A glycidyl methacrylate-based resin with pendant urea groups as a high capacity mercury specific sorbent

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Abstract

Polymer-supported pendant urea groups have been demonstrated to be very efficient in selective removal of mercuric ions from aqueous solutions. Methyl methacrylate (0.5 mol)–glycidyl methacrylate (0.4 mol)–divinylbenzene (0.1 mol) terpolymer beads have been prepared by suspension polymerisation. Urea functions have been incorporated into the bead polymer (210–420 \textmu m) via a two-step modification of the epoxy groups involving firstly reaction with excess of triethylenetetramine followed by acidic isocyanate. The resulting polymer resin has a urea group loading of 7.8 mmol g\textsuperscript{-1} and shows excellent mercury binding capacity > 6.7 mmol g\textsuperscript{-1}, even in the presence of excess chloride ions. The mercury sorption is strictly selective and Ca(II), Mg(II), Zn(II), Pb(II), Fe(II) and Cd(II) ions (0.2–0.3 M) do not give rise to any interference. The mercury can be recovered from loaded beads using hot acetic acid thereby regenerating the polymer. Recovered samples can be recycled more than 20 times without loss of activity as a result of the hydrolytic stability of the urea group in acetic acid.

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Keywords: Selective mercury removal; Polymer supported urea

1. Introduction

Quantitative separation of any metal ion from mixtures can be difficult and can require complex and costly chemical processing. Generally in most separations, one step alone is insufficient to recover all the desired metal ion from multicomponent mixtures. Recently, a metal ion template methodology using crosslinked polymers has offered some real promise in this respect. The shape memory and associated ion selectivity so obtained can be enhanced using high crosslinking densities. However, this gives rise to mass transfer limitation and slow reactions and the materials do not seem suitable yet for large scale separations [1]. Nevertheless the use of this methodology in designing electrodialysis membranes is promising, and with further improvements other applications may emerge [2]. In principle of course selective
metal ion separation can be achieved most efficiently using a ligand having unique affinity for the targeted metal ion. However most of the metal complex forming organic reagents do not provide such unique affinity and hence selective separation. Most common metal ligating groups indeed have comparable affinities for many metal ions. There are some exceptions however. Mercuric ions for instance interact extremely selectively with amide compounds since this ion is uniquely capable of forming a covalent bond with the amide nitrogen atom even in water at room temperature. Based on this key principle, we have previously demonstrated that cross-linked polyacrylamides [3,4] are very efficient in selective mercury separation from mixed metal ion solutions. Adequate hydrophilicity of the polymer is of crucial importance in capturing mercuric ion from aqueous solutions. Thus natural wool andnylons show only very low mercury sorption due to their hydrophobic nature. However the high and selective mercury uptake capacity of hydrophilic polyamides and the ability to strip the recovered mercury using hot acetic acid make these promising candidates for the cleaning up of contaminated drinking water. In a similar study polyacrylamide grafted onto coconut husk has also been demonstrated to be useful for mercuric ion removal [5].

Polymers with thiol or thioether groups have also been reported by other groups to be effective mercury sorbents [6–8] but these functional groups also tend to sorb Pb(II) and Cd(II) ions. There are a few commercially available resins with thiol functions [9] and others with diethyl dithiocarbamate functionality and these do seem to offer modest selectivity in mercury extraction. A number of papers dealing with the use of dithizone [10], pyridinium hydrochloride [11], and thioester [12] functions as mercury selective ligands have also been published.

The aim of the present study was to develop a mercury specific sorbent in spherical bead form which would be useful in column extractions. The sorbent was to have high Hg(II) capacity, high selectivity in the presence of possible interfering ions, and be readily regenerable. For this purpose, we have prepared a crosslinked resin bead polymer (210–420 μm) with pendant units each composed of four adjacent urea groups. We now report on the synthesis, characterisation and use of this resin in the selective recovery of mercuric ions.

2. Experimental

2.1. Materials

All the chemicals used were analytical grade products. Unless otherwise stated they were used as supplied: glycidyl methacrylate (GMA) (Fluka), methyl methacrylate (MMA) (Merck), divinylbenzene (DVB 55%) (Merck), triethylenetetramine (Merck), and KCNO (Fluka).

