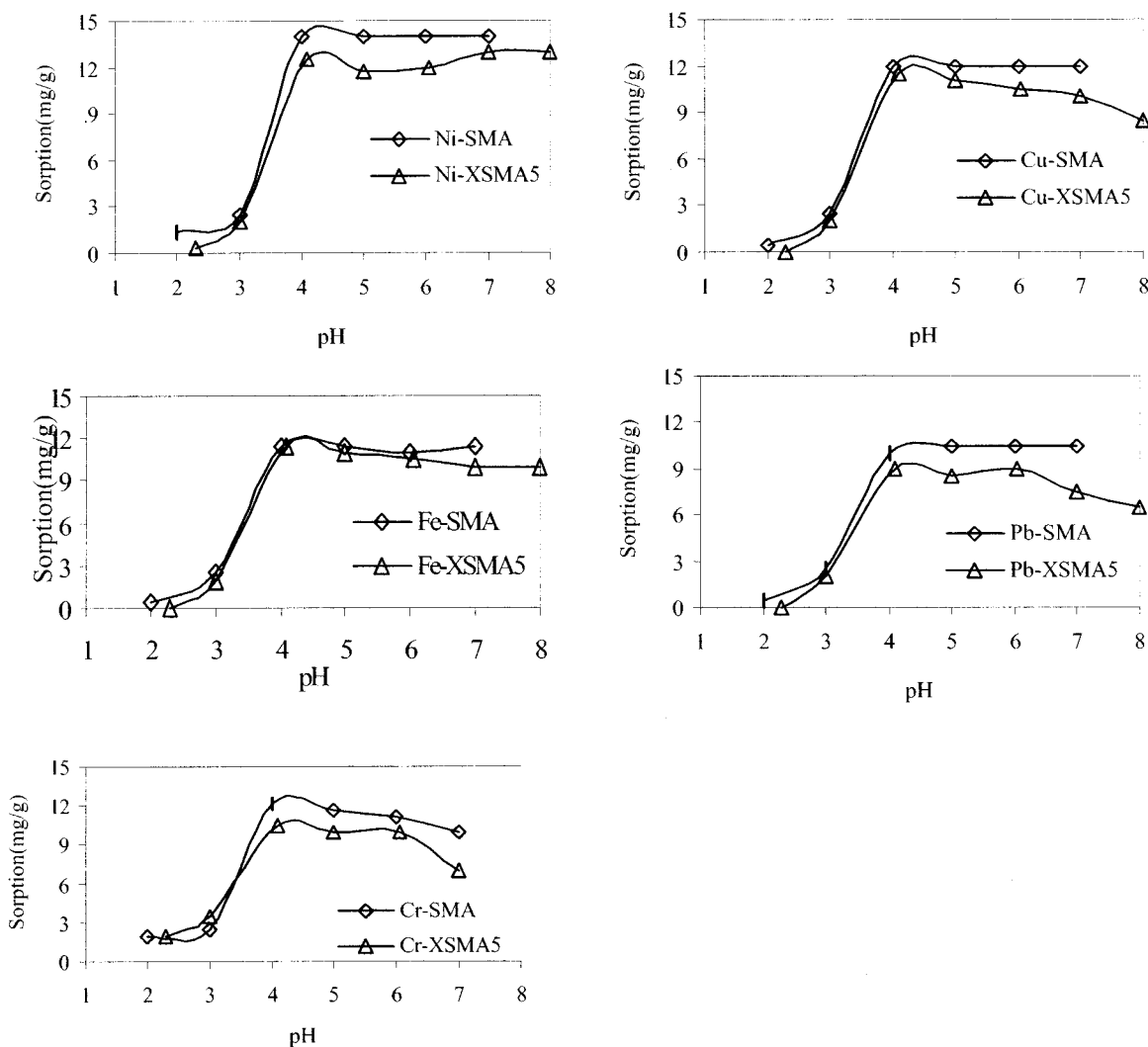


Figure 2 Relationship between the sorption and solution pH.

The swelling index of the polymer is reported in Table II. The results clearly indicate that the uptake of the solvent decreased with an increase in the crosslinking density. The resin became completely hydrophobic at 10% crosslinking, and so this composition could not be used for practical purposes.

