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Synthesis, characterization, and properties of an efficient and selective adsorbent to mercury (II)

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SUMMARY

The synthesis of a water-insoluble adsorbent resin was carried out by radical polymerization of [2-(methacryloyloxy)ethyl] trimethyl ammonium chloride by using ammonium peroxydisulfate as initiator and N,N'-methylene-bis-acrylamide (MBA) as crosslinking reagent. The adsorbent was characterized by elemental analyses, and FT-IR spectroscopy. The thermal stability was studied in the presence of Hg(II). The ability to bind Hg(II), Cd(II), Zn(II), Pb(II), Cu(II), Cr(III), and U(VI) as well as the maximum adsorption capacity, and elution of the Hg(II) from the loaded resin was studied. At pH 2 the adsorbent retained 95% of Hg(II) from an aqueous solution containing 1g/L in Hg(II). The retention of other metal ions was lower than 15%. Sorption selectivity from the binary mixtures Hg(II)-Cd(II), Hg(II)-Zn(II), Hg(II)-Pb(II), and Hg(II)-Cr(III) was studied at the optimum sorption pH value.

INTRODUCTION

The presence of heavy metal ions in the environment is one of the major concerns due to their toxicity to many life forms. Heavy metal ions can be removed by adsorption on solid carriers. There are nonspecific adsorbents, such as activated carbon, metal oxides, silica, and ion exchange resins (1-3), and specific ones which are considered among the most promising techniques (4-8). These specific sorbents consist of a ligand which interacts with the metal ion specifically, and the carrier may be an inorganic material or polymer microbead. The latter carrier matrices have attracted the most interest because they are easily produced in a wide range of compositions, and can be modified by polymer analogous reactions to introduce a new ligand.

In the last few years, we have prepared water-insoluble adsorbents from derivatives of acrylamide with different swelling capacity and ability to bind several heavy metal ions depending on the pH and concentration of the metal ion (9-16).

Now we report the synthesis, characterization, and metal ion binding ability of an adsorbent containing an ammonium group, for the removal of important heavy metal ions, i.e., Hg(II), Cd(II), Zn(II), Pb(II), Cu(II), Cr(III), and U(VI).

EXPERIMENTAL PART

Materials:

[2-(methacryloyloxy)ethyl] trimethyl ammonium chloride (MTA) (Aldrich), N,N'-methylene-bis-acrylamide (MBA) (Merck), ammonium peroxydisulfate (APS) (Merck)

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were of commercial grade and used without further purification. Reagent grade metal ions were used and solutions were prepared by dissolving appropriate weights of the acetate, chloride or nitrate of the metals in deionized water. Nitric acid (65%), perchloric acid (70 %), and sodium hydroxide standard solutions were used.

Synthesis of the adsorbent resin:

MTA (0.0130 mol) was polymerized in bulk with APS (0.5 mol%) and MBA (6 mol%) at 70ºC during 24h. The resin was dried under vacuum to constant weight. The yield was 79%. The dried resin was ground, sieved, and the 180-250 µm portion was used in all the sorption experiments.

Sorption of metal ions on the resin:

A batch equilibrium type procedure was used to determine the metal ion uptake from an aqueous solution containing 1g/L in the metal ion by the resin (0.1g). The pH of the aqueous solution (10 mL) varied between 1 and 5 depending on the metal ion. The two phases were shaken by a mechanical shaker at room temperature for 1h. After shaking, the two phases were separated, and the supernatant solution was analyzed for Hg(II), Cd(II), Zn(II), Pb(II), Cu(II), Cr(III), by atomic absorption spectrophotometry, and for U(VI) by colorimetry (17) by a CADAS 100 spectrophotometer.

Maximum adsorption capacity for Hg(II):

To obtain the maximum adsorption capacity for Hg(II), 50 mL of an aqueous solution were shaken with 0.5 g of the resin for 2h at room temperature (ca. 25ºC). The mixture in the flask was filtered and washed with water, and the filtered solution was transferred into a calibrated flask. The process was repeated three times, the volume was made up to 250 mL and then the metal was determined.

Separation of Hg(II) from binary mixture:

The following binary mixtures were evaluated: Hg(II)-Cd(II), Hg(II)-Zn(II), Hg(II)-Pb(II), Hg(II)-Cu(II), and Hg(II)-Cr(III). Thus, 10 mL of an aqueous solution containing 0.5 g/L of each metal ion were contacted for 1 h with 0.1 g of dry resin. The pH was adjusted to 2.0, then the resin was filtered and washed repeatedly with deionized water. Both metal ions were analyzed in the filtrates.