2.2. Preparation of GMA (0.4 mol)–MMA (0.5 mol)–DVB (0.1 mol) terpolymer beads

This resin was prepared by suspension polymerisation methodology using 1:1 v/v comonomers/toluene as a diluent, and styrene–maleic acid copolymer as the aqueous phase stabiliser. Details of the procedure have been given elsewhere [13]. The resulting crosslinked beads were fractionated by sieving and the 210–420 μm fraction was used in subsequent reactions.

2.3. Determination of the epoxy content

The epoxy content of the resin was determined using the pyridine–HCl method given in the literature [14]. This analysis indicated 3.40 mmol epoxy groups per g sample (theoretical value from comonomer feed ratio = 3.34 mmol g⁻¹).

2.4. Reaction with triethylenetetramine

The terpolymer resin (15 g 0.053 mol epoxide) was soaked in a mixture of triethylenetetramine (20 ml, 0.134 mol) and 2-methyl pyr-
rolidone (20 ml), shaken at room temperature for 20 h, and then heated for 2 h at 80 °C. The mixture was poured into water (1 l) the resin collected by filtration and washed well with water (3 × 300 ml). After drying at 60 °C for 6 h, the mass of resin was 19.2 g.

2.5. Determination of the amine content

Two methods were used for the determination of the amine content.

2.5.1. Method A

A sample of the modified polymer (0.2 g) was left in water (10 ml) for 24 h. Then 2 M HCl (10 ml) was added to the mixture which was shaken for 1 h. The resin was filtered off and the unreacted HCl in the supernatant liquid was assayed by titration with 2 M NaOH solution. The analysis indicated the amine content to be 11.2 mmol g⁻¹.

2.5.2. Method B

A second polymer sample (0.35 g) was added to 52% aqueous H₂SO₄ solution (10 ml) and the mixture refluxed for 2 h to digest the resin. The solution was diluted to 30 ml with distilled water, and was subjected to Kjeldahl nitrogen analysis. The nitrogen content of the resin was found to be 16.7% which equates to an amine content of 11.9 mmol g⁻¹.

2.6. Reaction with KCNO

The aminated resin from above was treated with concentrated hydrochloric acid, and then reacted with potassium cyanate solution. Thus, a sample of polymer (18.0 g, 0.214 mol of amine) was added to 36.5% HCl solution (40 ml) at 0 °C. The mixture was shaken for 1 h at room temperature. The resin was recovered by filtration then washed with water (200 ml). The sample was transferred into a screw top bottle and KCNO solution (100 ml 20 w/w%, 0.247 mol) was added. The bottle was closed tightly and shaken for 16 h at room temperature. The recovered resin was washed well with distilled water and dried. The nitrogen content was found to be 21.8% corresponding to 15.6 mmol N g⁻¹ resin.

2.7. Determination of the mercury uptake capacities

A resin polymer sample (about 0.2 g) was added to a Hg(II) solution (20.0 ml 0.15 M). After 1 h stirring at room temperature the resin was removed by filtration and 1.0-ml aliquots of the supernatant were used to estimate the residual mercury by a colorimetric method using diphenyl carbazide as the reagent according to a modified literature procedure [15]. In order to achieve a linear absorbance/[Hg(II)] response in the latter, appropriately diluted solutions of Hg(II) were mixed with a concentrated buffer solution (0.2 M sodium acetate/acetic acid) at pH 7, prior to addition of diphenyl carbazide reagent. Typically a solution of 10⁻⁵ M Hg(II) yields an absorbance of ~0.1. Hence the lower limit for the method is taken as an absorbance of 0.01 i.e. ~0.2 mg Hg l⁻¹ i.e. ~0.2 ppm. Application of this procedure indicated the HgCl₂ concentration to be 0.063 M. Thus, the mercury uptake capacity of the resin is given by:

\[(0.15 M - 0.063 M) \cdot 20 \text{ ml} / 0.2 \text{ g polymer} = 8.7 \text{ mmol g}^{-1}\]

The same experiment was repeated with the acetate and nitrate salts both in the absence and presence of NaCl. The data collected are shown in Tables 1 and 2.

