Chelating Resins Supporting Dithiocarbamate and Methylthiourea Groups in Adsorption of Heavy Metal Ions

A. LEZZI* and **S. COBIANCO**

Eniricerche S.p.A., Via Maritano, 26, 20097 S. Donato Milanese, Milan, Italy

SYNOPSIS

Two different sulfur atom containing functional groups were introduced into poly(styrene-*g*-ethylene glycols), PSR-ET(13)OH, consisting of a cross-linked polystyrene backbone grafted with linear poly(ethylene glycol) chains. Reaction of an amino derivative of the polymeric substrate with carbon disulfide and methylisothiocyanate produced new chelating resins of dithiocarbamate type, PSR-ET(13)CS_2Na, and methylthiourea type, PSR-ET(13)TU, respectively. The adsorption behavior of these resins was studied toward Hg(II), Cd(II), Cu(II), and Pb(II) ions in different experimental conditions. The order of metal adsorption for dithiocarbamate-supported resins was Hg(II) $>$ Pb(II) $\gg$ Cd(II) $>$ Cu(II) and for methylthiourea-supported resins was Hg(II) $\gg$ Cu(II) $>$ Cd(II) $\gg$ Pb(II). Different regeneration methods were performed with the dithiocarbamate and methylthiourea resins; the former was regenerated by complete mineralization of the metal complexes, the latter by treatment with a solution of 6 N HCl and 10% of thiourea.

INTRODUCTION

In a previous article[1] we described the synthesis and application of thiol-supporting poly(ethylene glycol)-graft-styrene-divinylbenzene copolymer in the purification of waste water from heavy metal ions. Two factors affect the chelating properties of the thiol groups supported on polymeric matrix: the presence and the length of the hydrophilic poly(ethylene glycol) chains and the pH of the metal containing solutions.

In the thiol-supporting resins we obtained the better compromise among the desirable properties of a chelating resin: high adsorption capacity for the metals of interest; high selectivity; fast kinetic, that is, rapid equilibration with metal containing solution. These properties depend on the structure of the resin, thus we tried to optimize its hydrophilic/hydrophobic balance by grafting poly(ethylene glycol) chains on the styrene-divinylbenzene copolymer.

The synthesis and the application in the removal of Hg(II), Cd(II), Pb(II), and Cu(II) ions from aqueous solutions of two different chelating resins supporting dithiocarbamate and methylthiourea groups are described.

In order to introduce these functional groups[2,3] into the resins, with the purpose of modifying their chelating properties, chemical modifications of the poly(ethylene glycol)-graft-styrene-divinylbenzene copolymer[1] were made by introducing primary amino groups.[4-6] The incorporation of the methylthiourea group, a neutral chelating agent, and the dithiocarbamate function, an anion-exchange group, was achieved by reaction of the amino-derivative copolymer with methylisothiocyanate and with carbon disulfide in alkaline medium, respectively. Both these functional groups contain nitrogen and sulfur atoms as potential coordinating sites to metal ions and have been widely used in analytical and biological fields.[7-10] They strongly collect a variety of metal ions from aqueous solutions with the notable exception of alkali and alkaline earth metal ions.

Many water-soluble and insoluble methylthiourea and dithiocarbamate-supporting resins were employed both in the liquid-phase polymer based re-

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 54, 889–897 (1994)
CCC 0021-8995/94/070889-09

tention (LPR) technique[11-14] and in column extraction procedures for concentrating trace metal ions from aqueous media. Polymeric matrixes usually employed are poly(ethyleneimine)s,[2] crosslinked polyacrylamide,[4,6] poly(ethyleneimine)-graft-styrene-divinylbenzene copolymer,[3] poly(vinylbenzylamine) beads, polyamine-polyurea resins, silica,[15,16] and porous glass beads. Regeneration methods for these resins have been investigated, but a disadvantage of dithiocarbamate-supporting resin is that the trace elements cannot be simply eluted and generally complete mineralization is necessary in order to recover the sequestrated metal ions. On the other hand methylthiourea ligand can be regenerated with an acid treatment.

EXPERIMENTAL

Materials and Methods

Merrifield Polymer Fluka was a styrene-2% divinylbenzene chloromethylated copolymer (1.6 meq Cl/g resin, 200–400 mesh). The bromo-poly(ethylene glycol)-graft-copolymer was prepared as previously described.[1] Ethylenediamine was purified as described in the literature.[17] Carbon disulfide and methylisothiocyanate were used as reagent grade. Dioxane was technical grade. Standard metal ion solutions were prepared with mercuric nitrate, cadmium chloride, lead nitrate, and copper chloride, all provided by Fluka. Lead, cadmium, and copper were estimated by inductive-coupled plasma spectrometry using an ICP AES, JY38 PLUS. Mercury was quantified by the cold vapor atomic-absorption technique (AAS) with a 5000 PE. The pH values were measured with a Metrohm 654 pH meter.

Preparation of PSR-ET(13)NH_2

PSR-ET(13)Br (3.5 g) was suspended in dioxane (50 mL) for 2 h under stirring. Then ethylenediamine (0.78 g) was added and the mixture was heated at 100°C for 24 h. The reaction mixture was then filtered and washed with a sodium chloride solution ($0.1M$) until the filtrate was free from ethylenediamine as indicated by the absence of blue coloration with ninhydrin reagent. Then the resin was washed with water, to remove NaCl, and with methanol and dried at 60°C under vacuum to constant weight.