Thermal characterization

The differential scanning calorimetry scans showed a shift in the baseline corresponding to the glass transition

at 124°C. The TGA scans revealed the high thermal stability of the polymer, with a weight loss of less than 20% at 300°C. This could be attributed to a loss of water during the formation of anhydride groups, followed by a partial loss of CO₂ from the polymer under 300°C.³⁰

Sorption of metal ions as a function of pH

The sorption behavior of some metals on the resins at different pH values was examined with a batch equil-

TABLE III
Sorption Capacity of the Chelating Resins at the Optimum pH

Metal	Optimum pH	Loading capacity of SMA		Loading capacity of XSMA5	
		mg/g	mmol/g	mg/g	mmol/g
Chromium	4-5	12.1	0.23	10.2	0.19
Iron	4-5	15.4	0.27	14.3	0.25
Nickel	4-5	16.5	0.28	14.2	0.24
Copper	4-5	16.9	0.26	15.4	0.24
Lead	3-4	10.3	0.05	8.8	0.04

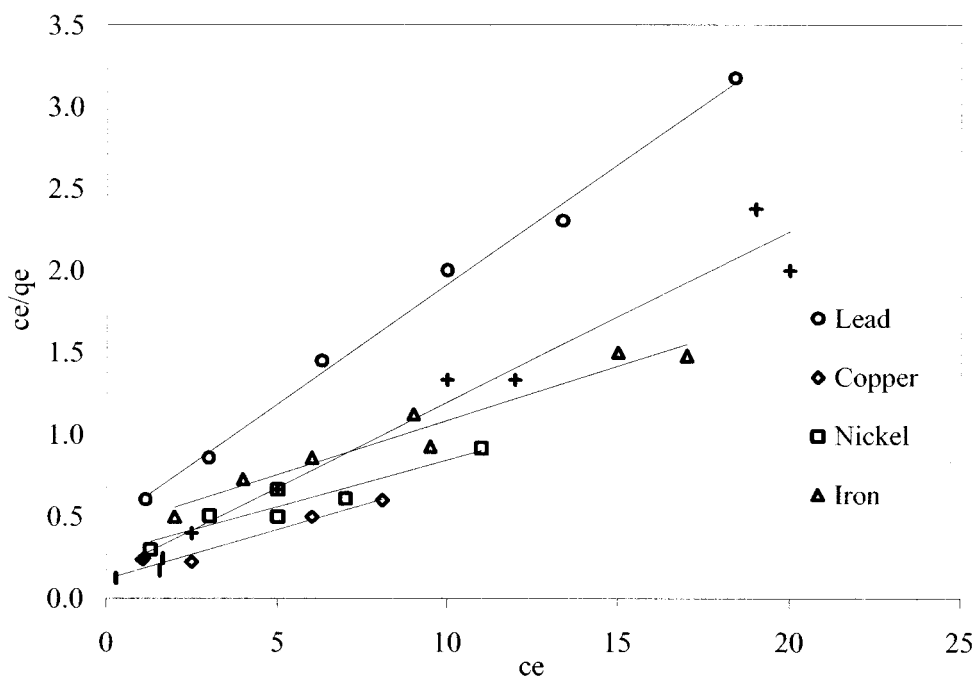


Figure 3 Langmuir isotherms for the adsorption of metals.

ibration technique. For this purpose, the resin (100 mg) was shaken with an excess solution of 30 ppm Cr(III), Fe(III), Ni(II), Cu(II), or Pb(II) for 2 h over the pH range of 2–8. After equilibrium, the concentration of each metal ion was determined by AAS. The pH of the metal test solution was measured during the sorption process. After equilibration with the resin, a decrease in the pH of the solution was observed that could be attributed to the release of protons from the resin.

In general, the adsorption of metal ions increased with an increase in pH, reaching a limiting value in each instance that was followed by a decrease in adsorption beyond the limiting value. Figure 2 shows the effect of pH on the sorption of different metal ions. The effect of crosslinking on the sorption is also shown. The sorption capacity decreased slightly with an increase in the crosslink density. A significant increase in the sorption was observed as the pH of the solution was raised from 2 to 4 for all the metals investigated. This could be related to the ionization and conformational behavior of the copolymer. The carboxylic groups on the copolymer exhibited two pK_a values, with pK_{a2} greater than pK_{a1} by three to five units. These copolymers were reported to undergo a transition from a compact form to an extended form upon the ionization of the primary carboxyl groups. The degree or percentage of metal sorption was calculated by the measurement of the metal content before and after the chelation.

Total sorption capacity

To determine the total sorption capacity of the resin, we determined the amount of metal ions sorbed per gram of the resin by immersing the required amount of the resin in the metal solution at the optimum pH and room temperature. The mixture was stirred with a mechanical shaker for 24 h, and this was followed by filtration. The metal-ion concentration in the supernatant and the residue was determined by AAS.