Kinetic measurements were carried out under the same conditions using a polymer sample (~0.2 g) in 50 ppm Hg(II) solution (100 ml 2.5 × 10⁻⁴ M) Hg(II) solutions. Aliquots were taken from the stirred solution at 1- to 10-min intervals. The level of sorbed Hg(II) was calculated from the mercury analysis of the filtrates as described above.
Table 1
Effect of accompanying anions on the mercury uptake of the urea resin

<table>
<thead>
<tr>
<th>Hg salt</th>
<th>Initial conc. (M)</th>
<th>Sorption capacity* (mmol g⁻¹)</th>
<th>Recovered mercury* (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(CH₃COO)₂</td>
<td>0.15*</td>
<td>9.4</td>
<td>9.0</td>
</tr>
<tr>
<td>Hg(NO₃)₂</td>
<td>0.15</td>
<td>9.1</td>
<td>8.9</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>0.15</td>
<td>8.7</td>
<td>7.9</td>
</tr>
</tbody>
</table>

* Solubility of mercuric acetate is limited. The solution was turbid.
* Based on dry urea functional resin.
* Eluted by hot acetic acid.

Table 2
Effect of chloride ion concentration on the mercury sorption capacity of the urea resin

<table>
<thead>
<tr>
<th>NaCl conc. (mol l⁻¹)</th>
<th>Hg(II) capacity* (mmol g⁻¹)</th>
<th>Recovered mercury* (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>8.0</td>
<td>7.4</td>
</tr>
<tr>
<td>0.05</td>
<td>7.3</td>
<td>6.6</td>
</tr>
<tr>
<td>0.10</td>
<td>7.1</td>
<td>6.4</td>
</tr>
<tr>
<td>1.0</td>
<td>6.9</td>
<td>6.3</td>
</tr>
<tr>
<td>1.5</td>
<td>6.7</td>
<td>6.0</td>
</tr>
</tbody>
</table>

* Based on dry urea resin.
* In the first contact with hot acetic acid.

2.8. Extractability of other ions

In order to investigate the extractability of metal ions, which are common in mercury ores, and also common contaminants in ground, river and waste water, loading experiments were repeated with single metal ion solutions of Ca(II), Mg(II), Zn(II), Pb(II), Cd(II) and Fe(III) ions (in the 0.2–0.3 M range).

The EDTA (ethylenediaminetetraacetic acid) titration method was used for these metal ion determinations. The results are summarised in Table 3.

2.9. Stripping of the sorbed mercury

Polymer resin samples loaded with mercury were dried superficially in the open atmosphere at room temperature to avoid sublimation of the mercury. The samples were then added to glacial acetic acid (20.0 ml). The mixtures were stirred at 80 °C in a thermostatted oil-bath for 2 h. The cooled mixtures were filtered and 1.0-ml aliquots were diluted to 100.0 ml with distilled water. The mercury contents of the solutions were determined as described earlier. Data on the recovered mercury are given in Tables 1 and 2.

Table 3
Metal ion sorption capacity of the urea resin measured using single metal ion solutions

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Feed conc. (mol l⁻¹)</th>
<th>Sorption capacity (mmol g⁻¹)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(II)</td>
<td>0.3</td>
<td>~0.00</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>0.3</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>0.2</td>
<td>0.06</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>0.3</td>
<td>0.12</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>0.3</td>
<td>0.03</td>
</tr>
<tr>
<td>Zn(II)+Hg(II)*</td>
<td>(0.2+0.15)</td>
<td>~0.00+8.74</td>
</tr>
</tbody>
</table>

* Based on dry urea resin.
* Mixed metal ion solution.

3. Results and discussion

3.1. Resin synthesis and chemical modification

Glycidyl methacrylate-based polymer beads with pendant urea functions have been prepared in three steps; (i) suspension polymerisation of a GMA (0.4 mol)–MMA (0.5 mol)–DVB (0.1 mol) mixture (Scheme 1), (ii) reaction with excess triethylenetetramine (TETA), and (iii) subsequent reaction of the HCl salt of the resin with KCNO (Scheme 2).

