Synthesis, Characterization, and Application of a New Chelating Resin Functionalized with Dithiooxamide

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ABSTRACT: Chloromethylated polystyrene-divinylbenzene has been functionalized with dithiooxamide. The resulting chelating resin (DTOA) has been characterized by elemental analyses, infrared spectroscopy, thermogravimetric analysis, and metal ion sorption capacities. It has been used for the preconcentration and separation of Cu(II), Zn(II), Cd(II), and Pb(II) prior to their determination by FAAS. Parameters such as the amount of the resin, effect of pH, equilibration rate, sorption and desorption of metal ions, and effect of diverse ions have been studied. The maximum sorption capacities found are 0.97, 0.12, 0.08, and 0.12 mmol g^{-1} for Cu(II), Zn(II), Cd(II), and Pb(II) at pH 6.0, 5.5, 1.0, and 5.5, respectively. The preconcentration factors are 100, 100, 50, and 50 for Cu(II), Zn(II), Cd(II), and Pb(II), respectively. Recoveries of the metal ions were 96 ± 5, 97 ± 6, 96 ± 5, and 96 ± 5 at 95% confidence level, whereas the limits of detection are 2.0, 1.3, 2.5, and 25.0 µg L^{-1} for Cu(II), Zn(II), Cd(II), and Pb(II), respectively. The calibration curves were linear up to 12 µg mL^{-1} (R^2 = 1.000), 2 µg mL^{-1} (R^2 = 0.998), 2 µg ml^{-1} (R^2 = 1.000), and 5 µg mL^{-1} (R^2 = 0.979) for Cu(II), Zn(II), Cd(II), and Pb(II), respectively. The reliability of the method has been tested by analyzing certified samples. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2281–2285, 2007

Key words: solid phase extraction; chelating resin; Cu(II); Zn(II); Cd(II); Pb(II); FAAS determination; microwave-assisted digestion; certified samples

INTRODUCTION

Accurate analysis of metal ions especially at trace level is one of the most difficult and complicated analytical tasks. Solvent extraction and solid phase extraction are the two most common methods for the preconcentration and separation of trace elements from various matrices. Solvent extraction has some disadvantages due to the use of excess solvent, which not only makes the method costly but is also contrary to the idea of green chemistry. During the past two decades, the use of chelating resin for metal ion preconcentration and separation has been considerably increased.[1–5] The basic advantages of most of the researches on chelating resin lie in the increased selectivity, high preconcentration factors, mechanical stability of the resin, reusability, and reproducibility. In fact, a good number of reports has been made from our groups.[6–11] For the quantification of metals at low concentrations, it is necessary to use very sensitive instrumental techniques or preconcentration methods, to achieve detection limits within the range of the available equipment.[12] Chelating resins are capable of preconcentrating metal ions selectively from a large aqueous volume and may be easily coupled with flame atomic absorption spectrometry (FAAS) detection to enhance its sensitivity.[13–15]

In the literature, many chelating resins are described that were synthesized using XAD,[1,16–18,19,20] amberlite-IRC,[21–23] chloromethylated PS-DVB[2,3,7,9] as the copolymer backbone. Generally, chelating ligands bound to copolymers by covalent bonds are much more resistant to external effects than those immobilized by simple impregnation, but the resulting metal retention capacities are only at medium level. Accordingly, various chelating resins have been synthesized on the basis of Pearson's hard and soft acids and bases (HSAB) approach and has been applied to various fields such as trace element analysis,[2] waste water treatment, precious metal recovery,[24] etc.

The combination of ''soft'' and ''borderline'' donor sites present in DTOA, bound to the copolymer by covalent linkage, is expected to result in a wider applicability and high exchange capacity. In this article, we report the synthesis of DTOA-functionalized chelating resin and its use in preconcentration and separation of Cu(II), Zn(II), Cd(II), and Pb(II) from aqueous solutions.

EXPERIMENTAL

Apparatus and reagents

A GBC Avanta atomic absorption spectrometer was used for absorbance measurement. The following conditions were used for determination of different metal

ions: Cu-lamp current 4 mA, wavelength 324.7 nm; Zn-lamp current 5 mA, wavelength 213.7 nm; Cd-lamp current 3 mA, wavelength 228.8 nm; and Pb-lamp current 3 mA, wavelength 283.3 nm. Elemental analysis was carried out in a Carlo-Erba CHNS-O EA 1108 elemental analyzer. The pH measurements were made with a Systronics digital pH meter (model 335). Infrared spectra were recorded on a 420 JASCO Fourier transform spectrometer. Thermogravimetric analysis was done on a Shimadzu TG50/DT50 instrument. A domestic Samsung CE 2933 microwave oven with a 2450 MHz frequency magnetron and 900 W maximum power was employed to carry out the digestion of different samples in a polytetrafluoroethylene (PTFE) reactor with 115 mL internal volume, 1-cm cell wall thickness, and hermetic screw caps.