The capacity of the resin is an important factor for determining the amount of resin required for the complete removal of a specific metal ion from a solution. From the carboxyl content determination, it was expected to have a maximum capacity of 0.01 equiv/g, but the experimental loading capacity of the resin was much less (Table III). This could be attributed to the steric factor.

Adsorption isotherms

The adsorption data for heavy metals (Cr, Fe, Ni, Cu, and Pb) were analyzed by a regression analysis to fit

TABLE IV
Langmuir Model

Metal	Langmuir equation	K	b	R^2
Cr	$C_e/q_e = 0.16 + 0.10C_e$	0.69	9.56	0.96
Fe	$C_e/q_e = 0.42 + 0.06C_e$	0.15	15.15	0.94
Ni	$C_e/q_e = 0.27 + 0.06C_e$	0.21	17.39	0.88
Cu	$C_e/q_e = 0.12 + 0.06C_e$	0.52	16.53	0.95
Pb	$C_e/q_e = 0.42 + 0.15C_e$	0.23	7.77	0.99

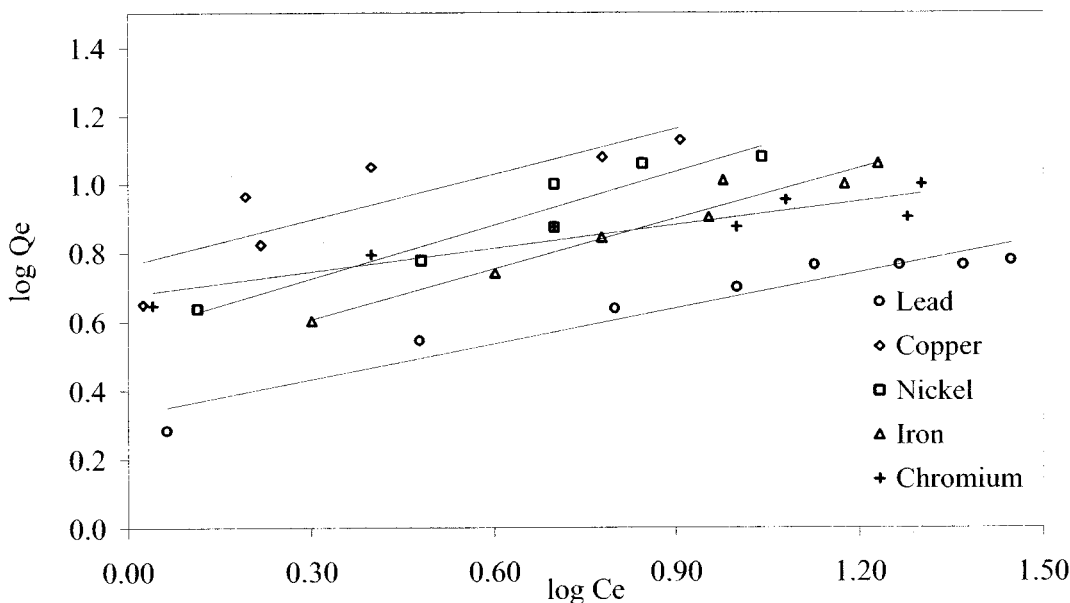


Figure 4 Freundlich isotherms for the adsorption of metals.

the Freundlich and Langmuir isotherm models. These data were plotted as a function of the amount of the heavy metal sorbed on the resin at equilibrium versus the heavy-metal concentration of the solution at equilibrium. The coefficients of these two models were computed with linear least-square fitting.

Langmuir isotherm

The Langmuir model was used to explain the observed phenomenon. The equilibrium data were analyzed with the following linearized equation:

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

where C_e is the equilibrium concentration (mg/L); q_e is the amount of metal adsorbed at equilibrium (mg/g); and k and b are the Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively. The linear plot (Fig. 3) of the four metal ions shows that the adsorption obeyed the Langmuir

model. The Langmuir constants were evaluated and are reported in Table IV.

Freundlich isotherm

The adsorption behavior was also confirmed with the Freundlich model:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

A linear plot (Fig. 4) of $\log q_e$ versus $\log C_e$ shows the applicability of the Freundlich model. The Freundlich constants k_f and n were calculated and are reported in Table V. Values of $1 < n < 10$ show the positive sorption of metal.³⁴ Correlation indices (R^2) were determined to compare the two models.