Optimisation of adsorption time for Hg(II):

The time required for the solid-liquid system to achieve the equilibrium conditions was determined by placing 10 mL of 1 g/L aqueous solution of Hg(II) with 0.1 g of the resin. At each time the supernatant was separated and the mercury ion determined.

Desorption of Hg(II):

Desorptions assay were carried out with the Hg(II)-loaded resin at maximum capacity. The ion was eluted by shaking 0.1 g of the resin with 10 mL of 1 M to 4 M

HNO_3 and $HClO_4$ at pH 2 for 1h. The resin was separated by filtration and the metal ion was analyzed in the supernatants as above.

Measurements:

Hg(II), Cd(II), Pb(II), Zn(II), Cu(II), Cr(III), were analyzed on a Perkin Elmer 1100 atomic absorption spectrophotometer, and U(VI) was analyzed with a CADAS 100 spectrophotometer. The pH were measured with a digital Extech Microcomputer pH-meter. The FT-IR spectra were recorded on a Magna Nicolet 550 spectrophotometer. Thermal stability analysis was performed on a Polymer Lab. STA 625 System with a heating rate of 10ºC/min under nitrogen.

RESULTS AND DISCUSSION

The crosslinked MTA resin was prepared by radical polymerization. The resin was completely insoluble in water and in organic solvents. The yield was 79%. The particle size of the resin immediately after the polymerization was higher 1000 µm (71%), between 1000 and than 500 µm (20%) and lower than 500 µm (9%). Subsequently, the resin was crushed to yield a material with a particle size between 180-250 µm. This fraction was used to study the metal ion binding capacity.

The sorption properties of the resin towards, Hg(II), Cd(II), Zn(II), Pb(II), Cu(II), Cr(III), and U(VI) were assayed by a batch method at different pH values (see Table 1).

Table 1. Influence of the pH on the sorption ability (%) of the resin for different metal ions. Concentration of metal ion:1g/L. Contact time: 1h.

Metal ion	Initial pH				
	1	2	3	4	5
Hg(II)	0	95			
Cd(II)	0		0		0
Zn(II)	18	25			
Pb(II)	0		0		0
Cu(II)	0		9		10
Cr(III)	0	0	0	0	54
U(VI)	13		13		13

At pH 1, the resin practically did not adsorb metal ions. At pH 2 the resin shows important sorption capacity and particularly high selectivity for Hg(II). Cr(III) is absorbed only at pH 5 (54%). According to these results the following runs were carried out for Hg(II) at pH 2.

The time required to attain the equilibrium conditions is approximately 30 min which is considered fast assuming that it is a heterogeneous system (see Figure 1).

Adsorption capacity of Hg(II) ions is presented in Figure 2 as a function of the initial concentration in the aqueous phase at pH 2 after the contact with 0.1g of the resin. The amount of Hg(II) ion adsorbed per unit mass of the resin decreases as increases the concentration from 0.05 to 4g/L which represents saturation of the active sites (available to bind Hg(II) ions) from low concentrations on the beads.

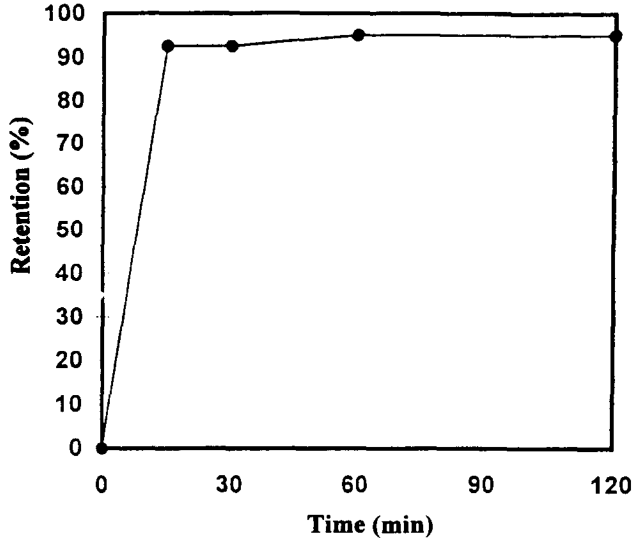

Figure 1. Plot of retention (%) of mercury(II) vs. time.