Spherical resin beads were obtained in good yields and the size fraction 210–420 μm was selected for further elaboration. The content of epoxy groups was determined to be 3.4 mmol g⁻¹. Using 10 mol% DVB as crosslinker with
considerably higher than expected. Since the triethylenetetramine precursor is only of technical grade, this could account in part for the discrepancy. However this excess could also arise as a result of direct aminolysis of the methacrylate ester segments. To account for the analytical result almost one-third of the incorporated nitrogen would need to arise from this aminolysis. Of course, by changing the reaction conditions, i.e. time, temperature, etc. the degree of aminolysis might well change. Perhaps most importantly however the nitrogen content is definitely not lower than the theoretical value.

Scheme 1. Synthesis of GMA resin by suspension polymerisation (note actual DVB content = 0.055 balance is ethyl styrene residues).

Scheme 2. Chemical modification of GMA resin to yield tetra urea pendant groups.

1:1 v/v toluene as a diluent, no phase separation would be expected in the beads [16–18] and so the resin is essentially of gel-type morphology with the polymer network expanded somewhat due to the presence of toluene. Treatment of the GMA resin with ~3-fold molar excess of TETA gave the corresponding aminated polymer having pendant tetraamine functions. The theoretical nitrogen content of the polymer is 12.6% (~9.0 mmol amine g⁻¹) assuming one epoxy ring opening per 1 mol of the TETA incorporated.

In fact the Kjeldahl nitrogen analysis gives 16.7% (i.e. 11.9 mmol amine g⁻¹) which is considerably higher than expected. Since the triethylenetetramine precursor is only of technical grade, this could account in part for the discrepancy. However this excess could also arise as a result of direct aminolysis of the methacrylate ester segments. To account for the analytical result almost one-third of the incorporated nitrogen would need to arise from this aminolysis. Of course, by changing the reaction conditions, i.e. time, temperature, etc. the degree of aminolysis might well change. Perhaps most importantly however the nitrogen content is definitely not lower than the theoretical value, as would be the case if TETA reacted with two (or more) epoxy groups. This is good evidence that the TETA residues are attached substantially as pendant groups as shown in Scheme 2.

The HCl salt of the aminated resin reacts readily with potassium cyanate to give the corresponding polymer bearing pendant urea functions. The nitrogen content of the final polymer (21.8%) indicates ~15.6 mmol nitrogen which corresponds to ~7.8 mmol urea function g⁻¹.

3.2. Mercury uptake

The urea function is reported to interact with Hg(II) ions [19,20] via formation of Hg–N covalent bonds as is the case with amide groups [21]. Indeed the urea containing resin provides a rapid and efficient mercury sorption from aqueous solution. The mercury capacity is ~8.7 mmol at equilibrium. In principle each pendant tetra-urea group contains five possible mercury binding sites. (Scheme 2: each of the four –CONH₂ groups seems capable of binding (only) one Hg, via formation of –CONH HgX as does the –CH₂N(HgX)CO– group via –CH₂N(HgX)CO–) and so the maximum theoretical capacity possible would be ~10.0 mmol Hg g⁻¹. Hence, the practical capacity of the resin is ~90% of the maximum theoretical value. This level of mercury binding is possible only by selective formation of monocarbamidomercury structures, i.e. there is no evidence for...
bridging Hg structures. The actual mercury sorption capacity is found to vary slightly depending upon the accompanying anion. This is shown in the data in Table 1.

Mercuric acetate yields the highest capacity \(9.4 \text{ mmol g}^{-1}\), probably because of the weak acidity of acetic acid and the lower interaction between Hg(II) ions and acetate. In the case of HgCl\(_2\), the sorption capacity is lowest, 8.7 mmol g\(^{-1}\). Chloride ions are known to have affinity towards Hg(II) ions. This affinity furnishes an analytical method for determination of chloride ions [22]. This means that chloride ions may compete with the resin urea function in the binding of mercury. To investigate this effect further, the mercury sorption experiments were also carried out in the presence of NaCl at various concentrations. The results in Table 2 indeed show that increasing the NaCl concentration reduces the mercury capacity. In 0.1 M NaCl solution (this is the average salt concentration of sea water), the capacity is 7.1 mmol g\(^{-1}\) and corresponds to \(\sim 82\%\) of the original capacity. The effect of chloride ion is therefore not dramatic and the urea resin could readily be employed in sea water and other similar saline solutions.

