Poly(acrylamide) Grafts on Spherical Bead Polymers for Extremely Selective Removal of Mercuric Ions from Aqueous Solutions

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ABSTRACT: Poly(acrylamide) grafted from solid polymer particles provides a simple solution for extremely selective removal of mercuric ions from aqueous solutions. The grafting of polyacrylamide has been performed, in high yields (164%), by redox initiation from iminoacetic acid groups created on crosslinked spherical beads $(210-420 \ \mu m)$ of glycidyl methacrylate/methyl methacrylate/ethylene glycol dimethacrylate terpolymer. In the grafting, homopolymer formation has been reduced greatly (22%) by the treatment of the bead polymer with ceric ammonium nitrate before the addition of acrylamide monomer. The mobility of the graft chains provides nearly homogeneous reaction conditions and rapid mercury binding ability, as for low molecular weight amides [mercury sorption by a 0.105-g polymer sample from 105 mL of a 7.74×10^{-4} mol L^{-1} (~155 ppm) Hg(II) solution shows first-order kinetics with respect to the Hg(II) concentration, $k = 1.1 \times 10^{-3} \text{ s}^{-1}$]. The mercury sorption capacity under nonbuffered conditions is around 3.6 mmol g^{-1} (i.e., 720 g of mercury/kg) and mostly occurs with the formation of diamido-mercury linkages, which result in the crosslinking of polyacrylamide brushes outside the spherical beads. The crosslinks can be destroyed by treatment with hot acetic acid, without hydrolysis of the amide groups. This process allows a complete elution of the mercury as mercury acetate, and the overall result is reversible crosslinking of the outer shell by mercuric ions. The material presented is efficient in the removal of mercury at concentrations measured in parts per million, and the mercury sorption is extremely selective over some foreign ions, such as Fe(III), Cd(II), Zn(II), and Pb(II). © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 3068-3078, 2002

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INTRODUCTION

All mercury compounds are known to be highly toxic chemicals. Their presence in municipal water is prohibited by health authorities almost everywhere in the world. Removal of toxic metals, in general, has been given great attention for environmental cleanup and hydrometallurgical applications. Conventional ion exchangers have limited success in the extraction of trace quantities, and the removal of toxic metals requires more efficient sorbent materials. Functional polymers specially designed with metal chelating groups (so-called polymeric sorbents) offer excellent metal-uptake abilities, and they have been discussed in many articles and reviews.^{1,2} However, most of those polymeric sorbents do not show desired selectivity, especially when multi-

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component mixtures are in question. Selective extraction of any desired metal ion is important not only for the isolation or removal of one chemical component but also for the effectiveness of the sorbent material because, during the extraction of any metal ion targeted, a waste amount of ligating groups should be spent for the extraction of common abundant metal ions such as Ca(II) and Mg(II) at the same time. In that case, only a few percent of the ligating groups of the sorbent serve in the removal of a target chemical, and this greatly reduces the effectiveness of the sorbent.

In some cases, selective metal ion removal can be achieved to some extent by the proper choice of conditions, such as pH adjustment.^{3–5} However, those polymeric sorbents described are applicable only for binary or ternary mixtures, and even in those cases, clear-cut selectivity has never been attained so far.

A more general approach for selective metal ion removal is template methodology, in which a complexed polymer ligand is postcrosslinked with a suitable reagent.⁶ Removal of the metal ion by any means gives rise to a product with microholes having high complexing affinity for the templated metal ion. The template methodology has been extended to organic and biomolecules by the groups of Wulff⁷ and Mosbach⁸ and has been termed *molecular imprinting*. The subject is now becoming a new area of research and is being exploited in the development of new permselective membranes⁹ and chiral membranes.¹⁰ In this technique, the success of the selectivity depends strictly on the crosslinked density of the material, and this makes the separation process slow. Because of this limitation, the technique is applicable only in small-scale separations for the time being, and it needs further improvements.

Ideally, the best method of selective separation is to find a suitable ligating group that is selective only for the target metal ion and not for any other metal ions. However, this is impossible in practice because most chelating groups show, more or less, coordination tendencies to many metal ions.

