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Adsorption of Some Metal Chelates on Polystyrene Divinyl Benzene Copolymers

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In the present work, adsorption of metal chelates (8-hydroxyquinoline and 1-nitroso-2-naphthol chelates) on the surface of polystyrene divinyl benzene copolymers (amberlite XAD-4 and diaion HP-20) resin were investigated by using flame atomic absorption spectrometry (FAAS) and scanning electron microscope (SEM). The optimal conditions for the quantitative adsorption and recovery of the metal ions on diaion HP-20 and amberlite XAD-4 were discussed.

Key Words: Amberlite XAD-4, Diaion HP-20, Preconcentration, Scanning electron microscope, Flame atomic absorption spectrometry, Adsorption, 8-Hydroxyquinoline, 1-Nitroso-2-naphthol, Trace metal.

INTRODUCTION

Studies on preconcentration and separation of the trace heavy metal ions are an important part of analytical chemistry[1–5]. Solvent extraction, cloud point extraction, electrodeposition, ion-exchange process, membrane filtration and solid phase extraction based on adsorption are important techniques for preconcentration and separation of trace metals[4–10].

Polystyrene-divinyl benzene copolymers have the lowest surface polarity and copolymers are not easily wetted and absorb little water because of their hydrophobic nature. They have an aromatic character and possess no ion-exchange capacity. The affinity of amberlite XAD and diaion HP resins for absorbable compounds correlates with their specific surface area, polarity and specific pore volume. Generally resins having the largest surface area are preferred (especially amberlite XAD-4 and diaion HP-20) with the same structure[11–14].

Use of polystyrene divinyl benzene copolymers including amberlite XAD and diaion HP resins with large surface area and macroporous structure convenient for preconcentration, isolation and chromatographic separation of various compounds is an improvement over activated carbon and other natural and artificial sorbents because they are more suitable for elution and are free from contamination risks.

Scanning electron microscope (SEM) is an important technique for the

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identification of surfaces. Also it can be used for identification of the adsorption of metal chelates on polystyrene divinyl benzene copolymers including XAD-4 and HP-20. In the present work, the adsorption of some metal chelates on polystyrene divinyl benzene copolymers was investigated by using scanning electron microscope (SEM) and flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

The instrumental detection system used was a Perkin-Elmer Model 3110 atomic absorption spectrometer. Atomic absorption measurements for model working were carried out in an air/acetylene flame. The operating parameters and other conditions were set as recommended by the manufacturer. Microstructural aspects of samples were studied employing a LEO 440 scanning electron microscope (SEM).

All solutions were prepared with deionized water. Otherwise stated analytical-grade acetone, acids, bases, salts and other chemicals used in this study were obtained from Merck, Darmstadt, Germany. Stock solutions of all the metals, containing 1000 mg/L (Merck, Darmstadt) were used. The chelating agents were 1-nitroso-2-naphthol (NN) and 8-hydroxyquinoline (oxine). The 1.0×10^{-2} M of the solutions of the ligands were prepared in a water/ethanol (75/25) mixture.

The buffers used were phosphoric acid/dihydrogen phosphate of pH 2, ammonium acetate/acetic acid of pH 4–6 and ammonium hydroxide/ammonium chloride of pH 8–10.

Diaion HP-20 and amberlite XAD-4 were purchased from Supelco, Bellefonte, US. They were (40–60 mesh) purified by washing with methanol, water, 1 M nitric acid in acetone, water, 1 M NaOH, water and acetone sequentially, in order to eliminate trace metal ions and other inorganic and organic contaminants in resin.

To 40–50 mL solution containing 5–20 μg of the metal ions was added 10 mL of buffer solution (desired pH between 2–10) and 1-nitroso-2-naphthol solution or 8-hydroxyquinoline. The resins were preconditioned by passing buffer solution. The metal/chelate solution was passed through the resin columns at a flow rate of 5 mL/min. The sample solution was permitted to flow through the column under gravity. After passing this solution completely, the columns were rinsed twice with 10 mL of water.

Prior to elution process for the desorption of the metal chelates from diaion HP-20 and amberlite XAD-4 colums, the SEM photographs of the metal chelates loaded resins were taken.