Preparation of PSR-ET(13)CS_2Na

PSR-ET(13)NH_2 (2 g) was suspended in a mixture of dioxane : NaOH (1 N) (1 : 1) for 2 h under stirring. A fivefold molar excess solution of CS_2 (0.38 g) in ethanol was added dropwise and the mixture was heated at 30°C for 24 h. The excess CS_2 was removed by heating at 50°C for 4 h under the fume hood. Beads were filtered and exhaustively washed with water and methanol and dried at 60°C under vacuum to constant weight.

Preparation of PSR-ET(13)TU

PSR-ET(13)NH_2 (4 g) was suspended in a mixture of water : dioxane (1 : 1) for 2 h under stirring. A solution of methyl isothiocyanate (1.1 g) in methanol was added dropwise. The mixture was heated at 50°C for 24 h. The beads were filtered and exhaustively washed with water and methanol and dried at 60°C under vacuum to constant weight.

Preparation of PSR-CS_2Na

PSR-Cl (10 g) was suspended in dioxane (100 mL) for 2 h under stirring. Ethylendiamine (9.85 g) was added successively and the mixture was heated at 100°C for 24 h. The reaction mixture was then filtered, washed with a sodium chloride solution ($0.1M$) until the filtrate was free from ethylendiamine, washed with water, to remove the NaCl solution, and with methanol and dried at 60°C under vacuum to constant weight. The amino-graft-copolymer, PSR-NH_2 (4 g), was suspended in a mixture of dioxane : NaOH 1 N (1 : 1) for 2 h. A solution of carbon disulfide (0.76 g) in ethanol was added dropwise and the mixture was heated at 30°C for 24 h. The excess CS_2 was removed by heating at 50°C for 4 h under the fume hood. Beads were filtered and exhaustively washed with water and methanol and dried at 60°C under vacuum to constant weight.

Preparation of PSR-TU

PSR-NH_2 (5 g) was suspended in a mixture of water : dioxane (60 mL) (1 : 1) for 2 h under stirring. A solution of methyl isothiocyanate (3.74 g) in methanol was added dropwise and the mixture was heated at 50°C for 24 h. The beads were filtered and exhaustively washed with water and methanol and dried at 60°C under vacuum to constant weight.

Complexation with Metals

The complexation reactions of dithiocarbamate and methylthiourea-supporting resins were carried out with Hg(II), Cd(II), Cu(II), and Pb(II) ions by the batch equilibration method. Resins (0.5 g) were shaken with different metal solutions (50 mL) containing about 20 ppm of metal ions at the suitable pH for each metal ion. The extent of the complexation reaction was followed by withdrawing aliquots of the reaction mixture after 2 and 7 h of shaking and estimating the metal ion content left in the supernatant liquid by atomic absorption spectrometric technique. The complexation experiments were conducted at different pH values.

Recovery of Metal Ions from Resins

These experiments were performed after the conditions for maximum uptake of metal ions were found. A known amount of PSR-ET(13)CS_2Na and PSR-ET(13)TU was first allowed to chelate the maximum amount of metal ions under optimum pH conditions, then dithiocarbamate/lead complex (0.5 g) was stirred with 3 N HNO_3 (7.5 mL) for 2 h. The desorbed metal ions were collected and estimated by AAS. The resin after the treatment with HNO_3 was washed with dilute NaOH and water and again subjected to dithiocarbamylation. Methylthiourea/cupric complex (0.5 g) was treated with a 6 N HCl solution containing 10% of thiourea (50 mL) for 2 h at 30°C. The resin was filtered and the concentration of metal ions released was determined by AAS.

RESULTS AND DISCUSSION

Polymer Synthesis

The dithiocarbamate and methylthiourea functions were introduced, in the styrene-divinylbenzene co-