However, there are a few exceptions, such as mercury ions with superior affinity toward thiol, thioether, and amide groups. According to this principle, a number of mercury selective polymer resins with thiol^{11,12} or thioether functions¹³ have been reported. Nevertheless, those materials presented are not strictly selective and also sorb other metal ions such as Pb(II) and Cu(II) to some extent.¹⁴

Another possibility of selective mercury extraction is to use polymer resins with amide groups; this is being studied extensively by our group. The chemistry of mercury-amide interactions has been known for about 100 years. Amide compounds readily react with mercuric ions, under ordinary conditions, to give monoamido-mercury or diamido-mercury compounds (Scheme 1). The mercury-amide linkage is believed to be covalent rather than coordinative.¹⁵

The amide group, however, is a weak donor because of an electron-withdrawing carbonyl group. Therefore, it shows very little tendency for coordination with transition-metal ions. This makes amide groups unique in mercury binding with extremely high selectivity. On the basis of this key principle, we have demonstrated that crosslinked polyacrylamide beads¹⁶ and celluloseg-polyacrylamide¹⁷ are able to bind mercury selectively. Those materials are effective in the removal of mercuric ions. The regeneration of the loaded sorbents can be achieved by hot acetic acid without hydrolysis of amide groups.

In this study, this analogy has been extended to glycidyl methacrylate (GMA)-based spherical bead polymers carrying polyacrylamide graft chains. In doing so, we have expected to combine two important characteristics in such a structure, the physical advantage of bead-shaped particles and the mobility of graft chains, which allow semihomogeneous reaction conditions for the mercury sorption.

In this study, the efficiency and selectivity of mercury sorption over some common metal ions such as Pb(II), Cd(II), Fe(III), and Zn(II) have also been investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA; Fluka) and ethylene glycol dimethacrylate (EGDM; Fluka) were dis-

tilled before use. The other chemicals were analytical-grade chemicals: GMA (Aldrich), propylamine (E. Merck), monochloroacetic acid (E. Merck), HgCl₂ (E. Merck), and $Ce(NH_4)_2(NO_3)_6$ (E. Merck). Unless otherwise stated, they were used as supplied.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs were taken with small amounts of dry samples on disk covers coated with gold. The analyses were performed with a JEOL JSM-840 scanning microscope. The particle sizes of the beads were determined by a comparison of the particles to the bar in the right-hand corner of the images.

Preparation of GMA (0.05 mol)-MMA (8.5 mol)-EGDM (1.0 mol) Terpolymer Beads

Styrene/maleic anhydride copolymer (0.25 g) was dispersed in 350 mL of distilled water. NaOH (0.2 g, 5×10^{-3} mol) was added to the mixture and heated to 80 °C. The mixture was stirred at that temperature until the polymer was dissolved. Then, the solution was cooled to room temperature and transferred into a 1-L, three-necked flask equipped with a nitrogen inlet, a mechanical stirrer, and a reflux condenser. A mixture of 3.4 mL (0.025 mol) of GMA, 45.5 mL (0.425 mol) of MMA, 9.4 mL (0.05 mol) of EGDM, and 0.41 g (2.5 \times 10⁻³mol) of azobisisobutyronitrile in 60 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) under a nitrogen atmosphere for 3 h. The bead product was filtered and washed with an excess of water, acetone (100 mL), and ethanol (50 mL). Then, it was dried in vacuo at room temperature for 24 h, and the yield was 48.6 g.

Determination of the Epoxy Content

The epoxy content of the polymer beads was determined by a pyridine–HCl method described in the literature.¹⁸ Titration of the filtrated pyridine–HCl solution with NaOH (0.05 M) gave a 0.44 mmol g^{-1} epoxy content.

Modification of the Bead Polymer with Propylamine

The bead polymer (20 g) was added portionwise to a stirred solution of 20 mL (0.243 mol) of propylamine in 30 mL of 2-methylpyrrolidone at 0 °C. The mixture was shaken with a continuous shaker for 12 h at room temperature. The reaction content was poured into water, filtered, and washed with an excess of water. The product was dried at 40 °C *in vacuo* for 24 h. The yield was 20.5 g.

