Crosslinked Poly(glycidyl methacrylate)-Based Resin for Removal of Mercury from Aqueous Solutions

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ABSTRACT: Glycidyl methacrylate–based resin crosslinked beads with acetamide functions were demonstrated to be efficient in the removal of mercury. Beaded polymer supports were prepared by suspension polymerization of glycidyl methacrylate (0.9 mol) and ethylene glycol dimethacrylate (0.1 mol). The resulting copolymer beads were modified through epoxy functions in two steps: (1) by treatment with excess dibutyl amine and (2) by subsequent reaction with chloroacetamide. The resulting polymer resin, which had a chloroacetamide content of 2.5 mmol/g, was effective in extracting mercury from aqueous solutions. The mercury sorption capacity was around 2.2 mmol/g in non-buffered conditions. Experiments performed in identical conditions with several metal ions revealed that Cd(II), Pb(II), Zn(II), and Fe(III) ions also were extractable in low quantities (0.2–0.8 mmol/g). The sorbed mercury could be eluted by repeated treatment with hot acetic acid without hydrolysis of the amide groups. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 348–352, 2006

Key words: modification; resins; crosslinking; metal-polymer complexes

INTRODUCTION

Removal of inorganic pollutants from wastewater is a tedious process compared to the removal of organics because most of the latter can be removed relatively simply by activated carbons without much regard to their origin. Inorganic pollutants, however, need to use sorbents with ligating groups able to bind to them by forming chemical bonds.

Ion exchangers have been widely used in the removal of inorganics. Chelating polymers, on the other hand, can be regarded as a second generation for sorption of inorganics. These sorb metal ions by coordination, yielding chelate complexes that are efficient even for trace quantities of as little as a few parts per million (ppm).

Many articles[1–3] and reviews[4–12] in the literature have taken up metal sorption and heavy-metal uptake using polymer sorbents with chelating groups.

Among the heavy metals rejected by industries, mercury is one of the most environmentally unfriendly. The selective removal and recovery of metal ions, in general, has a potentially vast range of applications for conserving the environment and using its resources.

Mercury-selective polymeric resins with thiol[13–14] or thioether[15] functions have been reported. Nevertheless, these materials are not strictly selective and also to some extent sorb other metal ions, such as Pb(II), Cd(II), and Cu(II).[16]

Another possibility for selective mercury extraction is the use of polymer resins with amide groups. These kinds of polymers have been studied extensively by our group.

Amide compounds readily react with mercuric ions under ordinary conditions to give mono- or diamidomercury compounds (Scheme 1). The mercury–amide linkage is believed to be covalent rather than coordinative.[17]

In this study, we used glycidyl methacrylate–ethylene glycol dimethacrylate copolymer beads as reactive support. By incorporating dibutylamine via the ring opening of the epoxide groups following quaternization with chloroacetamide, a new sorbent that is efficient at removing mercury ions was produced. The conditions for regeneration of the resulting resin and for affinity of the sorbent for other metal ions such as Cd(II), Pb(II), Zn(II), and Fe(III) also were investigated.

EXPERIMENTAL

Materials

The chemicals used—glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA), dibutylamine, and 2-chloroacetamide, all supplied by Fluka (Buchs, Switzerland)—were analytical grade and used as supplied.

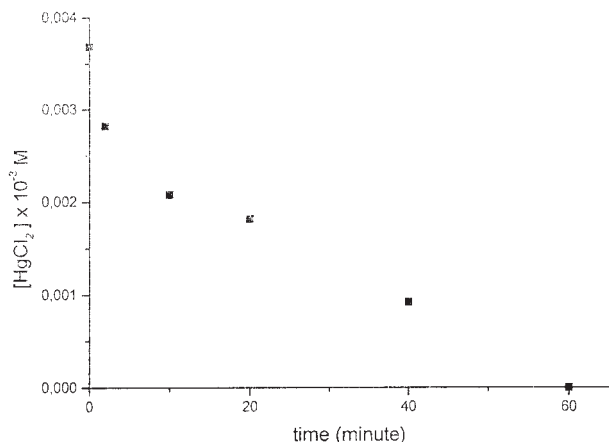*Correspondence to:* B. F. Şenkal (bsenkal@itu.edu.tr).

