

Investigation of Adsorption of Metal Ions on Polystyrene Divinyl Benzene Copolymers by Scanning Electron Microscopy and Flame Atomic Absorption Spectrometry

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The adsorptions of some metal ions as chelates or complexes on two polystyrene divinyl benzene copolymers (amberlite XAD-1180 and amborsorb 563) were examined for preconcentration-separation of trace heavy metal ions. Flame atomic absorption spectrometry (FAAS) and scanning electron microscope (SEM) were used in the identification of the adsorption of metal ions on the resins. The optimal analytical conditions for the quantitative adsorption and recoveries of the heavy metal ions on amborsorb 563 and amberlite XAD-1180 were discussed.

Key Words: Amberlite XAD-1180, Amborsorb 563, Preconcentration, Scanning electron microscope, Flame atomic absorption spectrometry, Adsorption, Chomotrope 2R, Ammine complexes.

INTRODUCTION

Solvent extraction, cloud point extraction, membrane filtration, ion exchange, electrodeposition, coprecipitation are some of the separation-preconcentration techniques for trace metal ions¹⁻⁷. Solid phase extraction based on adsorption is also an efficient separation/preconcentration technique^{8,9}. In the solid phase extraction based on adsorption of trace heavy metals, the analytes were converted to a suitable form including metal chelates or metal complexes. Then this form was adsorbed on an adsorbent with various procedures including batch or column techniques. The adsorbed metal forms were desorbed by a suitable eluting solution in a small volume. The metal concentrations in the effluent were determined by an instrumental technique like atomic absorption spectrometry, spectrophotometry, ICP-MS etc.⁹⁻¹¹

Activated carbon, silica gel, cellulose, chelating resins, alumina, titanium dioxide, C-18, C-70, chromosorb-102, microcrystalline naphthalene, chromosorb-105, amborsorb 563, fullerenes, amborsorb 572, sepiolite, diaion HP-20,

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etc.¹²⁻²⁰ are important solid phase extractors for trace metal ions in solid phase extraction studies. The main requirements with respect to solid phase materials are as follows: the possibility of extracting lots of metal ions in a wide pH range, fast and quantitative adsorption and easy elution, repeated usability and accessibility. Solid phase extraction has many advantages. It is a simple technique. Several analytes can be enriched and separated simultaneously. Furthermore, high preconcentration factors can be obtained by using solid phase extraction procedures^{9, 11, 13}.

The use of polystyrene divinyl benzene copolymers with large surface area and macroporous structure convenient for preconcentration, isolation and chromatographic separations 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.

Amberlite XAD-1180 resin is polystyrene-divinyl benzene (PS-DVB) copolymer having a hydrophobic nonpolar surface and is a member of amberlite XAD resin family. Its surface area and size are $650 \text{ m}^2 \text{ g}^{-1}$ and 20–60 mesh, respectively. It has the lowest surface polarity among XAD resins. Amberlite XAD-1180 is not easily wetted and absorbs little water because of its hydrophobic nature. It has an aromatic character and possesses no ion-exchange capacity¹⁰.

Ambersorb 563 is also a member of the ambersorb resin family. Its surface area and size are $600 \text{ m}^2 \text{ g}^{-1}$ and 20–60 mesh, respectively. Ambersorb 563 is also a partially pyrolyzed resin of sulfonated styrene/divinylbenzene copolymer, like other members of this family. It has also an aromatic character and possesses no ion-exchange capacity²¹.

In the present work, the adsorption of some metal chelates on polystyrene divinyl benzene copolymers (Chromotrope 2R coated amberlite XAD-1180 and ambersorb 563) were investigated by using scanning electron microscope (SEM) and flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

All solutions were prepared with deionized water. Otherwise stated analytical-grade acetone, mineral acids, bases, salts and other chemicals were obtained from Merck, Darmstadt, Germany. Stock solutions of all the metals, containing 1000 mg/L (Merck, Darmstadt) were used. The ligand, chromotrope 2R (Fig. 1) (0.2% (w/v)) was dissolved in water and prepared daily.