Determination of the Amine Content

The amine content of the aforementioned polymer was determined titrimetrically. Therefore, 0.51 g of the polymer sample was added to 10 mL of a 0.3 M HCl solution. The mixture was left to stand for 16 h in a tightly closed bottle. The mixture was filtered, and 5 mL of the filtrate was titrated with a 0.1 M NaOH solution. The titer (13.9 mL) for the unreacted acid indicated a 0.43 mmol g^{-1} amine content.

Reaction with Potassium Chloroacetate

Chloroacetic acid (9.45 g, 0.1 mol) was dissolved in 20 mL of distilled water and cooled to 0 °C in an ice bath. A solution of 6.9 g (0.05 mol) of K_2CO_3 in 15 mL of distilled water was added dropwise to the acid solution, with stirring, in about 30 min. Eighteen grams of the aforementioned polymer was added to this solution. The reaction content was placed on a continuous shaker and was shaken for 24 h at room temperature. The mixture was filtered, washed with water and alcohol (25 mL), and dried *in vacuo* at 40 °C for 24 h. The yield of the carboxymethylated polymer was 18.4 g.

Determination of the Carboxyl Content

The carboxyl content of the carboxymethylated polymer was estimated as follows. Of the polymer sample, 0.47 g was left in contact with 10 mL of a 0.1 M NaOH solution for 4 h. The unreacted NaOH content was determined by the titration of 2 mL of the filtrate with 0.1 M HCl; 1.5 mL of the titer corresponds to 0.42 mmol of the carboxyl group.

Graft Copolymerization of Acrylamide from Iminoacetic Acid Groups

The aforementioned polymer (10.765 g) with iminoacetic acid function was wetted with 25 mL of distilled water and left to stand overnight. To this mixture, 0.3 g (0.55 mmol) of $Ce(NH_4)_2(NO_3)_6$ in 5

mL of distilled water was added and shaken for 5 min at room temperature. A solution of 45 g (0.63 mol) of acrylamide in 100 mL of distilled water was added to the mixture and shaken for 24 h at room temperature with the continuous shaker. The mixture was filtered, and 10 mL of the filtrate was added to 50 mL of acetone so that the free polymer content could be assigned. A white precipitate was filtered and washed with acetone; 0.76 g of the dried polymer corresponds to 22% of the overall free polymer yield.

The bead product was left in contact with 100 mL of water and was filtered. Then, it was washed again with water and acetone (40 mL). The product was soaked in 50 mL of acetone and left to stand overnight to remove water. After filtering, it was dried *in vacuo* at 40 °C for 12 h. The yield was 28.7 g (166.6% grafting). The beads were fractionated by sieving, and a $210-420-\mu$ m fraction was used in the graft reaction.

Determination of the Grafting Degree

The degree of grafting was determined by Kjeldahl nitrogen analysis, as follows. Of the graft polymer sample, 0.5 g was placed in 10 mL of concentrated H_2SO_4 and boiled for 10 h. The mixture was filtered and diluted to 50 mL with distilled water. The nitrogen content of the filtrate was assayed by the Kjeldahl method, as given in the literature. This analysis gave a 12.46% nitrogen content.

Swelling of the Graft Copolymer

Because of hydrophilic polyacrylamide brushes, the bead polymer was expected to show water absorbency. The water sorption ability was simply determined by a mass increase of the polymer sample (0.2 g) soaked in distilled water in a crucible. After contact for 24 h, the mass of the filtered sample (1.36 g) indicated a 680.0% (w/w) water sorption.

Determination of the Mercury-Loading Capacity

The polymer sample (0.2 g) was wetted with 5 mL of distilled water (24 h). A 0.14 M HgCl₂ solution (20 mL) was added to the mixture and stirred for 24 h at room temperature. The mixture was filtered, and the residual Hg(II) concentration was determined colorimetrically by the diphenylcarbazide method.¹⁹ Therefore, a 0.107 M residual

Hg(II) concentration in the filtrate indicated a 3.6 mmol g^{-1} mercury-uptake capacity.

Sorption Tests for Foreign Ions

The sorption affinity of the resin toward foreign ions [i.e., Cd(II), Zn(II), Pb(II), and Fe(III)] was examined by simple contact of the aqueous solutions of those ions with 0.15 M initial concentrations for 24 h. Residual metal analysis was performed by complexometric ethylenediaminetetraacetic acid (EDTA) titrations, as described in the literature.²⁰ The results are collected in Table 3 (shown later).