Scheme 1

Preparation of GMA–EGDMA copolymer beads

Poly(vinyl pyrrolidone) (1 g) was dissolved in 115 mL of water. Then the solution was transferred to a 1-L three-necked flask equipped with a nitrogen inlet, mechanical stirrer, and reflux condenser. A mixture of 20 mL (0.147 mol) of GMA, 3.1 mL (16.3 mmol) of EGDMA, and 0.5 g (3.05×10^{-3} mol) of azobisisobutyronitrile (AIBN) in 23 mL of toluene was added to the flask under a nitrogen stream. The mixture was heated to 70°C and stirred continuously (ca. 400 rpm) in a nitrogen atmosphere for 5 h.

The bead product was filtered and washed consecutively with excess water, acetone, and methanol. Then the beads were dried in vacuum at room temperature for 24 h, and the yield was 23.8 g.

Determination of epoxy content

The epoxy content of the polymer beads was determined by a pyridine-HCl method described previously.[18] Titration of the filtrated pyridine-HCl solution with NaOH (0.052M) yielded an epoxy content of 6.15 mmol/g.

Modification with dibutylamine

The GMA–EGDMA copolymer resin (10 g) was added to 10 mL of dibutylamine in a 100-mL flask. The mixture was stirred for 10 h at room temperature, and then it was heated at 90°C in a thermostated oil bath for 5 h.

The reaction content was poured into water, filtered, and washed with excess water. The product was dried at room temperature in vacuum for 24 h. The yield was 14.0 g.

Determination of amine content

To determine the amine content, 0.105 g of the polymer sample was left in contact with 5.2 ml of HCl (0.1M) for 10 h. After filtration, 2 mL of the filtrate was taken, and the acid content of the solution was determined by titration with a 0.052M NaOH solution in the presence of phenolphthalein as a color indicator.

The total amine content of the polymer was found to be 3.4 mmol/g of resin.

Reaction of crosslinked amine-containing beads with chloroacetamide

Tertiary amine containing 6 g of beads 420–590 μm in size was soaked in a solution of 10 g (0.107 mol) of 2-chloroacetamide in 50 mL of dimethylformamide. The mixture was shaken by a continuous shaker for 2 days at room temperature, and then heated to 80°C in a constant temperature bath for 48 h. Beads were filtered and washed consecutively with dimethylformamide, excess water, and acetone. The vacuum-dried sample weighed 7.3 g.

Chloride analysis

The quaternization yield was followed by analysis of the chloride ions in the final product. Thus, 0.1 g of the quaternized beads was boiled in 9 mL of 10% NaOH solution for 3 h. Analysis of the chloride ion solution was performed by the mercuric thiocyanate method as described in the literature.[19] This method produced a chloride content of 2.5 mmol/g.

Mercury uptake

The mercury uptake experiments were performed in nonbuffered conditions. In these experiments a quantity (0.2 g) of the quaternized polymer was added to Hg(II) solution (20 mL, 0.1M). The mixture was shaken on a continuous shaker for 24 h and filtered. A sample (1 mL) of the supernatant solution was transferred to a volumetric flask and diluted to 100 mL with water. Residual mercury content of the solution was assayed using a colorimetric method as described previously.[20]

Analysis of the final supernatant indicated a Hg(II) concentration of 0.067M in the final solution, corresponding to a mercury-loading capacity of 2.2 mmol/g.

Kinetics of mercury uptake

To test the efficiency of the sorbent for trace quantities of mercury, batch kinetic experiments were carried

Figure 1 Soprtion time plots of 0.1-g resin sample with 90 mL of 3.638×10^{-3} M HgCl$_2$ solution.

out with a very diluted Hg solution (3.683×10^{-3} M). For this purpose, the polymer resin sample (0.1 g) was wet with distilled water (1.5 mL) and added to a solution of Hg (90 mL of 0.1 g of HgCl$_2$ in 100 mL of water), and the mixture was stirred magnetically. Variation in the mercury concentration was monitored by analysis of samples (5 mL) taken at appropriate time intervals. The data collected are pictured in Figure 1.

RESULTS AND DISCUSSION

Glycidyl methacrylate (GMA)–based crosslinked polymer has advantages over other polymer supports because of its ease of functionalization through the epoxide groups involved. The remarkable resistance of its ester linkage to acid and to base hydrolysis is an additional advantage to using it as the ligand-carrying polymer.

In the present study, copolymer beads were prepared by suspension polymerization; a product 210–420 μm in size was used in further elaborations (Scheme 2).

Analysis of the bead polymer sample by the pyridine-HCl method found an epoxy content of 6.15 mmol/g.