TABLE V
Freundlich Model

Metal	Freundlich equation	K	n	R ²
Cr	$\log q_e = 0.68 + 0.22 \log C_e$	1.98	4.55	0.86
Fe	$\log q_e = 0.46 + 0.49 \log C_e$	1.58	2.04	0.95
Ni	$\log q_e = 0.57 + 0.52 \log C_e$	1.77	1.92	0.92
Cu	$\log q_e = 0.76 + 0.44 \log C_e$	2.15	2.27	0.73
Pb	$\log q_e = 0.32 + 0.34 \log C_e$	1.38	2.94	0.93

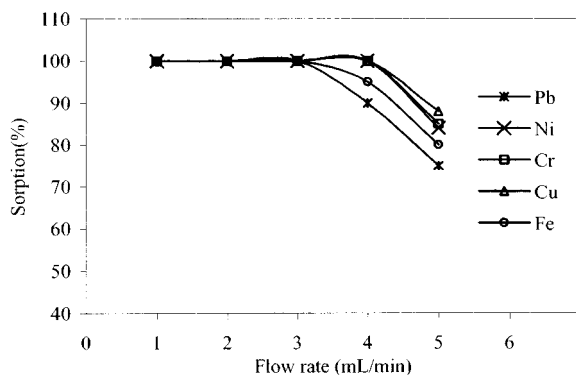


Figure 5 Effect of the flow rate on the metal sorption.

Effect of the flow rate

The dependence of the uptake of the metal on the flow rate was studied for Cr(III), Fe(III), Ni(II), Cu(II), and Pb(II) at the optimum pH, the flow rate of the solution being varied from 1 to 5 mL/min. The results are shown in Figure 5. At a flow rate greater than 3, there was a decrease in the sorption percentage.

Resin stability tests

To test the resin stability, we subjected the resin to several loading and elution column operations. The tests revealed that the sorbent was highly stable and could be used repeatedly. There was no decrease in the sorption capacity even after 15 cycles of operation (Fig. 6).

Preconcentration and recovery

Experiments on the recovery of metal ions from the resin were carried out with a column technique at their optimum pH. A 20-mL metal solution (10 ppm) at the optimum pH was passed through the column at a flow rate of 3 mL/min. The metals were recovered with 5 mL of 2N HCl. The eluent was then diluted to 20 mL before determination by AAS. The effect of interfering ions was also studied. Metal solutions of Cr, Fe, Ni, Cu, and Pb containing Na, Mg, and Ca ions (10 ppm each) as interferents were analyzed, and Table VI reports the recovery rates in the absence and excess of these foreign ions. The alkali and alkaline earth metals did not affect the recovery of the metal ions from the solutions. This suggests the use of this resin for trace concentrations from natural samples.

CONCLUSIONS

This article describes the synthesis, characterization, and analytical evaluation of a crosslinked styrene/

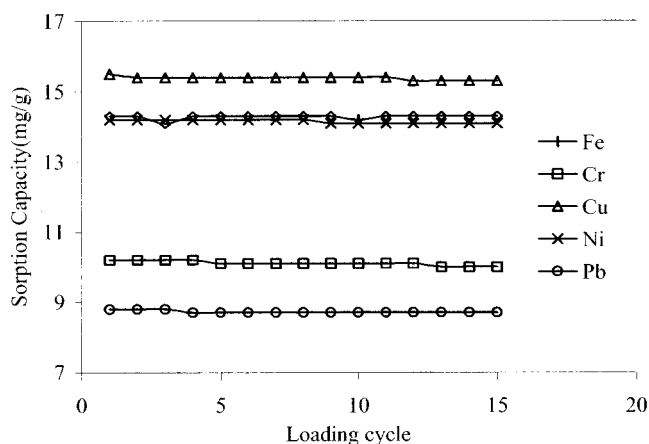


Figure 6 Effect of the loading and elution cycle on the sorption capacity.

TABLE VI
Preconcentration and Recovery of Metal Ions

Metal	Metal-ion concentration (mg/L)	Volume of eluent (mL)	Recovery (%) ^a	Recovery in the presence of Na, Mg, and Ca (10 ppm, %) ^a
Cr	10	5	98.3	98.0
Fe	10	5	97.7	97.5
Ni	10	5	96.6	96.3
Cu	10	5	99.3	99.1
Pb	10	5	98.5	98.5

^a The relative standard deviation was 0.1–2% for triplicate analysis.

maleic acid copolymer as an adsorbent. The crosslinked polymer was stable over the entire pH range as compared to an analogous linear polymer, which was soluble in a basic medium. The developed resin showed high metal uptake, and the sorbed metal could be readily eluted by 2N HCl/HNO₃. The metal-uptake data followed both Langmuir and Freundlich adsorption isotherms. The resin could be used several times without its efficiency being affected.

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