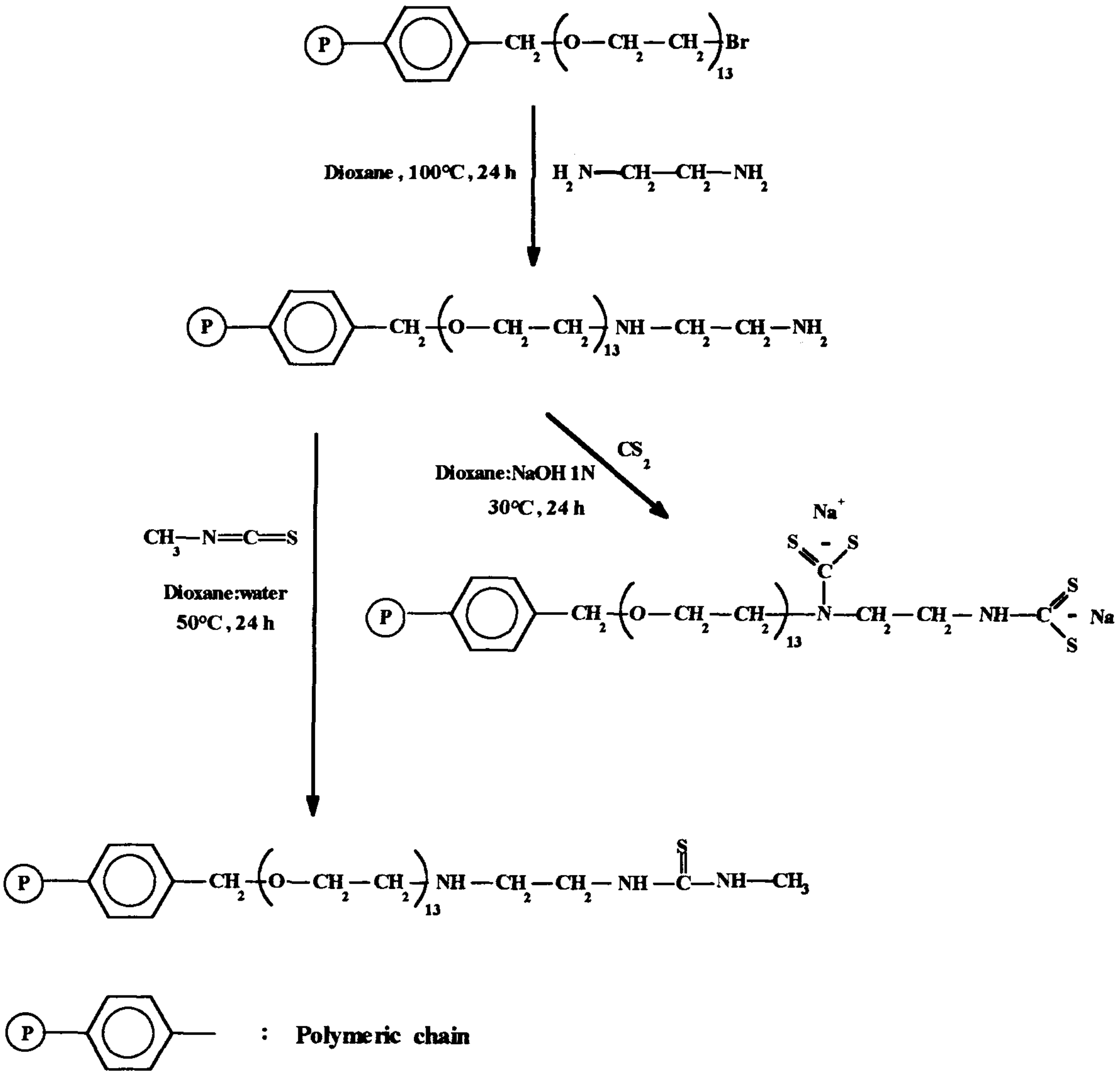

Figure 1 Synthetic pathway.

polymer grafted with poly(ethylene glycol) chains, by a two-step reaction (Fig. 1).

The first step of the synthetic pathway involves the incorporation of the amino groups at the end of the poly(ethylene glycol) chains by reaction of the PSR-ET(13)Br (bromo-derivative of the functionalized styrene-divinylbenzene copolymer, PSR-ET(13)OH) with ethylenediamine in dioxane, a good swelling solvent of the resin, at 100°C for 24 h. Chemical reactivity of the amino groups allowed the introduction into the resin of many functional groups, such as dithiocarbamate and methylthiourea ligands. The amino function content was estimated by elemental analysis (Table I).

Dithiocarbamate-Supporting Resins

The amino-poly(ethylene glycol)-graft-styrene-divinylbenzene copolymer, PSR-ET(13)NH_2, was converted to the corresponding dithiocarbamate beads, PSR-ET(13)CS_2Na, by treatment with a fivefold molar excess of carbon disulfide in a mixture of dioxane : NaOH, 1 N. In this way, the chelating groups were obtained as sodium salts. The dithiocarbamylation is depicted in Figure 1.

In order to demonstrate the importance of the hydrophilic chains in the metal ions complexing reaction in aqueous medium, the resins with the chelating groups directly bound to the backbone (PSR-CS_2Na) were also prepared.

In Table I the nitrogen and sulfur elemental analysis data and the number of equivalents of functional groups by weight (g) of resin calculated both from the nitrogen and sulfur contents of each resin were reported. Comparing the number of dithiocarbamate groups calculated from the nitrogen content and from the sulfur content for the resin PSR-ET(13)CS_2Na, note that the former is almost half of the latter. That is probably due to the reaction of the available secondary amino groups of the ethylendiamine bound to the hydrophilic chains in the dithiocarbamylation. In the PSR-CS_2Na, in which the ethylenediamine is directly bound to backbone, this effect was not observed and not even all the primary amino groups of the beads were converted in the dithiocarbamate function. We can suppose a lower steric hindrance and consequently a higher chemical reactivity of the secondary amino groups in the PSR-ET(13)NH_2 than in the PSR-NH_2.