Stock solutions of Cu(II), Zn(II), Cd(II), and Pb(II) used were obtained from E. Merck (Germany) and working solutions were prepared by appropriate dilutions. Dithiooxamide (BDH, UK), chloromethylated polystyrene resin (Fluka, Switzerland), 5-sulfosalisylic acid (SSA; BDH, Bombay), sodium fluoride (SRL, India) were used. All other chemicals used were of analytical reagent grade. The glass apparatus used were soaked in $4M$ nitric acid overnight and cleaned with double-distilled water before use. The following reference materials were analyzed: tomato leaves (1573, SRM, National Bureau of Standards), citrus leaves (1572, SRM, National Bureau of Standards), and pond sediment (NIES 2).

Microwave-assisted digestion of certified samples

Hundred to hundred and fifty milligrams of the samples was taken in a hermetically-sealed PTFE reactor. 1.5 mL HF (450 W, 2.5 min), 4 mL aqua regia (450 W, 2.5 min), and 3 mL H_2O_2 were used stepwise for complete digestion of the samples. An additional treatment with 5 mL saturated boric acid for 10 min in boiling water bath removed excess HF to avoid glass apparatus damage.

Synthesis of the resin

Air-dried chloromethylated polystyrene copolymer containing 2% divinyl benzene was used as the starting material. The copolymer bead (1 g, 200–400 mesh) was treated with 241 mg of dithiooxamide (DTOA) in the presence of sodium carbonate (400 mg) in *N,N*-dimethylformamide (DMF) to obtain a new orange-brown polymer. The new resin was washed thoroughly with DMF to remove excess ligand and then by $1M$ HCl to remove excess base. Finally, it was washed with double-distilled water, dried, and preserved at room temperature for further use.

Stability of the resin

Half gram of the resin was shaken with 100 mL of acid or alkali with different concentrations viz. 1–7M HNO_3, HCl, and NaOH solutions for 7 days. No significant change in nitrogen or sulfur content was observed after filtration and drying of the resin. The stability of the resin toward temperature was also studied thermogravimetrically.

Metal ion capacity as a function of pH

Batch technique was used taking metal ion in excess to the resin. Capacities for Cu(II), Zn(II), Cd(II), and Pb(II) were determined in the pH range 1–6. The lower pH (i.e., 1–3) was adjusted with 0.1M HCl, while pH 4–6 was adjusted with 0.2M sodium acetate buffer. To 100 mg of the chelating resin, 30 mL of M(II) [M = Cu, Zn, Cd, Pb] solution (1000 µg mL^{-1}) was added. The pH of the solution was adjusted to the desired value and equilibrated for 24 h. It was then filtered and washed with double-distilled water to remove the unbound metal ions. The sorbed metal ions were then eluted with suitable eluants and concentrations of the metal ions were measured.

Studies of various eluting agents for desorption

The resin (0.1 g) containing adsorbed metal ions were shaken with 30 mL of different concentrations of 0.01–2M HNO_3, 0.01–2M HCl, 1M SSA (sulfosalisylic acid), and 1M NaF. The amount of each of the desorbed metal ions was determined.

Column operation

A 130 mm × 10 mm glass column was used for the present work. Air-dried resin (1.5 g) was immersed in double-distilled water and allowed to swell for 24 h. The column was then packed with the swollen beads and the bed volume was 2 mL.