Then, the adsorbed metal chelates on the diaion HP-20 and amberlite XAD-4 columns were eluted with 8–10 mL portion of 1 M HNO_3 in acetone. The eluent was evaporated over a hot plate to near dryness. The residue was diluted to 2–5 mL with 1.0 M HNO_3. The eluent was analyzed for the determination of metal concentrations by flame atomic absorption spectrometer.

RESULTS AND DISCUSSION

In this pilot work, for the investigation of adsorption of the traces heavy metal ions on diaion HP-20 and amberlite XAD-4 resins, flame atomic absorption spectrometry and scanning electron microscopy have been used. The quantitative recovery values of metal ions were investigated by flame atomic absorption spectrometry. The identification of the surface of both the resins and metal-chelate loaded resins was performed by using scanning electron microscopy.

Studies with flame atomic absorption spectrometry

The optimal analytical conditions including pH of the model solutions, amounts of ligands, matrix effects, amounts of resins, etc. for the quantitative recovery of the metal chelates on diaion HP-20 and amberlite XAD-4 were examined in the model solutions that were containing analyte ions at trace levels by flame atomic absorption spectrometry. The analyte ions in this work were iron(III), copper(II), cobalt(II) and cadmium(II). The results are summarized in Table-1. The metal/8-hydroxyquinoline and metal/1-nitroso-2-naphthol chelates were quantitatively recovered from the amberlite XAD-4 and diaion HP-20 resins at pH 8 and 9, respectively.

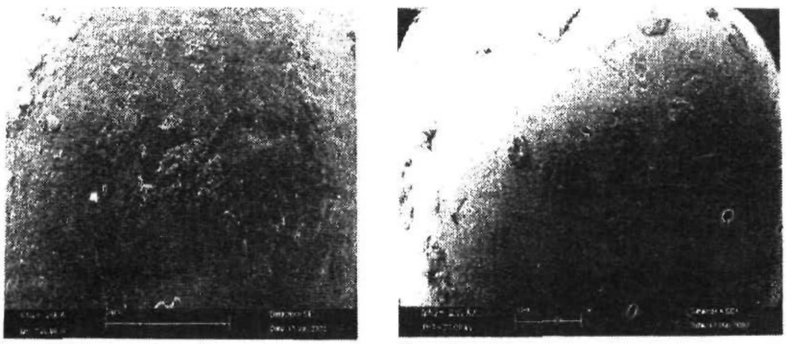
TABLE-1
OPTIMAL ANALYTICAL CONDITIONS FOR SOLID PHASE EXTRACTION ON AMBERLITE XAD-4 AND DIAION HP-20

Parameters	Optimal value	
	8-Hydroxyquinoline system	1-Nitroso-2-naphthol system
Resin	XAD-4	Diaion HP-20
pH	8	9
Concentration of ligand (10^{-3} M)	1.0	1.0
Resin amount (mg)	700	700
Sample volume (mL)	1000	1000
Eluent	1 M HNO_3 in acetone	1 M HNO_3 in acetone
Desorption volume (mL)	5–10	5–10
Matrix	No effects	No effects
Sample flow rate (mL/min)	5	5
Eluent flow rate (mL/min)	5	5

The recovery of metal chelates was not quantitative in the acidic pH of the sample solutions. The concentrations of the ligands for the quantitative recovery of analytes were 1.0×10^{-3} M. Also 700 mg of the XAD-4 and diaion HP-20 resins were enough for quantitative recovery. Higher concentrations of the alkaline and earth alkaline ions and some anions as matrix were not effected on the retentions of analytes on diaion HP-20 and amberlite XAD-4 resins. The results agree with the results of the studies of Elci *et al.*[14] and Soylak *et al.*[15]