Mercury Sorption in the Presence of Fe(III) Ion

This was performed by the mercury-loading experiment being repeated in the presence of Fe(III) ion as follows. A binary mixture of HgCl₂ and $FeCl_3 \cdot 6H_2O$ was prepared so that the final concentration of each component was $0.15 \text{ mol } \mathrm{L}^{-1}$. Ten milliliters of this solution was interacted with 0.235 g of the resin sample for 24 h at room temperature. The mixture was filtered, and 1 milliliter of the filtrate was treated with 5 mL of 0.3 mol L^{-1} KSCN and 5 mL of a dithizone solution (2 g in 50 mL of CCl₄). The mixture was shaken vigorously in a separatory funnel. The iron was retained as a thiocyanate complex in the aqueous phase. For analysis of the residual iron, 1 mL of the aqueous phase was taken and diluted to 100 mL. Absorption measurements at 460 nm²¹ gave 0.15-mmol Fe(III) sorption per gram of the polymer.

An analysis of the mercury in the extract phase was performed by monitoring of the absorbance of the mercury–dithizone complex at 496 nm, as described in the literature.²² For this purpose; 0.5 mL of the extract phase was taken and diluted to 100 mL with CCl₄. This analysis gave 3.52 mmol of Hg(II)/g of polymer.

Mercury Sorption in the Presence of Zn(II)

The same experiments described previously were repeated with a Hg(II)–Zn(II) binary mixture. Analyses of unreacted Hg(II) and Zn(II) in the solution were performed by the EDTA titration method with potassium iodide as a masking agent for the mercury, according to a general procedure given in the literature.²³ This analysis gave 0.06 and 3.5 mmol g⁻¹ Zn(II) and Hg(II) sorptions, respectively.



Figure 1. Concentration–time plot for the HgCl₂ solution (100 mL, initial concentration = 7.735×10^{-4} M) interacting with 0.275 g of a graft polymer sample.

Kinetics of Mercury Sorption

Batch kinetic experiments were performed with dilute $HgCl_2$ solutions $(7.74 \times 10^{-4} \text{ mol } \text{L}^{-1})$. A polymer sample (0.105 g) was wetted with 5 mL of distilled water and left to stand overnight. To the mixture, 100 mL of a $HgCl_2$ solution was added with continuous stirring by a magnetic stirrer (at 300-350 rpm). The sorption kinetics were followed by monitoring of the residual mercury content. This was carried out by an analysis of samples taken from the stirred mixture in 10-min intervals. The mercury contents of the sample solutions were assayed by the diphenyl carbazide method, as described previously. The relevant data are pictured in Figure 1.

Regeneration of the Polymer Sorbent

The mercury-loaded sample (0.2 g) was interacted with 10 mL of glacial acetic acid and stirred at 80 °C for 1 h. After cooling, the mixture was filtered, and 2 mL of the filtrate was taken out for colorimetric analysis of the mercury. The colorimetric analysis gave 0.36 mmol of stripped mercury, which corresponded to 1.82 mmol/g of loaded polymer sample.

RESULTS AND DISCUSSION

Polyacrylamide brushes were created on GMAbased crosslinked polymer beads for the preparation of a mercury-specific sorbent. The brush polymer chains were anchored to the bead surfaces by graft polymerization of acrylamide from iminoacetic acid groups on the crosslinked support. Preparation of the crosslinked bead polymer, its modification to yield iminoacetic acid groups, and subsequent grafting by redox initiation from the surfaces are depicted in Scheme 2. In the first step, terpolymer beads with reactive GMA segments are prepared by suspension polymerization; a 210–420 μ m size of the product is used in further elaborations. An analysis of the bead polymer sample by the pyridine-HCl method gives a 0.44 mmol of epoxy content per gram. Obviously, this analytical result indicates the oxirane groups in the accessible positions in the crosslinked matrix. However, the feed composition of the suspension mixture implies 0.446 mmol of theoretical epoxy content per gram. The minor difference represents the nonreactive epoxy groups embedded in the crosslinked polymer matrix. It is noteworthy that this fraction is not involved in the following modifications. Further reactions beyond this stage must proceed quantitatively when proper conditions are provided because the next modification steps proceed through the accessible epoxy groups and yield accessible reaction sites in each following step. Therefore, the reaction with an excess of propylamine is quantitative, as shown by amine analysis (0.43 mmol g^{-1}).