Reaction with excess dibutyl amine produced a tertiary amine containing 3.4 mmol/g of amine functions. Reaction of crosslinked amine function resin in dimethylformamide with excess 2-chloroacetamide yielded a product with a chloride content of 2.5 mmol/g, corresponding to about 73.5% quaternization. However, quaternization of ethanol amines have been reported to rearrange to diethylamino ether moieties spontaneously.[21]

FTIR spectra of the starting compound C—O showed that the stretching vibration band of the CH—OH group became weak after reaction. This can be ascribed to ether formation during quaternization. On the basis of this observation the structure of the resulting material can be depicted as shown in Scheme 3.

Mercury uptake

The quaternary amide-amide-containing resin obtained was an efficient sorbent to remove mercury through the amide groups.

On the basis of the basic reaction of the mercuric ions with amide groups, which yielded covalent mercury–amide linkages,[17] the mercury binding of the resin can be depicted as shown in Scheme 4.

In the mercury uptake experiments, we deliberately used mercuric chloride because the Hg(II) ion has a reasonable affinity to chloride ions. In previous studies,[22] we found mercury uptake to be somewhat higher when mercuric acetate is used. For this reason, in the present study, HgCl$_2$ was used to determine the capacity of the polymeric sorbent under extreme conditions. The loading experiments indicated a mercury capacity of about 2.2 mmol/g in each case, and no significant change in capacity was observed at different initial mercury concentrations (Table I). The pH of HgCl$_2$ solutions remained almost constant, in the 3.1–3.9 range, throughout the extraction process. We did not use buffer solutions in the experiments because their use is not practical in real application conditions.

To inspect mercury efficiency of the resin, metal extraction experiments were repeated with Cd(II), Pb(II), Zn(II), and Fe(III) solutions. Each showed a small sorption capacity (0.2–0.8 mmol/g) relative to
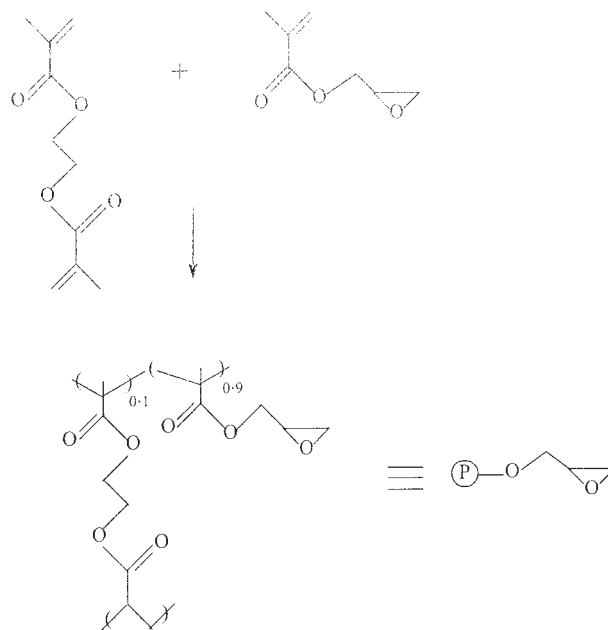
Scheme 2
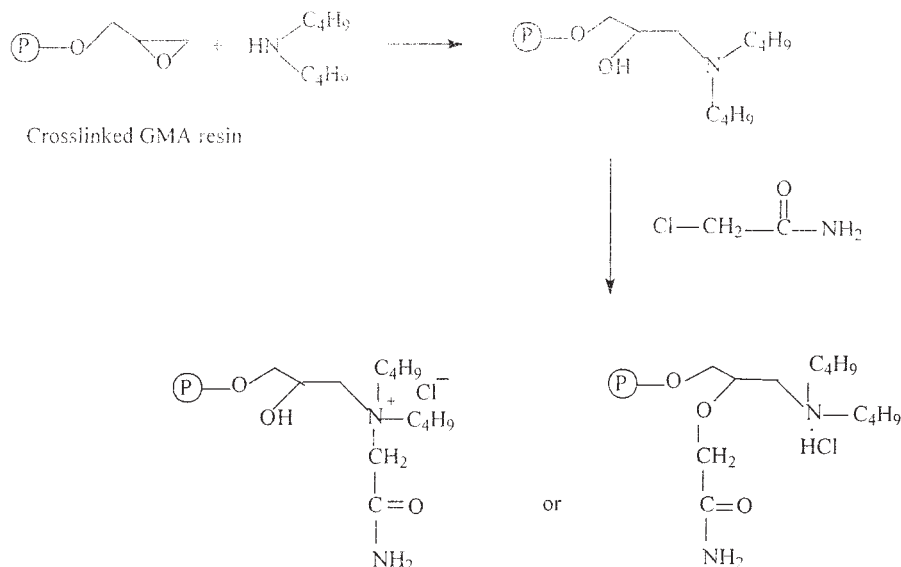
Scheme 3

mercury sorption capacity (Table I). Therefore, the overall results clearly showed that mercury sorption is very efficient.