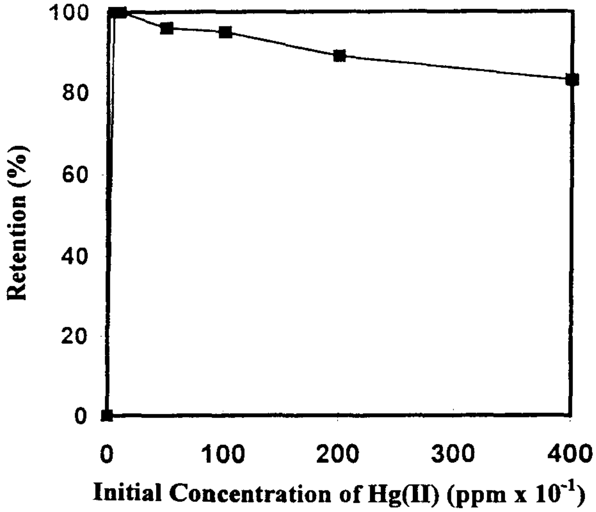

Figure 2. Effect of the initial concentration of Hg(II) on the sorption behavior of the resin.

The selectivity sorption from binary mixtures containing mercury ions was then studied. The resin was suspended for 2h in an aqueous solution containing equal amounts of two kinds of metal ions: Hg(II)-Cd(II), Hg(II)-Zn(II), Hg(II)-Pb(II), Hg(II)-Cu(II), and Hg(II)-Cr(III). The adsorptivity was determined by observing the concentration of two ions in the aqueous phase. Adsorption selectivity for Hg(II) at pH 2 was excellent in these binary systems as is shown in Table 2.

Table 2. Adsorption selectivity of the resin for Hg(II) ions from binary mixtures at pH 2.

Metal 1	Metal 2	Sorption (%) of Hg(II)	Sorption (%) of Metal 2	Selectivity* (%)
Hg(II)	Cd(II)	75	4	95
Hg(II)	Zn(II)	73	4	95
Hg(II)	Pb(II)	73	0	100
Hg(II)	Cu(II)	75	0	100
Hg(II)	Cr(III)	83	3	97

*Defined by percent adsorption of metal 1, Hg(II) in total adsorbed metal ions (metal 1+metal 2).

In the Hg(II)-Pb(II) and Hg(II)-Cu(II) systems, the Hg(II) ions were adsorbed in the resin exclusively, and even in the Cr(III), Cd(II) and Zn(II) systems, the adsorption selectivity exceeds 90% for Hg(II). The adsorption in the binary systems decreases around a 20% for Zn(II), Pb(II), and Cu(II) but only about 12% for Cr(III) in respect to the adsorption behavior of individual metal ions, shown in Table 1. Thus the coexisting ion affects the selective adsorption on the metal ions and that the selectivity for two kinds of metal ions cannot completely be predicted from sorption results obtained in the single ion system.

This high preference of the resin for the adsorption of Hg(II) may be attributed at least two factors, i.e. stability constant for complex formation and conformational requirements.

Due to the low adsorption capacity for the other metal ions, particularly at pH 2, the maximum load capacity was determined only for Hg(II). After three contacts it was 82% .

The FT-IR spectra of the unloaded resin show, among other characteristic absorption signals (in cm-1), at 3436 (N-H) , 1728 (stretching of C=0, carboxylic acid), 1647 (stretching of C=O, amide group), and the corresponding to the loaded with Hg(II), a shifting of the signals and the presence of the signal at 1386 cm^{-1} (see Figure 3).

To recover the resin, nitric acid and perchloric acid at different concentrations were added to the Hg(II)-loaded resin (see Figure 4).

The elution of Hg(II) ions after only one contact ranged between 55 and 65%. Perchloric acid showed a slight higher elution than nitric acid, and for either acids the concentration is unimportant.