This amount is almost equal to the theoretical value, 0.435 mmol g^{-1} . The subsequent reaction with potassium salt of chloroacetic acid gives high-conversion yields, as established by titrimetric analysis of the carboxyl groups. The carboxyl content is 0.42 mmol g^{-1} , which is almost equal to the theoretical value, 0.424 mmol g^{-1} .

Grafting

Grafting from iminoacetic acid groups by redox initiation with $Ce(NH_4)_2(NO_3)_6$ is a very complicated process because of homopolymer formation as a side reaction. For fast initiation, the reactivity of the reducing groups on the surface is of prime importance in grafting by the Ce(IV) method (Scheme 3). This requirement is fulfilled by the iminoacetic acid functions, as described in reports dealing with Ce(IV)–aminoacid redox couples.²⁴ However, the grafting depends on the processing conditions and still tends to give homopolymers. Most likely, chain transfer to the solvent molecules is responsible for the homopolymer formation. Bearing this fact in mind, we have







Initial Concentration	Sorbed Mercury $(mmol \ g^{-1})$	Mass Increase (%)	pH	Stripped Mercury ^a
$0.025 \mathrm{M}$	3.7	76.1	3.6 - 3.72	_
$0.05 \ \mathrm{M}$	3.2	73.6	3.71 - 3.72	
0.1 M	3.6	76.0	3.41 - 3.66	1.8
$0.14 \mathrm{M}$	3.246	75.8	3.3 - 3.5	1.82

Table 1. Mercury Sorption Characteristics of the Graft Resin

^a Mmol Per gram of mercury-loaded polymer.

found that pretreatment of the bead polymer particles with a Ce(IV) solution, at least 5 min before the addition of the acrylamide monomer, is a suitable way to suppress homopolymer formation. In this way, we have attained high mass increases (166%) in a 24-h reaction period at room temperature. Under these circumstances, the free polymer yield is around 22%. Longer interaction periods with Ce(IV), before the monomer addition, cause the consumption of vast amounts of the initiator groups in direct oxidation, and the grafting degree falls sharply to low levels.

Initiation through iminoacetic acid functions is believed to proceed via CO_2 elimination, as reported before.²⁵

Kjeldahl nitrogen analysis (12.46%) of the graft polymer corresponds to 8.9 mmol of nitrogen/g of polymer. The nitrogen content can be related to the degree of grafting x (g/g of starting polymer)

$$\frac{(x/71)10^3 + 0.42}{1+x} = 8.9$$

where $(x/71) \times 10^3$ mmol of acrylamide graft/g of polymer and 0.42 denote the nitrogen content of the prepolymer with iminoacetic acid groups (mmol g⁻¹).

This gives x = 1.64 g of graft polyacrylamide (23.1 mmol). In other words, nitrogen analysis indicates a 164% grafting, which is very close to the found by mass increase.

If we assume that all the initiation sites are involved in grafting, the number of acrylamide repeating units per initiation site will be 23.1/0.42 = 55. In other words, 55/56 = 98.2% is the total nitrogen in polyacrylamide graft chains. This accounts for 23.1/2.64 = 8.75 mmol g⁻¹ acrylamide groups.

Mercury Uptake

The polyacrylamide graft on bead particles is anticipated to have superior peculiarities over common polymer sorbents carrying small reactive sites on solid surfaces because, in this structure, the insolubility and processing facility of the bead-shaped support are combined with the flexibility of the suspended graft chains, providing semihomogeneous reaction conditions.

The product shows considerable water sorption ability due to the hydrophilicity of polyacrylamide chains involved. Dry beads soaked in distilled water exhibit a 680.0% mass increase. The wettability of the polymer sorbent, in general, is beneficial for enhancing polymer–solute interactions, which cause the sorption from aqueous solutions to speed up.