KINETICS OF MERCURY SORPTION

To investigate the efficiency of the resin in the presence of trace quantities, we performed batch kinetic
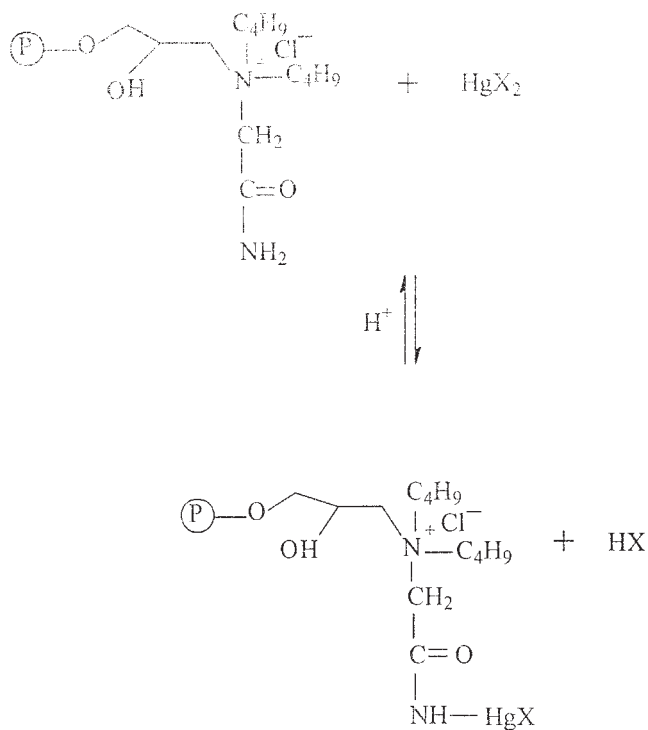

Scheme 4

sorption experiments with highly diluted $HgCl_2$ solutions (3.683×10^{-3} M).

The kinetics of the sorption obeyed second-order kinetics ($k = 0.323$ M^{-1} s^{-1} with a correlation factor of 0.980) as with many metal complexations involving solid surfaces.

Regeneration of resin

In the regeneration of mercury from loaded polymer, hot acetic acid was used as an appropriate agent. Mineral acids can be considered extracting agents. However, strong acids would inevitably cause hydrolysis of the amide groups. Therefore, mineral acids are not suitable in the regeneration process.

Although acetic acid is less effective and slower in regeneration, it does not cause hydrolysis. When loaded samples were heated in glacial acetic acid at 80°C for 1 h, the amount of recovered mercury was around 2.0 mmol/g (Table I), about 86% of the capacity of fresh polymer.

TABLE I
Metal Uptake Characteristics of Quaternized Beads

Metal ion	Initial concentration (M)	Resin capacity (mmol/g)	Recovered metal (mmol/g)
Hg(II)	0,10	2.20	1.90
Hg(II)	0,05	2.23	2.00
Hg(II)	0,025	2.12	2.02
Cd(II)	0.150	0.30	—
Pb(II)	0.150	0.20	—
Zn(II)	0.150	0.22	—
Fe(III)	0.150	0.80	—

Although we did not investigate the efficiency of the regenerated polymer, according to the literature,[23] polymer samples can be recycled and are reusable without loss of activity.

CONCLUSIONS

The resin produced was highly effective in removing mercury, and its format makes it of interest for technological use as a column-packing material. Under nonbuffered conditions, the mercury uptake capacity was around 2.2 mmol/g. The resin also contains tertiary amine groups; therefore, other metal ions can be bind to it, but the sorption capacity of the other metal ions was small compared to that of bound mercury.

The recovery of mercury can be achieved by treatment with hot acetic acid without hydrolysis of the amide groups. In addition, the conditions of regeneration of the resin are easy, which is important for industry.

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