Table I Elemental Analysis Data

Resins	Elemental Analysis N %	Elemental Analysis S %	Content of Functional Group (meq funct. Group/g) Calc. from % N	Content of Functional Group (meq funct. Group/g) Calc. from % S
PSR-NH_2	2.64	—	0.94	—
PSR-CS_2Na	2.47	3.21	0.88	0.50
PSR-TU	3.16	1.39	0.75	0.43
PSR-ET(13)NH_2	0.59	—	0.21	—
PSR-ET(13)CS_2Na	0.53	2.36	0.19	0.37
PSR-ET(13)TU	1.08	0.60	0.26	0.19

Methylthiourea-Supporting Resins

The conversion of the amino beads, PSR-ET(13)NH_2 and PSR-NH_2, in the methylthiourea beads, PSR-ET(13)TU and PSR-TU, was performed by treatment with methylisothiocyanate in a water : dioxane mixture at 50°C (Fig. 1).

In Table I we can observe two important data: PSR-ET(13)TU shows a higher conversion value of functional groups than PSR-TU; the number of functional groups calculated from the nitrogen content is higher than that calculated from the sulfur content, both for PSR-ET(13)TU and PSR-TU.

These results can be understood if it is assumed that the primary amino groups are less available in PSR-TU than in PSR-ET(13)TU and if we suppose that the secondary amino groups of the beads do not react at all because the methylisothiocyanate agent has a higher steric hindrance than the carbon disulfide molecule in the dithiocarbamylation.

Characterization of Resins

The structures of the dithiocarbamate and methylthiourea-supporting resins were confirmed by infrared (IR) spectra (Fig. 3). Elemental analysis data are also reported (Table I).

The IR spectra of the resins are complicated and only a few peaks could be assigned with reasonable certainty. In Figure 2 the IR spectra of (a) PSR-Cl, (b) PSR-ET(13)OH, (c) PSR-ET(13)Br, and (d) PSR-ET(13)NH_2 are reported.

The IR spectrum of PSR-Cl is characterized by a sharp band at 620 cm^{-1} assigned to the $\nu_{(C-Cl)}$ [Fig. 2(a)]. This band disappears in the spectrum of PSR-ET(13)OH, in which a broad band at 3400 cm^{-1} due to the $\nu_{(O-H)}$ and a very strong absorption at 1090 cm^{-1} due to $\nu_{(C-O-C)}$ of the hydrophilic poly(ethylene glycol) chains appear [Fig. 2(b)].

By treatment of PSR-ET(13)OH with phosphorus tribromide, the peak of the stretching absorption band of hydroxyl group disappears and a sharp absorption appears at 608 cm^{-1} due to the $\nu_{(C-Br)}$. Amino groups introduced by reaction of PSR-