The mercury sorption capacity of the polymer sample is about 3.6 mmol g^{-1} under nonbuffered conditions. Interestingly, different initial concentrations of mercury do not change the capacity of the polymer. This behavior seems to be unusual with respect to Langmuir- or Brunauer–Emmett– Teller (BET)-type common adsorption isotherms. However, in our case, there is no any limitation of diffusion inside the polymer particles because all the reactive sites are located on flexible polyacrylamide chains lining the particle surfaces outside. Also, the mercury binding takes place as if under homogeneous conditions.

An average mass increase of 76% after mercury sorption implies that most of the mercury ions have been bonded in the diamido-mercury form because 3.6 mmol of Hg(II) sorption accounts for about $3.6 \times 200.5 \cong 0.720$ mg of mercury/g of polymer (Table 1).

A more precise assignment can be made on the basis of the mass balance of the sorbed mercury $(3.6 \text{ mmol g}^{-1})$ as follows. Let *x* be the millimoles of mercury bonded in the monoamido form and *y* be the millimoles of mercury in the diamido form (per gram of the polymer sample). The incorporation of each millimole of HgCl results in a 0.235-g mass increase. Similarly, each millimole of diamido–mercury formation yields a 0.1985-g mass

increase. The sum of these two should give a mass increase of 0.76 g:

$$0.235x + 0.1985y = 0.760g$$

Because the total amount of mercury uptake is 3.6 mmol

$$x + y = 3.6$$

Then, we get $x \approx 1.24$ mmol and y = 2.36 mmol.

This result clearly indicates that under nonbuffered conditions, 65.5% of the mercuric ions are bounded in the diamido-mercury form and $2.36 \times 2 + 1.24 = 5.96$ mmol of amide groups are involved in mercury binding. Therefore, the unreacted part of the acrylamide units is 8.75 - 5.96= 2.79 mmol g⁻¹, or 31.9% of total acrylamide units.

These results reveal that the $HgCl_2$ solution acts as a crosslinker for the polyacrylamide outer shells and that the bead particles are surrounded by a tightly crosslinked layer, as depicted in Scheme 2. Because of the high crosslinking density of the outer layer, no more mercury can penetrate into the matrix, and about one-third of the acrylamide units remain unreacted.

SEM pictures in Figure 2 represent dense polyacrylamide brushes surrounding the spherical beads. The diameters of the beads clearly have been doubled after grafting [Fig. 2(b)]. The structure of the grafted polymer can be depicted as shown in Scheme 4. Of course, the grafting of polyacrylamide starts not only from outer surfaces of the spheres but also from inner surfaces of the permanent pores remaining open during the reaction. The crosslinking effect of mercury on the outer layer [Fig. 2(c)] can be inferred from the closing of the large pores observed. Binding in the diamido-mercury form also takes place between the acrylamide chains on different particles. The interparticle connections observed in the SEM picture explain the coalescence of the particles that was observed visually during treatment with the Hg(II) solution. These observations are confirmatory evidence for the aforementioned proposal.

In buffered solutions, the mercury uptake rises to 6.1 mmol g^{-1} (Table 2). This result implies that, at neutral pHs, mercury binding occurs mostly via monoamido-mercury formation because of the competition of the buffer components (0.2 M).







b

Figure 2. SEM micrographs of the bead polymers with (a) iminoacetic acid groups (original magnification, $90\times$), poly(acrylamide) grafts (original magnification, $150\times$), and (c) mercury-loaded graft copolymer (original magnification, $100\times$).

Selectivity of the Mercury Uptake

The selectivity of the Hg(II) uptake was investigated by the testing of the extractabilities of some foreign ions: Cd(II), Zn(II), Pb(II), and Fe(III).



Scheme 4

Those ions are the most abundant ions in mercury ores. These experiments revealed that only minor amounts of sorption were detected from the solutions with 0.15 M initial concentrations (Table 3).

Most likely, those negligible amounts of sorption found are due to the precipitation of the metal hydroxides on the polymer particles rather than coordination with the metal ions. Weak basicity of the amide groups must be responsible for the metal hydroxide precipitations.

Extracted amounts of mercury from Hg(II)-Fe(III) and Hg(II)-Zn(II) binary mixtures are al-

Table 2. pH-Dependent Mercury Uptake

pH	Capacity (mmol g^{-1}) ^a		
2.74	3.45		
4.05	5.17		
5.23	6.0		
7	6.1		

 $^{\rm a}$ The initial mercury concentration was 0.15 M at room temperature.

most the same as those observed in the absence of Fe(III) and Zn(II) ions.