Studies with scanning electron microscopy

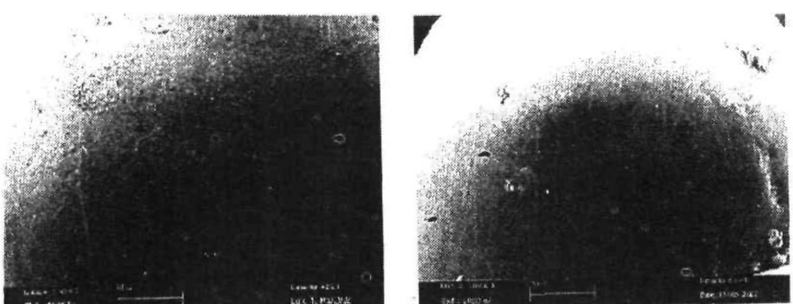
In order to investigate the adsorption of the metal chelates on the amberlite XAD-4 and diaion HP-20 resins, firstly, the scanning electron microscope (SEM) photographs of the polystyrene divinyl benzene copolymers were taken. These photographs were given for XAD-4 and HP-20 in Figs. 1a and 1b, respectively. As can be seen from these photographs, both amberlite XAD-4 and diaion HP-20 have some cavities from their surfaces. The surface areas of amberlite XAD-4 and diaion HP-20 resins were 750 m^2/g and 600 m^2/g, respectively[14, 15]. Because of their high surface area, amberlite XAD-4 and diaion HP-20 have been firstly used for the preconcentration, isolation and separation of the organic species from the various media.



(a) (b)

Fig. 1. Scanning electron microscopy photographs of (a) amberlite XAD-4; (b) diaion HP20

The SEM photographs of the metal chelates loaded amberlite XAD-4 and diaion HP-20 resin are also given in Figs. 2a and 2b, respectively. The cavities on the amberlite XAD-4 and diaion HP-20 resins were filled thereafter by metal



(a) (b)

Fig. 2. Photographs of scanning electron microscopy (SEM) of (a) amberlite XAD-4/metal-8-hydroxyquinoline chelates; (b) Diaion HP-20 /metal-1-nitroso-2-naphthol chelates

chelate adsorption process (Figs. 2a and 2b). Also the surfaces of both the metal chelates loaded resins are smooth and regular according to Figs. 1a and 1b.

In conclusion, the comparison of the scanning electron microscopy (SEM) photographs of the diaion HP-20 and Amberlite XAD-4 resins and metal chelates loaded resins can give some important information on the adsorption process of the metal chelates of the investigated resins. Also, the retention of the iron(III), copper(II), cobalt(II) and cadmium(II) ions on these resins was quantitative as 8-hydroxyquinoline and 1-nitroso-2-naphthol chelates.

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REFERENCES

1. M. Soylak, L. Elci and M. Dogan, *J. Trace Microprobe Tech.*, **19**, 329 (2001).
2. M.Y. Khuhawar and P. Das, *J. Chem. Soc. Pakistan*, **18**, 6 (1996).
3. M.G. Pereira and M.A.Z. Arruda, *J. Braz. Chem. Soc.*, **14**, 39 (2003).
4. A. Uzun, M. Soylak, L. Elci and M. Dogan, *Asian J. Chem.*, **14**, 1277 (2002).
5. C. Ortega, S. Cerutti, R.A. Olsina, M.F. Silva, L.D. Martinez, *Anal. Bioanal. Chem.*, 375, 270 (2003).
6. M.J. Ahmed and M. Mamun, *Talanta*, **55**, 43 (2001).
7. M. Soylak, S. Saracoglu, L. Elci and M. Dogan, *Kuwait J. Sci. Eng.* (2003) (in press).
8. M. Soylak, A.U. Karatepe, L. Elci and M. Dogan, *Turk. J. Chem.*, **27**, 235 (2003).
9. R. Lima, K.C. Leandro and R.E. Santelli, *Talanta*, **43**, 977 (1996).
10. M. Soylak, L. Elci and Dogan, *Coll. Spectro. Int.* (Ankara, Turkey), **31**, 55 (1999).
11. A.K. Saxena, A.K. Singh and S S. Sambi, *Anal. Chim. Acta*, **295**, 199 (1994).
12. R.G. Wuilloud, H.A. Acevedo, F.A. Vazquez and L.D. Martinez, *Anal. Lett.*, **35**, 1649 (2002).
13. M.C. Yebra, L. Rodriguez, L. Puig and A.A. Moreno-Cid, *Mikrochim. Acta*, **140**, 219 (2002)
14. L. Elci, M. Soylak and M. Dogan, *Fresenius J. Anal. Chem.*, **342**, 175 (1992).
15. M. Soylak, Y. Akkaya and L. Elci, *Int. J. Environ. Anal. Chem.*, **82**, 197 (2002).

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