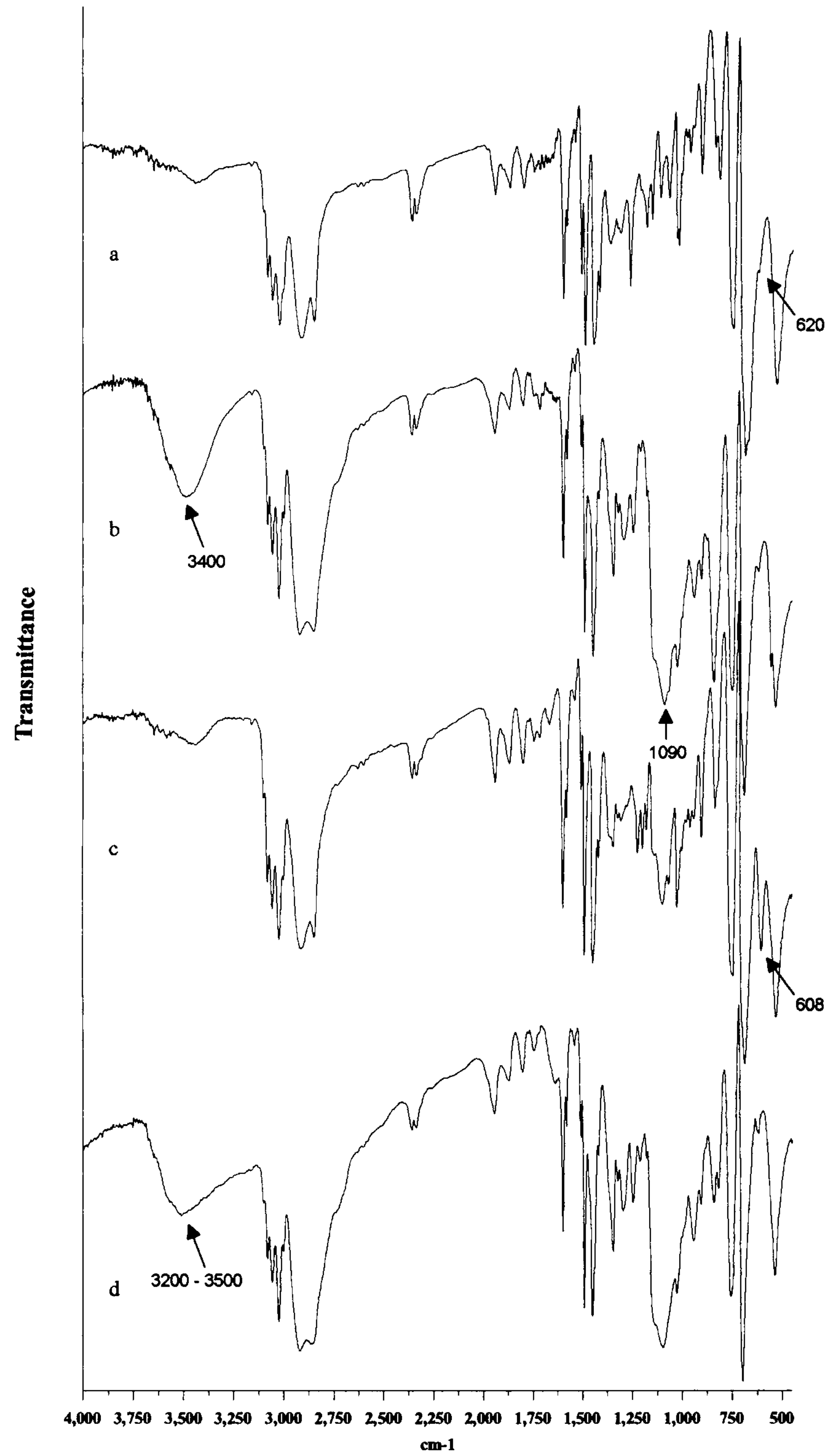

Figure 2 IR spectra (KBr disk) of (a) PSR-Cl, (b) PSR-ET(13)OH, (c) PSR-ET(13)Br, and (d) PSR-ET(13)NH_2.

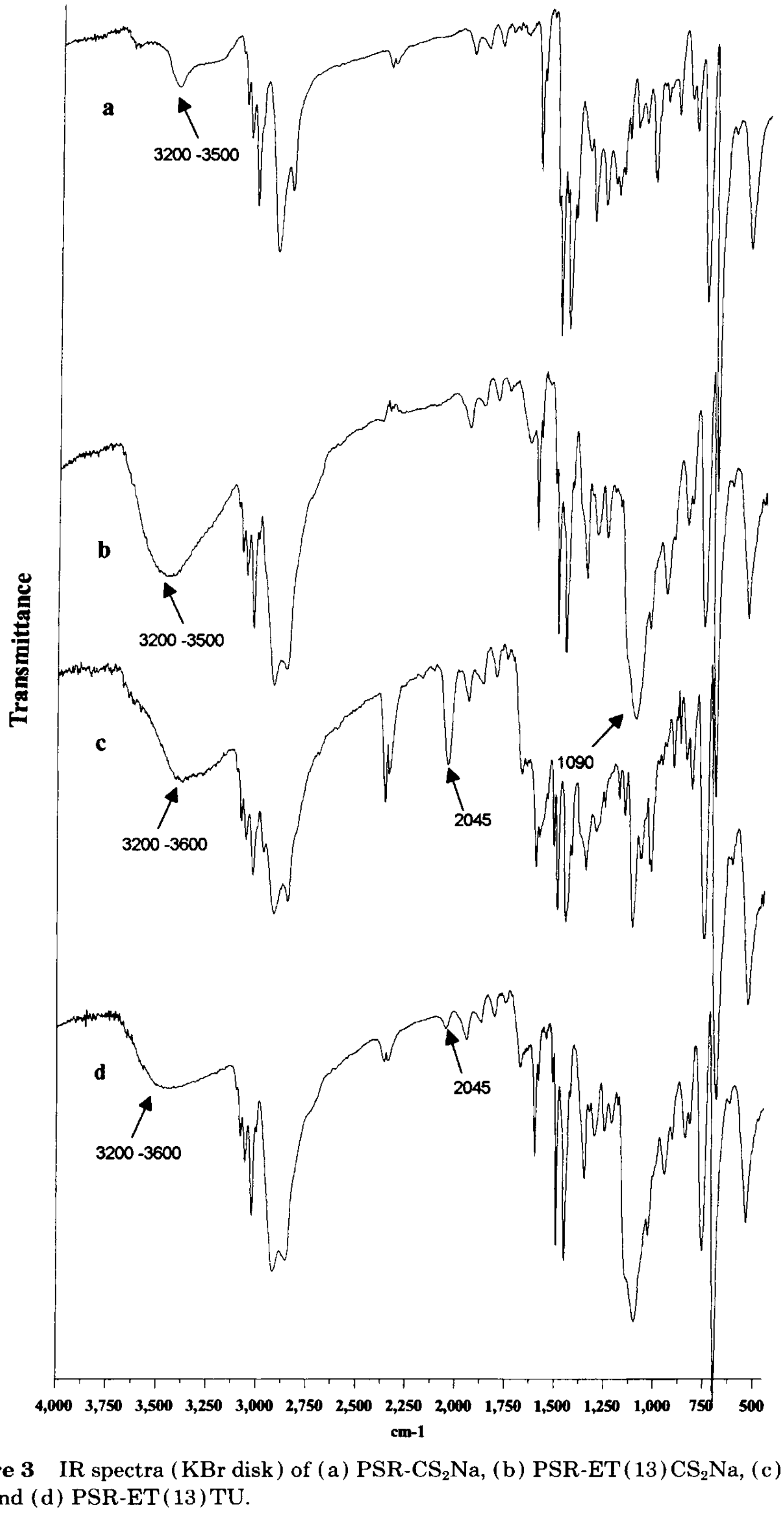

Figure 3 IR spectra (KBr disk) of (a) PSR-CS_2Na, (b) PSR-ET(13)CS_2Na, (c) PSR-TU, and (d) PSR-ET(13)TU.