Kinetics of the Mercury Sorption

The kinetics of the mercury sorption depend on many external factors, such as the stirring rate and pH of the solution. To obtain information about kinetic profiles of the mercury sorption, we performed experiments by the batch method with low mercury concentrations under nonbuffered conditions. At moderate stirring rates (ca. 350 rpm), the mercury concentration (155 ppm) falls to zero levels in about 10 min of contact time (Fig. 1). The concentration-time plots obey first-order kinetics $(k = 1.1 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1})$ with respect to the Hg(II) concentration. As can be inferred from the figure, the mercury binding is reasonably fast. The fast reaction can only be ascribed to the flexibility of the dangling polyacrylamide chains in water.

At relatively high initial concentrations, kinetic plots differ considerably. The extracted mer-

Hg(II)	Foreign Ion	Initial Foreign Ion Concentration	Sorbed Metal $(mmol \ g^{-1})$	$\begin{array}{c} \mbox{Mercury Uptake} \\ (mmol \ g^{-1}) \end{array}$
_	Cd(II)	$0.15 \mathrm{~M}$	0.14	_
	Pb(II)	$0.15 \mathrm{M}$	0.06	_
_	Zn(II)	$0.15 \mathrm{M}$	0.07	_
	Fe(III)	$0.15 \mathrm{M}$	0.16	_
0.15 M	Fe(III)	$0.15 \mathrm{M}$	0.15	3.52
0.15 M	Zn(II)	$0.15 \mathrm{~M}$	0.06	3.5

Table 3. Extractabilities and Effects of Some Foreign Ions in the Mercury Uptake

cury-time plot in Figure 3 shows a sharp increase in 30 min. Beyond this point, the curve reaches the saturation limit. A relevant graph of $\ln(c_0/c)$ versus t gives two linear plots bisecting around 30 min. Obviously, the first part of the kinetic plot represents the mercury uptake before the crosslinking of the polyacrylamide brushes. The rate constant of this part is slightly different, (k= $1.3 \times 10^{-3} \text{ s}^{-1}$) from the one obtained in trace kinetics. The second part of the plot with a smaller slope indicates slow sorption rates. In other words, the mercury sorption is fast at the beginning, but after crosslinking of the shell layer, the penetration of mercuric ions into the crosslinked matrix becomes much more difficult, and the process becomes diffusion-controlled.

Splitting of the Sorbed Mercury

The regeneration of the polymer sorbent can be achieved by acid treatment, but the use of min-



Figure 3. Mercury-loading kinetics of a graft polymer sample (0.2 g) from 25 mL of a 0.112 M HgCl₂ solution.

eral acids is not advisable because strong acids may cause hydrolysis of the amide groups. To avoid such hydrolysis, we have found that acetic acid is the most suitable for splitting mercury. When mercury-loaded samples are heated at 80 ° C in acetic acid, about 90% of the mercury is re-extracted into the acetic acid. Small percentages of mercury remaining can be eluted by a second acetic acid treatment. Therefore, 1.8 mmol of mercury extracted from bead particles in the first contact corresponds to 92.0% of the loaded mercury (3.6 mmol of mercury should be equivalent to $3.6/1.635 \approx 2.2$ mmol of mercury/g of loaded polymer sample). Another advantage of acetic acid is its environmentally safe nature for large-scale treatments.

In conclusion, polyacrylamide can be grafted efficiently onto spherical bead polymers by redox initiation of acrylamide from supported iminoacetic acid groups with Ce(IV). Mobile polyacrylamide chains selectively bind mercuric ions and give a second crosslinked layer. Partial mobility of the graft chains provides queasy homogeneous reaction conditions in mercury binding. Moreover, reversible crosslinking with mercuric ions leads to an interesting topology of the polyacrylamide brushes on the spherical bead particles. The excretion of sorbed mercury can be achieved with acetic acid and yields mercury-free polymer. The procedure presented offers a feasible pathway for removing mercuric ions, even at concentrations measured in parts per million.

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