Sodium phosphate buffer (0.1 M) was prepared by adding an appropriate amount of phosphoric acid (Merck, Darmstadt) to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 M) were prepared by adding an appropriate amount of acetic acid (Merck, Darmstadt) to ammonium acetate solutions to result in solutions of pH 4–6 and ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia (Merck, Darmstadt) to ammonium chloride solution to result in solutions of pH 8–10.

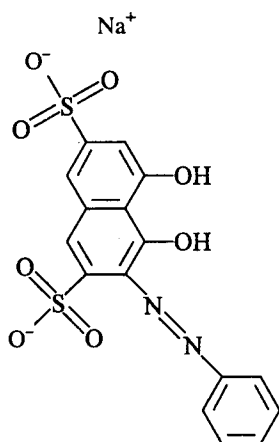


Fig. 1. Chromotrope 2R

Amberlite XAD-1180 and ambersorb 563 resin were purchased from Sigma Chem. Co., St. Louis, US and Supelco, Bellefonte, US, respectively. Amberlite XAD-1180 and ambersorb 563 were washed successively with methanol, water, $1 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone, water, $1 \text{ mol L}^{-1} \text{ NaOH}$ and water, sequentially, in order to eliminate trace metal ions and other inorganic and organic contaminants in the resin.

A bead size of resin 20–60 mesh was selected for the preconcentration procedure. Smaller resin particles could have improved retention capacity, but the flow rates of sample solution and eluent solution ought to have been reduced, with subsequent increase in preconcentration-separation time.

The instrumental detection system used was a Perkin-Elmer Model 3110 atomic absorption spectrometer. Atomic absorption measurements for model working were carried out in the 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).

Procedures for Amberlite XAD-1180

The preparation of chromotrope 2R coated amberlite XAD-1180 resin is based on procedure reported by Saracoglu *et al.*²² Amberlite XAD-1180 (1.0 g) resin was added to 2 mL of chromotrope 2R solution and diluted to 20 mL with water using continuous stirring for 20 min. Afterwards the 2R-1180 resin was filtered off, washed with water and dried at 110°C .

4 mL of buffer solution were added to 50 mL of solution containing 5–20 μg of each working element. The resin was preconditioned with the buffer solution. Buffered metal solution was passed through the column at a flow rate of 5 mL/min. After passing this solution, the resin was washed twice with 10 mL of water. The adsorbed metals on the chromotrope 2R coated amberlite XAD-1180 resin were eluted with 5–10 mL portion of 1 M HNO_3 at a flow rate of 5 mL/min. The eluate was analysed for metals by atomic absorption spectrometry.

Procedures for Ambersorb 563

A sample volume of 100 mL, containing copper(II) ions, was transferred into a beaker; 10 mL of the relevant buffer solution was added. After shaking, 250 mg of ambersorb 563 was added and the mixture was shaken again for 10 min. The system was then filtered under vacuum through cellulose nitrate membrane (5 cm diameter). Then the filter and constituents were washed with distilled water. In order to get elution of adsorbed lead on ambersorb 563, 10 mL of 0.25 M HNO₃ was used. The final volume was completed to 5.0 mL with 0.25 M HNO₃. Copper content of the final solution was determined by flame atomic absorption spectrometry. The same procedure was applied to the blank solution.

Prior to each experimental step, the scanning electron microscopy (SEM) photographs of ambersorb 563 and amberlite XAD-1180 resin were taken.

RESULTS AND DISCUSSION

In the light of our previous work²³ on the investigation of the SEM images and flame atomic absorption works of the adsorption of some metal chelates on polystyrene divinyl benzene copolymers, the present work was performed. In this work different polystyrene divinyl benzene copolymers including ambersorb 563 and amberlite XAD-1180 were used. In the amberlite XAD-1180 system, firstly the ligand (chromotrope 2R) was impregnated to amberlite XAD-1180. Then the analytes were added to this new resin (chromotrope 2R coated amberlite XAD-1180 resin) for the adsorption. After this step, the elution was performed with 1 M nitric acid.