ET(13)Br with ethylendiamine are characterized by the disappearance of the peak at 608 cm^{-1} and the appearance of a broad band in the region at 3200–3500 cm^{-1} due the stretching of the primary and secondary amino groups.

The IR spectra of the chelating resins with the functional groups supported at the end of the poly(ethylene glycol) chains and directly bound to the polymer matrix are reported in Figure 3.

The spectrum of PSR-ET(13)CS$_2$Na presents a broad band in the region 3200–3500 cm^{-1} due to the stretching of amino groups like the spectrum of PSR-CS$_2$Na. PSR-ET(13)CS$_2$Na is also characterized by the strong absorption at 1090 cm^{-1} due to the poly(ethylene glycol) chains.

The spectrum of the PSR-ET(13)TU showed a broad band at 3200–3600 cm^{-1} assigned to $\nu_{(N-H)}$ of secondary amino groups, a strong peak at 1090 cm^{-1} due to $\nu_{(C-O-C)}$, and a weak sharp band at 2045 cm^{-1}, which is probably assigned to an overtone absorption of the (C$=$S) group. This absorption at 2045 cm^{-1} has a higher intensity in the spectrum of PSR-TU because its number of functional groups by weight of resin is higher than in PSR-ET(13)TU.

Chelating Properties of Resins

Effect of Poly(ethylene glycol) Chains

The investigations on adsorption capacities of dithiocarbamate and methylthiourea-supporting resins were performed on dilute metal ions solutions by the batch equilibration technique. Chelating experiments were performed with 1% by weight of each resin in 50 mL of a solution containing about 20 ppm of metal ion at different pH values. The influence of three important factors on the chelating properties of the resins was considered: the nature of the chelating group, its mobility and accessibility toward metal ions, and the pH of metal solutions.

In order to show the importance of the poly(ethylene glycol) chains grafted to the resins in the metal chelating reactions, we compared the adsorption capacity of the resins containing the hydrophilic chains with the resins having the chelating group directly bound to the main polymeric chain. The adsorption results reported in Table II show that the amount of chelated Hg(II) and Pb(II) ions by PSR-ET(13)CS$_2$Na was higher by three orders of magnitude than that chelated by PSR-CS$_2$Na. After 7 h of treatment, the functionalized resin reduces the amount of Hg(II) ions in solution from 18.1 ppm to less than 0.005 ppm and the amount of Pb(II) ions from 19.5 to 0.05 ppm.

Poly(ethylene glycol) chains enhance the hydrophilic character of ligands; act as spacers reducing the steric hindrance exercised by the matrix on the ligands; and furthermore, due to their flexibility, they improve the mobility and the accessibility of the ligands, which are able in this way to catch metal ions in a more efficient way.

On the other hand PSR-CS$_2$Na and PSR-ET(13)CS$_2$Na present almost the same complexation behavior toward Cd(II) and Cu(II) ions. The former reduces the amount of Cd(II) and Cu(II) ions from 19.3 and 18.6 ppm to 2.4 and 0.13 ppm, respectively, and the latter to 1.3 and 0.18 ppm (Table II). A greater mobility of Cu(II) and Cd(II) than Hg(II) and Pb(II), and a faster kinetic of adsorption, qualitatively speaking, can be invoked to explain (in the time of our observation) the same chelating behavior toward Cu(II) and Cd(II) of resins with and without poly(ethylene glycol) chains. When the methylthiourea-supporting resins are used, the effect of poly(ethylene glycol) chains is again more remarkable for Hg(II) uptake than for Cd(II) and Cu(II) (Table III). PSR-ET(13)TU reduces the amount of Hg(II), Cd(II), and Cu(II) ions from 18, 19.3, and 18.6 ppm to 0.02, 1, and 0.14 ppm; and PSR-TU to 0.24, 3.1, and 0.10 ppm, respectively. The methylthiourea group does not show any chelating affinity for Pb(II) ions.

Table II Comparison of Adsorption Capacity of PSR-CS$_2$Na and PSR-ET(13)CS$_2$Na

Sample	Ethylene Oxide Units	Metal	pH	Mother Solution (ppm)	After 2 h (ppm)	After 7 h (ppm)
PSR-CS$_2$Na	0	Hg^{2+}	4.5	18.1	8.80	8.30
PSR-ET(13)CS$_2$Na	13	Hg^{2+}	4.5	18.1	1.90	<0.005
PSR-CS$_2$Na	0	Pb^{2+}	5.6	19.5	16.90	16.20
PSR-ET(13)CS$_2$Na	13	Pb^{2+}	5.6	19.5	0.10	0.05
PSR-CS$_2$Na	0	Cd^{2+}	9.1	19.3	1.10	2.40
PSR-ET(13)CS$_2$Na	13	Cd^{2+}	9.1	19.3	0.90	1.30
PSR-CS$_2$Na	0	Cu^{2+}	7.6	18.6	0.47	0.13
PSR-ET(13)CS$_2$Na	13	Cu^{2+}	7.6	18.6	0.44	0.18