3.3. Selectivity of the mercury sorption

To evaluate the selectivity of the urea resin in mercury sorption (Ca(II), Mg(II), Zn(II), Pb(II) and Fe(III)) the capacity of the resin was determined using a number of single metal ion solutions, i.e. under similar conditions to those used for the mercury sorption measurements. The results are shown in Table 3.

Perhaps not surprisingly essentially no sorption of Ca(II) and Mg(II) ions is observed. Indeed the maximum metal ion sorption detected (for Fe(III)) is only 0.12 mmol\(^{-1}\). Clearly therefore the urea resin is unable to coordinate to these ions and the small absorbivities observed may be due to metal hydroxide precipitation in the resin as a result of the weak basicity of the urea function.

In the case of Zn(II), sorption measurements were also made under competitive conditions when the Zn(II) uptake was zero and indeed a small enhancement was observed in the mercury uptake (last entry Table 3). The Hg–N bond formation proceeds with simultaneous liberation of protons and under these slightly more acidic conditions, Zn hydroxide formation may be suppressed.

3.4. Hg sorption kinetics

Batch kinetic experiments indicate reasonably fast mercury binding from mercury solutions of low concentration (50.0 ppm, \(2.5 \times 10^{-4}\) M). The results from the batch method used depend to some extent on factors such as the stirring rate, but the data do give an order of magnitude for the sorption rate. At moderate stirring speeds (350–400 rpm), the concentration of mercury falls to the 0–1 ppm level in about 40 min contact time (Fig. 1). For the acetate, nitrate and chloride salts, the sorption displays roughly second-order kinetics \((k = 1.58 \times 10^2, 3.9 \times 10^2\) and \(0.59 \times 10^2\) M\(^{-1}\) s\(^{-1}\) with 0.967, 0.947 and 0.986 correlation factors, respectively). The kinetic measurements therefore demonstrate how efficient the urea resin is in recovering Hg(II) from trace concentration solutions.

Fig. 1. Sorption of Hg(II) by urea resin from 50 ppm solution as a function time: ▲, chloride salt; ■, acetate salt; ●, nitrate salt.
3.5. Stripping of the mercury and regeneration of the urea resin

Use of mineral acids to strip the Hg-loaded resin resulted in hydrolysis and loss of resin functionality although the site of hydrolysis was not established. Fortunately, it was found as with earlier amide polymers [3] that hot acetic acid (80–90 °C) is a suitable Hg stripping reagent and does not cause degradation of the urea resin. All the mercury however is not stripped in a single treatment with acetic acid; typically though more than 60% is recovered in a first treatment (Tables 1 and 2). However repeated back-extraction using acetic acid yields almost complete mercury recovery. Ultimately of course depending upon particular applications and associated costs, the stripping of Hg(II) may not be necessary and loaded resin may be discarded. Where stripping does prove essential the environmental impact of using hot acetic acid would need to be assessed, and some closed continuous extraction methodology may be appropriate.

3.6. Recycling of the urea resin

The mercury-free resin recovered from the stripping experiments was washed with water and then recycled. To evaluate recyclability one resin sample was subjected to 20 sorption and desorption experiments without measuring the capacities on each cycle. In the last loading step the Hg(II) capacity of the resin (loaded from HgCl₂ solution) was found to be 8.63 mmol g⁻¹ essentially within the experimental error of the figure found for the initial loading (Table 1).

4. Conclusions

A divinylbenzene crosslinked glycidyl methacrylate resin has been derivatised with pendant tetra-urea functions. The resin shows a very high capacity for Hg(II) sorption, and extremely low affinity for a selection of common potentially interfering metal ions. The resin can be stripped of Hg by multiple treatment with acetic acid, and one sample cycled through 20 loading and stripping steps displayed no loss of capacity for Hg(II).

References