The sorption and recovery characteristics for Cu(II), Zn(II), Cd(II), and Pb(II) in the presence of various other metal ions were thoroughly studied. A 100 mL portion of the mixture of the test metal ion was allowed to flow through the resin column at the flow rate of 0.5 mL min^{-1}. The metal ion that was not sorbed was completely washed out by using solution of appropriate pH. The sorbed Cu(II), Zn(II), Cd(II), and Pb(II) ions were completely eluted by 1M SSA, 1M NaF, 2M HNO_3, and 2M HCl, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization of the resin

The resin was synthesized through the steps shown in Scheme 1. The nitrogen and sulfur contents of the
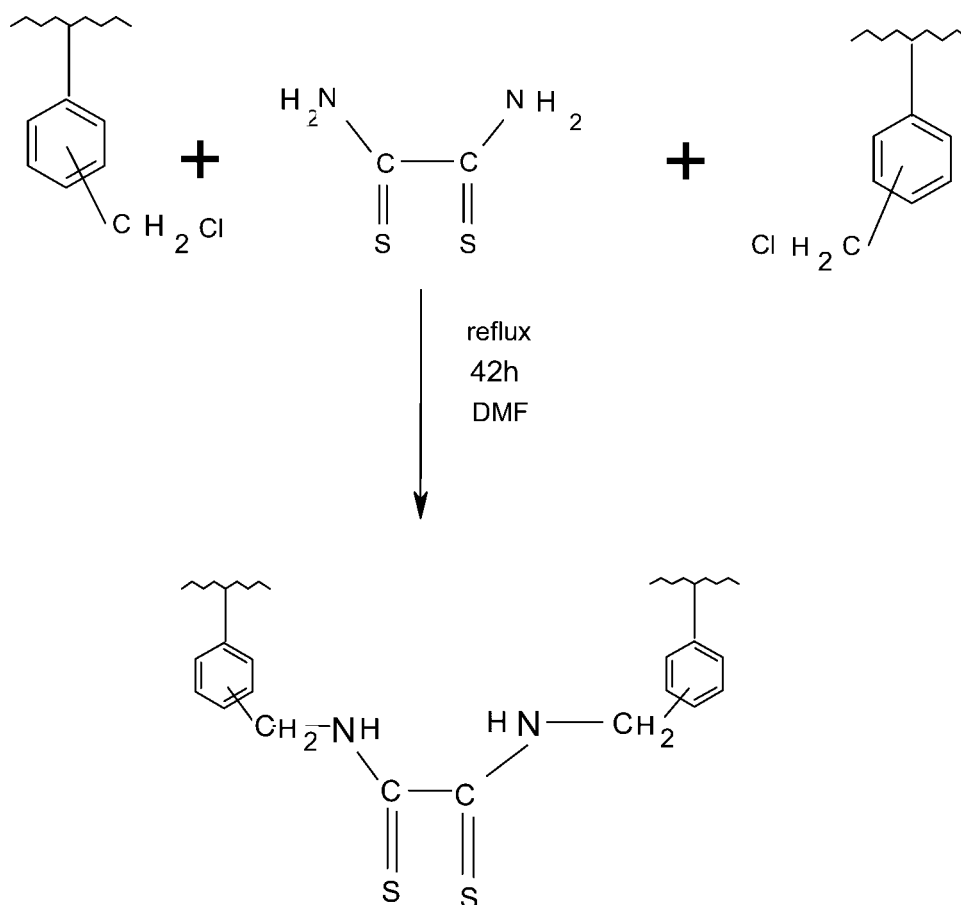
Scheme 1 Synthesis of DTOA resin.

resin were found to be 2.78 and 6.61%, respectively. Assuming that all the nitrogen and sulfur are part of the chelating group, the capacity should be 1.0 mmol g^{-1}, but actually it is 0.97 mmol g^{-1}. The lower value may be due to the rigidity of the polymeric matrix and inability of all the chelating groups to participate in chelation for steric restriction.

The IR spectra of the final resin were compared with those of the chloromethylated resin and chelating ligand. It is to be noted that FTIR spectra of polymers are complicated. Therefore, only a few peaks could be assigned with reasonable certainty. The band at 668 cm^{-1} for —C—Cl stretching had disappeared in the final resin. A few new bands appeared, e.g., those at 3295, 3211, and 3139 cm^{-1} may be due to —NH stretching. The presence of —NH and the absence of free —NH$_2$ groups in the resin were confirmed by nonaqueous titration. The band at 1198 cm^{-1} may be due to C=S stretching and at 2365, 1772, 1685, and 1384 cm^{-1} are due to dithiooxamide moiety.

The chemical stability of the resin was checked by treatment with 1–7M HNO$_3$, HCl, and NaOH for 7 days. No significant change in nitrogen or sulfur content was observed. Thus, the resin is fairly stable in acid and alkali. Thermogravimetric analysis showed that the resin is stable up to 210°C.