In the ambersorb 563 system, copper ions in the ammonia/ammonium chloride buffer were adsorbed on ambersorb 563 resin and then the elution was performed with 0.25 M nitric acid. The quantitative recovery values of metal ions were investigated by flame atomic absorption spectrometry. The identification of the surface of both the resins and the metal loaded resins was performed by using scanning electron microscopy (SEM).

The optimal analytical conditions including pH, matrix effects, amounts of the resins, etc. for the quantitative recovery of analytes on ambersorb 563 and amberlite XAD-1180 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 are copper(II), iron(III) and lead(II) for XAD-1180 system and copper(II) for ambersorb 563 system. The optimal conditions are given in Table-1 for XAD-1180 system and for ambersorb 563 system. Higher concentrations of the alkaline and alkaline earth ions and some anions as matrix were not effected on the retentions of analytes on ambersorb 563 and amberlite XAD-1180 resins. The results agree with the results of the studies of Saracoglu *et al.*²², Soyak *et al.*²⁴ and Saracoglu *et al.*²⁵

In order to investigate the adsorption of the metal chelates on the amberlite XAD-1180 and ambersorb 563 resins, firstly, the scanning electron microscope photographs of the polystyrene divinyl benzene copolymers were taken. These photographs for XAD-1180 and Ambersorb 563 are given in Figs. 2 and 3, respectively. As can be seen from these photographs, both amberlite XAD-1180 and ambersorb 563 have some cavities in their surfaces.

TABLE-1
OPTIMAL ANALYTICAL CONDITIONS FOR SOLID PHASE EXTRACTION ON
AMBERLITE XAD-1180 AND AMBERSORB 563

Parameter	Optimal values	
	Amberlite XAD-1180	Amborsorb 563
Resin	Amberlite XAD1180/Chromotrope 2R	Amborsorb 563
Analyte metals	Cu, Fe, Pb	Cu
pH	8	9
Buffer	Ammonia/ammonium chloride	Ammonia/ammonium chloride
Resin amount	500 mg	250 mg
Sample volume	250 mL	100 mL
Eluent	1 M HNO ₃	0.25 M HNO ₃
Desorption volume	10 mL	0.5-1.0 mL
Number of usage	50	200
Matrix	No effects	No effects
Sample flow rate	5 mL/min	5 mL/min
Eluent flow rate	5 mL/min	5 mL/min

The scanning electron microscope image of amberlite XAD-1180 loaded chromotrope 2R ligand is given in Fig. 4. The rough structure of amberlite XAD-1180 resin changed after loading chromotrope 2R. Also the SEM image was obtained after adsorption of the metal ions on the chromotrope 2R loaded amberlite XAD-1180 resin.