Table III Comparison of Adsoption Capacity of PSR-TU and PSR-ET(13)TU

Sample	Ethylene Oxide Units	Metal	pH	Mother Solution (ppm)	After 2 h (ppm)	After 7 h (ppm)
PSR-TU	0	Hg^{2+}	2.3	18.0	1.10	0.24
PSR-ET(13)TU	13	Hg^{2+}	2.3	18.0	0.23	0.02
PSR-TU	0	Pb^{2+}	5.6	17.1	17.10	16.50
PSR-ET(13)TU	13	Pb^{2+}	5.6	17.1	17.00	17.00
PSR-TU	0	Cd^{2+}	7.0	19.3	2.50	3.10
PSR-ET(13)TU	13	Cd^{2+}	7.0	19.3	0.70	1.00
PSR-TU	0	Cu^{2+}	7.6	18.6	0.10	0.10
PSR-ET(13)TU	13	Cu^{2+}	7.6	18.6	0.18	0.14

Effect of pH

The dependence of pH on the reactivity of dithiocarbamate and methylthiourea-supporting resins toward Hg(II), Pb(II), Cd(II), and Cu(II) ions was also investigated.

If the affinity of a chelating group toward a metal ion is very strong the metal complex formation is not influenced by the pH. In fact Hg(II) ions uptake both from dithiocarbamate and methylthiourea-supported resins does not change by increasing pH (Figs. 4, 5).

On the other hand the pH of the metal solution greatly influences the chelating properties of PSR-ET(13)CS_2Na and PSR-ET(13)TU toward Cd(II) and Cu(II) ions. When PSR-ET(13)CS_2Na is used (Fig. 4) Cd(II) uptake remains constant (at low levels) at $pH < 6$; for $pH > 6$ the amount of chelated ion increases rapidly while the amount of Cu(II) uptake increases gradually from pH 5 to 7.6. The dithiocarbamate group acts as a weak acid; thus in slightly acidic conditions it is present in solution both as dithiocarbamic acid and in the delocalized anion forms. Probably only the latter species is active in the Cd(II) and Cu(II) complexes formation. The suitable pH values for the complexation of Cd(II) and Cu(II) ions with PSR-ET(13)CS_2Na are 9.1 and 7.6, respectively.

When PSR-ET(13)TU was used, Cu(II) and Cd(II) ions uptake increased gradually with increasing pH (Fig. 5) and the more suitable pH values were 7 for Cd(II) ions and 7.6 for Cu(II) ions. The alkaline medium makes the methylthiourea groups more available for complexation.

Methylthiourea ligand has two donor atoms, the nitrogen and the sulfur atoms, but in acidic conditions the amino groups are fully protonated and so they are not active in the complexation.

The pH of metal ion solutions also influences the chemical stability of dithiocarbamate resin. In acidic media, dithiocarbamate resin is less stable than methylthiourea resin and it decomposes to give carbon disulfide and the protonated amine resin.

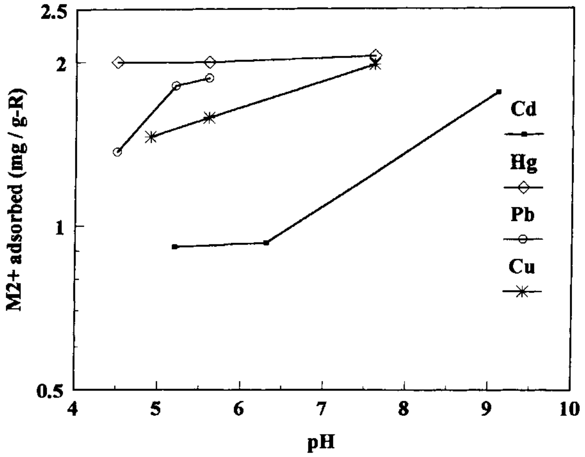

Figure 4 Effect of pH on the adsorption of metal ions with PSR-ET(13)CS_2Na resin (0.5 g) in 50 mL of metal ion solution at room temperature and after 7 h of treatment.

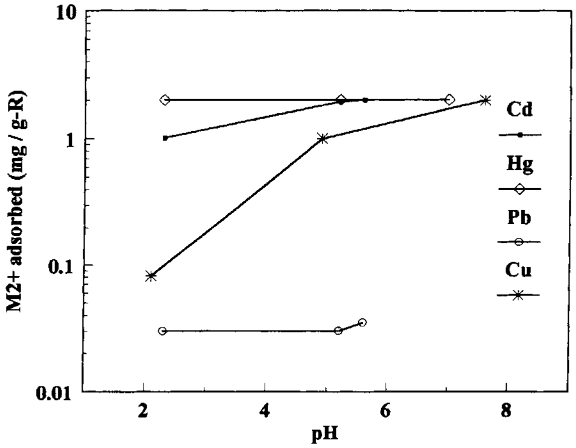

Figure 5 Effect of pH on the adsorption of metal ions with PSR-ET(13)TU resin (0.5 g) in 50 mL of metal ion solution at room temperature and after 7 h of treatment.