From the retention and elution cycle, it is found that the resin can be reused, with the same exchange capacity, even after 30 times regeneration without appreciable loss of ligating sites.

The $\tau_{1/2}$ for Cu(II), Zn(II), Cd(II), and Pb(II) are 15, 21, 23, and 27 min, respectively. This shows that the resin is suitable for column operation under low flow rate condition.
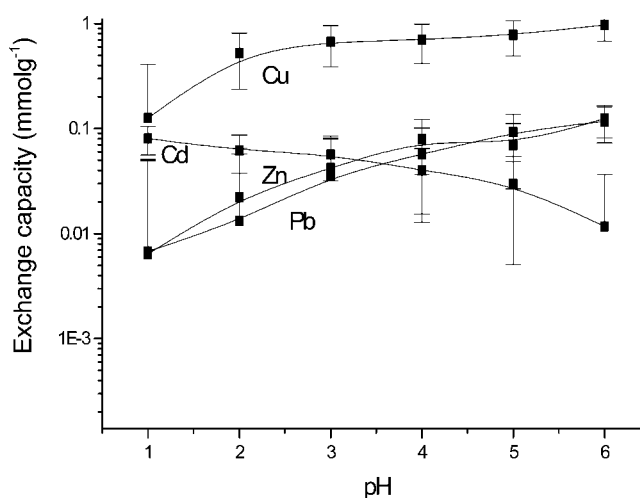
Figure 1 Uptake of M(II) with variation of pH.

TABLE I
Desorption of Cu(II), Zn(II), Cd(II), and Pb (II) by
Different Eluants

Eluants	% Recovery			
	Cu(II)[a]	Zn(II)[a]	Cd(II)[a]	Pb(II)[a]
0.01M HCl	19	68	22	59
0.1M HCl	44	82	35	74
1M HCl	79	100	48	87
2M HCl	99	99	68	99
0.01M HNO$_3$	21	88	36	57
0.1M HNO$_3$	52	93	53	68
1M HNO$_3$	77	99	79	93
2M HNO$_3$	90	100	99	99
1M SSA	101	nd	nd	nd
1M NaF	nd	98	nd	nd

nd: Not detected.
[a] The amount in each case was 100 μg.

Sorption and desorption of metal ions

The sorption behavior of the metal ions on the resin by batch method is shown in Figure 1. For Cd(II), sorption capacity decreases with increase in pH. The sorption at low pH may be due to the protonation of nitrogen atoms of the dithiooxamide moiety that subsequently attacks the negative species like $[CdCl_4]^{2-}$. In acidic solution, the metal ions may exist as negatively-charged chloro complex when HCl was added for pH adjustment. For Cu(II), Zn(II), and Pb(II), the sorption capacities increase with increase in pH. The effect of different eluants on desorption of metal ions is given in Table I.

Effect of diverse ions

Separation of 2 μg mL^{-1} each of Cu(II), Zn(II), Cd(II), and Pb(II) from several binary mixtures was carried out (Table II). The presence of macro amounts of diverse metal ions like alkali, alkaline earth, and the first transition series including mercury and silver did not interfere. Hence, attempts were made to separate Cu(II), Zn(II), Cd(II), and Pb(II) from ternary synthetic mixtures and some certified samples.

TABLE II
Separation of 2 μg mL^{-1} Each of Cu(II), Zn(II),
Cd(II), and Pb(II)

Foreign ions[a]	% Recovery			
	Cu(II)	Zn(II)	Cd(II)	Pb(II)
Hg(II)	95	94	98	96
Ag(II)	97	97	94	94
Co(II)	96	95	95	95
Fe(II)	98	97	97	97
Ni(II)	98	97	99	97
Na(I)	100	98	99	99
Ca(II)	98	98	99	98
Ba(II)	99	98	100	99

[a] In each case, the amount of the foreign ion added was 2000 μg.

Analytical figures-of-merit

The calibration curve for the determination of Cu(II), Zn(II), Cd(II), and Pb(II) was found to be linear up to 12 μg mL^{-1} ($R^2 = 1.000$), 2 μg mL^{-1} ($R^2 = 0.998$), 2 μg mL^{-1} ($R^2 = 1.000$), and 5 μg mL^{-1} ($R^2 = 0.979$), respectively. The detection limit was calculated as the concentration corresponding to a 3σ value of the blank signal and was found to be 2.0, 1.3, 2.5, and 25.0 μg L^{-1} for Cu(II), Zn(II), Cd(II), and Pb(II), respectively. The preconcentration factors are 100, 100, 50, and 50 for Cu(II), Zn(II), Cd(II), and Pb(II), respectively. The precision of the method was evaluated by five successive elution and retention cycles with 0.1 g of M(II) in 100 mL of solution. It was observed that the recoveries were 96 ± 5, 97 ± 6, 96 ± 5, and 96 ± 5 at 95% confidence level for Cu(II), Zn(II), Cd(II), and Pb(II), respectively.