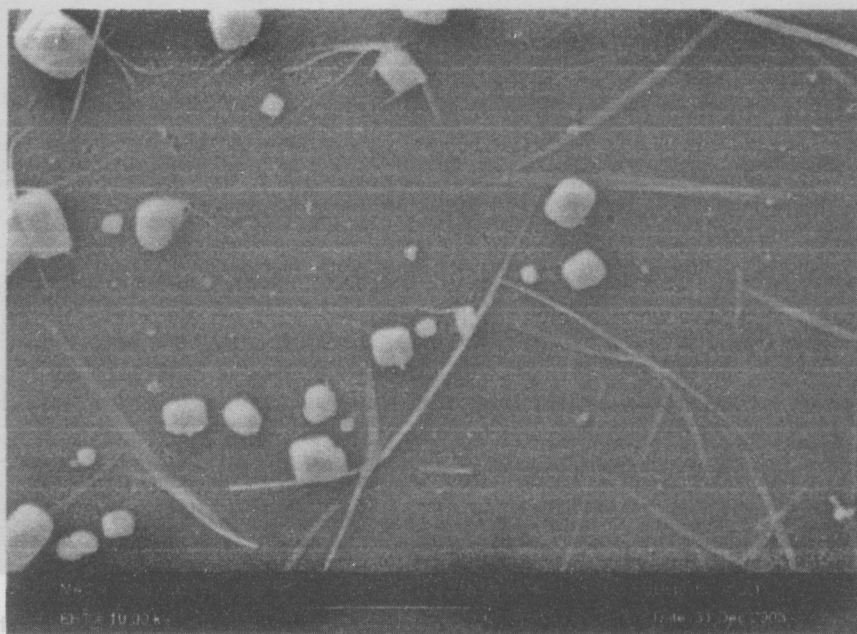


Fig. 2. Scanning electron microscope photograph of amberlite XAD-1180

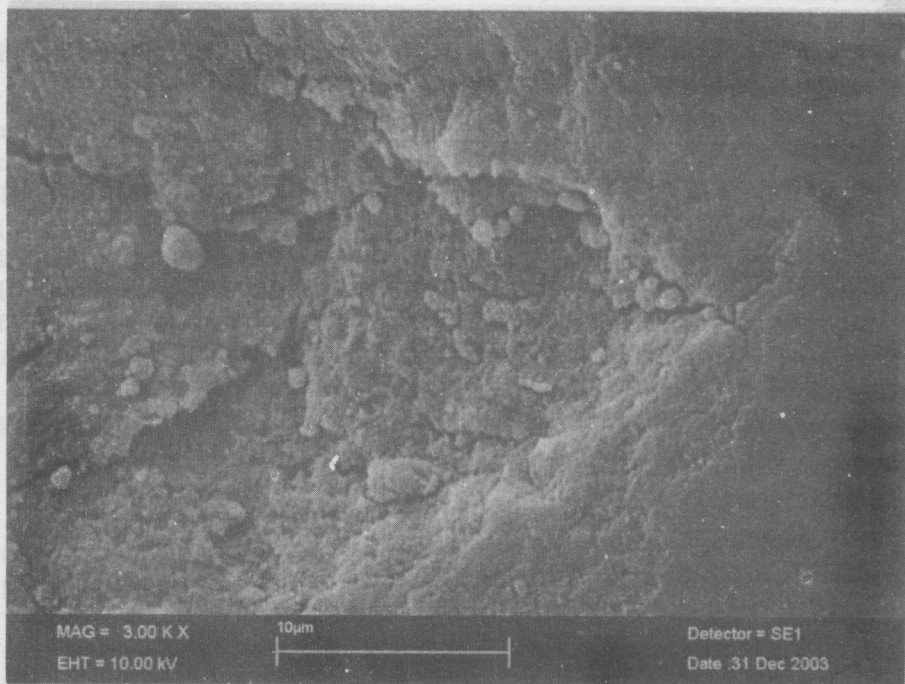


Fig. 3. Scanning electron microscope image of ambersorb 563

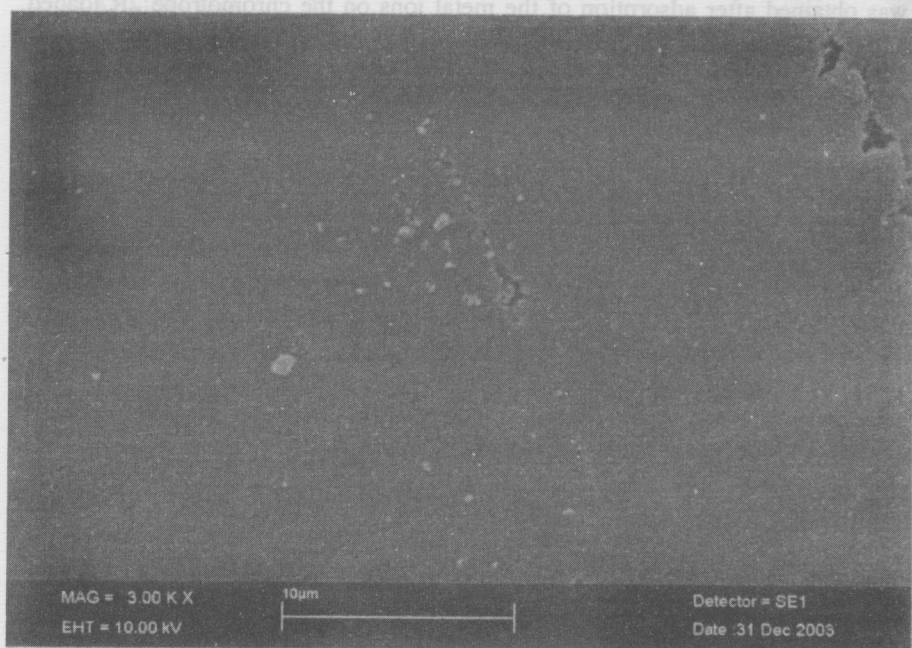


Fig. 4. Scanning electron microscope photograph of amberlite XAD-1180 loaded with chomotrope 2R

The SEM photograph of the copper ammine complexes loaded ambersorb 563 resin is given in Fig. 5. The cavities on ambersorb 563 resin were filled by adsorption of copper ammine complexes (Fig. 5). Also the surfaces of both metal chelates loaded resins (Figs. 4 and 5) are smooth and regular according to the Fig. 2 for XAD-1180 and Fig. 3 for Ambersorb 563.

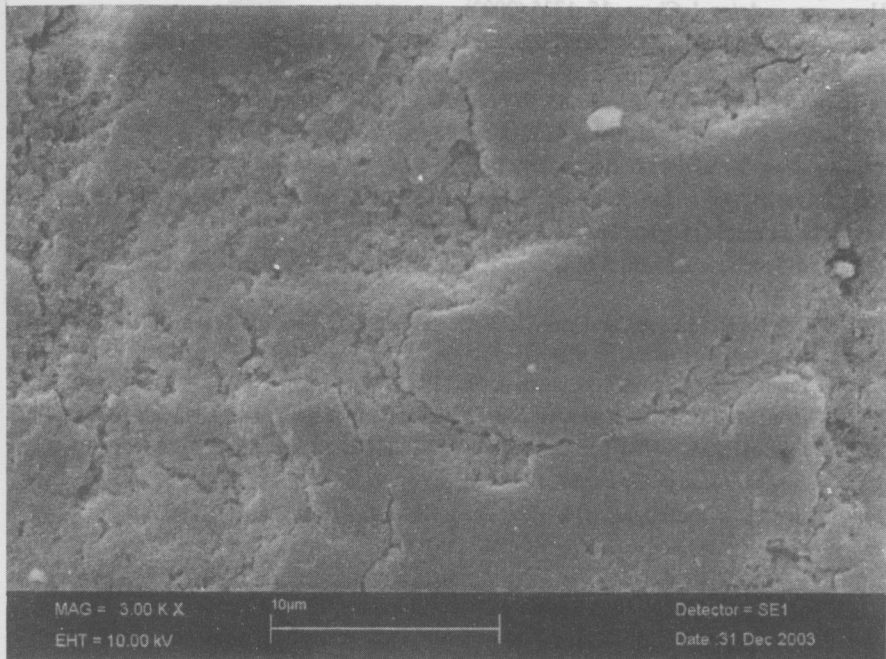


Fig. 5. Scanning electron microscope photograph of ambersorb 563 loaded with copper ammine complexes

The comparison of the scanning electron microscopy (SEM) images of ambersorb 563 and amberlite XAD-1180 resins and metal ion loaded resins can give some information on the adsorption process of the metal ions of the resins. The results found in the present work agree with our work about this subject²³.

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