Therefore adsorption experiments with dithiocarbamate resins were carried out in slightly acidic conditions or in alkaline conditions.

Regeneration of Resins

Because of different chemical stabilities of dithiocarbamate and methylthiourea resins, two different regeneration methods must be employed in the removal of adsorbed metal ions. From methylthiourea resin, metal ions could be selectively removed by treatment with an acidic solution of thiourea, a water-soluble chelating agent of heavy metal ions. Cu(II) ions were completely desorbed.

Regeneration of dithiocarbamate resin was investigated for the Pb(II) complex by treatment with concentrated acid (HNO_3). Metal ions were desorbed quantitatively and the acid-treated resin, which liberated carbon disulfide, was neutralized and again subjected to dithiocarbamylation.

CONCLUSIONS

1. Chelating resins containing dithiocarbamate and methylthiourea groups were synthesized and employed in the removal of heavy metal ions from water.
2. Resins were prepared by reaction of a styrene-divinylbenzene macromolecular beads grafted with poly(ethylene glycol) chains with ethylendiamine, followed by reaction with carbon disulfide in alkaline medium or methylisothiocyanate.
3. The results obtained from the chelating experiments performed with dithiocarbamate-supporting resins, PSR-ET(13)CS_2Na and PSR-CS_2Na, show that the hydrophilic chains have a remarkable effect in the complexation of Hg(II) and Pb(II) ions, but they have no effects in the complexation of Cd(II) and Cu(II) ions. It is likely due to the different sizes of the ions, Cd(II) and Cu(II) ions are smaller than Hg(II) and Pb(II) ions, that can easily penetrate the pore of the resin and are easily chelated.
4. PSR-ET(13)CS_2Na can reduce the amount of Hg(II) and Pb(II) ions in solution from 18 and 19.5 ppm, respectively, to 0.005 and 0.05 ppm after 7 h of treatment.
5. Methylthiourea-supporting resins, PSR-ET(13)TU and PSR-TU, present almost the same chelating behavior toward Hg(II), Cd(II), and Cu(II) ions than dithiocarbamate resins, but they do not show any chelating affinity toward Pb(II) ions. PSR-ET(13)TU can reduce the amount of Hg(II) ions in solution from 18 to 0.020 ppm after 7 h of treatment.
6. Dithiocarbamate resins can be regenerated by complete mineralization of the metal complexes and then dithiocarbamylated again; methylthiourea resins can be regenerated by an acid treatment.

The authors acknowledge the Eni Fund for financial support. We thank E. Sobacchi and N. Sommariva who performed elemental and AAS analysis measurements.

REFERENCES

1. A. Lezzi, S. Cobianco, and A. Roggero, *J. Polym. Sci. A, Polym. Chem.*, to appear.
2. H. Tbal, M. Delporte, J. Morcellet, and M. Morcellet, *Eur. Polym. J.*, **28**(6), 671 (1992).
3. T. Saegusa, S. Kobayashi, K. Hayashi, and A. Yamada, *Polym. J.*, **10**(4), 403 (1978).
4. B. Mathew and V. N. Rajasekharan Pillai, *Polym. Bull.*, **26**, 603 (1991).
5. Yi-Yong Chen, Zhen-Mei Gu, X. M. Ren, and Xin-Liang Cheng, *J. Macromol. Sci.-Chem.*, **A24**(3/4), 319 (1987).
6. B. Mathew and V. N. Rajasekharan Pillai, *Polym. Int.*, **28**, 201 (1992).
7. C. K. Wagner, G. Hall, B. Riegel, J. De Virgilio, V. Kamath, and G. Germann, *J. Appl. Polym. Sci.*, **31**, 1797 (1986).
8. K. Minagawa and Y. Takirawa, *Anal. Chim. Acta*, **115**, 103 (1980).
9. J. F. Dingman Jr., K. M. Gloss, E. A. Milano, and S. Siggia, *Anal. Chem.*, **46**(6), 774 (1974).
10. K. Hiratani, Y. Onishi, and T. Nagakawa, *J. Appl. Polym. Sci.*, **26**, 1475 (1981).
11. K. Geckeler, G. Lange, H. Eberhardt, and E. Bayer, *Pure & Appl. Chem.*, **52**, 1883 (1980).
12. B. Ya. Spivakov, K. Geckeler, and E. Bayer, *Nature*, **315**, 313 (1985).
13. K. E. Geckeler, E. Bayer, B. Ya. Spivakov, V. M. Shkinev, and G. A. Vorob'eva, *Anal. Chim. Acta*, **189**, 285 (1986).
14. V. M. Shkinev, V. M. Gomolitskii, B. Ya. Spivakov, K. E. Geckeler, and E. Bayer, *Talanta*, **36**(8), 861 (1989).
15. D. E. Leyden, G. H. Luttrell, A. E. Sloan, and N. J. De Angelis, *Anal. Chim. Acta*, **64**, 97 (1976).
16. F. K. Chow and E. Grushka, *Anal. Chem.*, **50**(9), 1346 (1978).
17. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, New York, 1980.

Received February 24, 1994
Accepted May 2, 1994