Applications

Separation of Cu(II), Zn(II), and Pb(II) from ternary synthetic mixtures

Hundred microgram of each of Cu(II), Zn(II), and Pb(II) were mixed in 100 mL of double-distilled water and passed through the column after adjusting the pH to 5.5. At first, the sorbed Cu(II) was eluted completely by 20 mL of 1M SSA, then Zn(II) by 1M NaF, and finally Pb(II) by 2M HCl. The results of the recovery of the metal ions show 98, 96, and 97%, respectively.

Separation of Cu(I), Zn(II), Cd(II), and Pb(II) from certified samples

Various certified biological samples were digested in a microwave oven by the procedure described earlier. Then each metal ion, viz. Cu(II), Zn(II), Cd(II), and

TABLE III
Determination of Cu(II), Zn(II), Cd(II), and Pb(II)
in Certified Samples

Sample	Certified value (μg g^{-1})	Value obtained[a] (μg g^{-1})	% Error
Tomato leaves (100 mg)	Cu: 11 ± 1	Cu: 10.6 ± 1.1	3.6
	Zn: 62 ± 6	Zn: 61.3 ± 6.5	1.1
	Cd: 3	Cd: 3.2 ± 1.2	−6.6
	Pb: 6.3 ± 0.3	Pb: 6.0 ± 0.9	4.7
Citrus leaves (125 mg)	Cu: 16.5 ± 1.0	Cu: 16.3 ± 1.2	1.2
	Zn: 29 ± 2	Zn: 29.3 ± 1.5	−1.0
	Cd: 0.03 ± 0.01	Cd: 0.027 ± 0.051	10.0
	Pb: 13.3 ± 2.4	Pb: 13.5 ± 1.8	1.5
Pond sediment (130 mg)	Cu: 210 ± 12	Cu: 211.2 ± 13.1	−0.6
	Zn: 343 ± 17	Zn: 345.5 ± 16.3	−0.7
	Cd: 0.82 ± 0.06	Cd: 0.78 ± 0.08	4.9
	Pb: 105 ± 6	Pb: 107.2 ± 4.3	−2.1

[a] Average of five determinations.

TABLE IV
A Comparative Study of DTOA Resin with Some Other Resins

Active group	Exchange capacity (mmol g^{-1})				References
	Cu(II)	Zn(II)	Cd(II)	Pb(II)	
DTOA	0.97	0.12	0.08	0.12	Present work
Pyrogallol	0.07	0.069	0.046	0.032	16
Tiron	0.22	0.169	0.084	0.060	17
Quinalizarin	0.049	0.021	0.015	0.025	20
o-Vanillinthiosemicarbazone	0.013	0.023	–	0.009	5
o-Aminophenol	0.053	0.044	0.030	0.016	19
Pyrocatechol	0.092	0.028	0.049	–	18
o-Aminobenzoic acid	–	0.116	0.080	0.059	1
4-(2-Thiazolylazo)resorcinol	0.81	–	0.27	0.32	6
Acid red 88	0.012	0.016	0.011	–	3

Pb(II), was analyzed after separation through DTOA resin and the results are shown in Table III.

CONCLUSIONS

The sorption capacities of DTOA resin are compared with those of some other previously reported resins as shown in Table IV. No doubt this resin exhibits best exchange capacities for Cu(II) in comparison to all other resins in the list. It is clearly seen that, except for the exchange capacity of Zn(II) with Tiron and of Pb(II) with 4-(2-thiazolylazo)resorcinol, the exchange capacity of Cd(II) are comparable with DTOA resin.

Evidently, the resin is highly selective for Cu(II), Zn(II), Cd(II), and Pb(II) which may be due to the presence of soft S and borderline N atoms. Sulfur atom plays the key role in binding the metal ions and nitrogen helps in chelation. This resin can be very effective for the separation and preconcentration of the Cu(II), Zn(II), Cd(II), and Pb(II) ions from environmental samples.

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