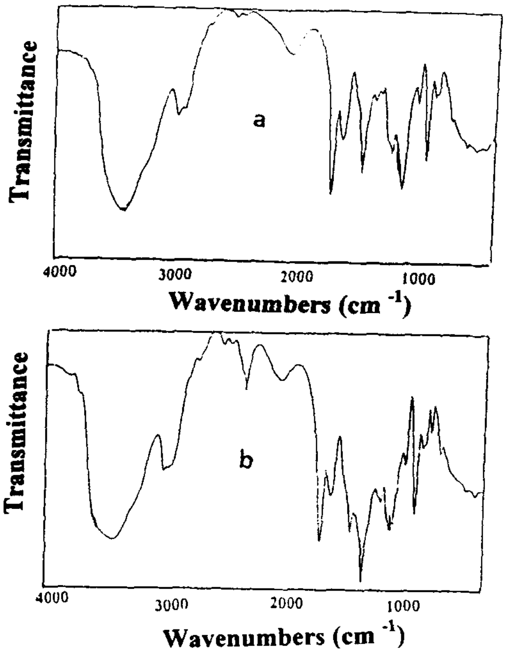

Figure 3. FT-IR spectra of the resin, unloaded (a) and loaded with Hg(II) (b)

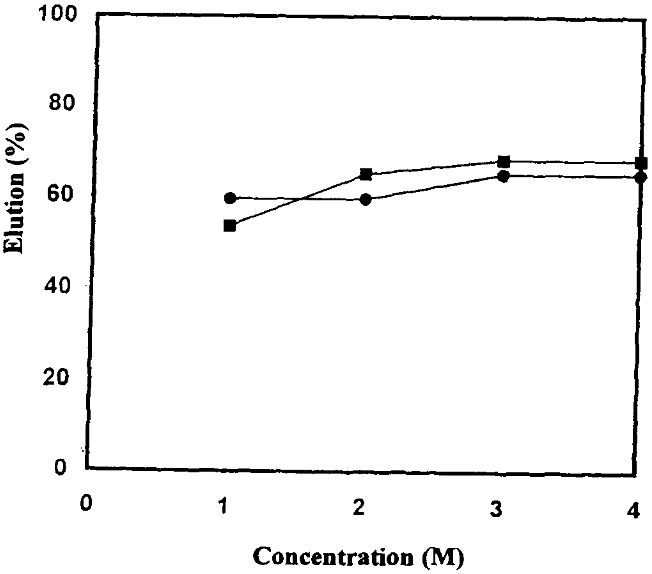

Figure 4. Elution behavior with nitric acid (●) and perchloric acid (■) of the loaded resin with Hg(II).

To determine the effect of Hg(II) adsorbed on the thermal stability of the resin, thermogravimetric analyses were carried out. The resin was loaded with Hg(II) at pH 2 according to the maximum capacity. Up to 200°C for both resins the weight-loss was less than 8%. Therefore, the weight-loss of the loaded resin was higher (10-20%) than that of the unloaded resin (see Figure 5).

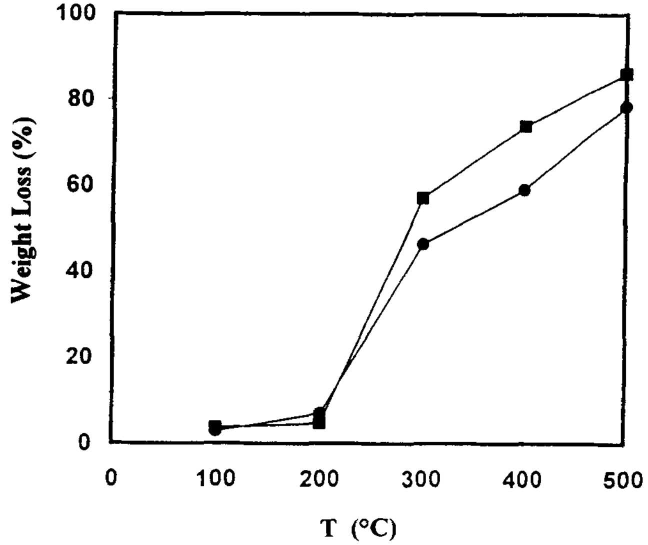

Figure 5. Thermal stability under nitrogen of the unloaded resin (●) and the loaded resin with Hg(II) (■). Heating rate: 10ºC/min.

CONCLUSIONS

The radical polymerization of MTA yielded a crosslinked matrix completely insoluble in water. It showed high efficiency to adsorb Hg(II) (95%) at pH 2 and excellent selectivity in respect to the other metal ions like Cd(II), Zn(II), Pb(II), Cu(II), and Cr(III) either from individual metal ion solutions and from binary mixtures. It is possible partially recover the resin by treatment of the loaded resin with nitric acid or perchloric acid.

Both loaded and unloaded resins showed high thermal stability up to approximately 200°C, with a weight loss lower than 8%.

ACKNOWLEDGEMENTS

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