Poly(acrylamide) Grafts on Spherical Polymeric Sulfonamide Based Resin for Selective Removal of Mercury Ions from Aqueous Solutions

Bahire Filiz Şenkal, Erdem Yavuz, Niyazi Bicak*

Istanbul Technical University, Department of Chemistry, 34469, Maslak-Istanbul, Turkey
E-mail: bsenkal@itu.edu.tr

Summary: Poly (acrylamide) was grafted from carboxylic acid groups onto cross linked poly (styrene) beads using a redox polymerization methodology. A beaded polymer with a poly(acrylamide) surface shell was prepared in three steps, starting from poly(styrene-divinyl benzene) (PS-DVB) (10% crosslinking) based beads with a particle size of 420-590μm, according to the synthetic protocol; chlorosulfonation, sulfamidation with glycine and grafting using a concentrated aqueous acrylamide solution with cerium ammonium nitrate.
The resulting polymer resin with 220 wt % of grafted poly (acrylamide) has been demonstrated to be an efficient mercury-specific sorbent, able to remove Hg (II) from solutions at ppm levels. The mobility of the graft chains provides nearly homogenous reactions conditions and rapid mercury binding ability. The mercury sorption capacity under non-buffered conditions is around 5.75 mmol/g. No interference arises from common metal ions such as Cd (II), Fe (II), Zn (II), and Pb (II).The sorbed mercury can be eluted by repeated treatment with hot acetic acid without hydrolysis of the amide groups.

Keywords: graft poly(acrylamide); mercury extraction; mercury specific sorbent; polymer modification; poly(styrene); selectivity

Introduction

Among the different industrial heavy metal rejections, mercury is among those with the greatest impact on environment. 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 clean up and hydrometallurgical applications [1].

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Conventional ion exchangers have limited success in the extraction of trace quantities and it is necessary to remove toxic metals by using more efficient polymeric sorbents.

Two common ligands types, sulfur and amide, are currently used in the design of polymeric sorbents for binding mercuric ions selectively.

The superior reactivity of sulfur compounds toward mercuric ions is the key principle behind anchoring thiol [2, 3] and thio ether [4] functions for laboratory or industrial levels of applications. Unfortunately, thiol and thioether functions react also with other metal ions. Therefore the mercury-thiol interaction is not specific. There are many articles about some other sulfur-containing polymer-supported ligands such as xanthate [5], thiourea [6], pyridine-based thiols [7] and dithiozone [8] in highly selective mercury removal. Sinner et al showed that polymers possessing dipyridyl amide functions have highly selective mercury sorption abilities [9].

Another important ligating group for selective mercury binding is the amide group, which forms covalent mercury-amide linkages under ordinary conditions.

In this study, poly(acrylamide) groups carrying polymeric sorbents were synthesized using a redox methodology. Linear polymers grafted onto crosslinked polymer resin particles offer numerous potential applications due to the combination of resin insolubility and the flexibility of the graft polymer side chains as the functional group carrier.

The flexible side-chains can provide pseudo–homogenous reaction conditions and better accessibility of the functional groups involved.

For this purpose, chlorosulfonated polystyrene beads have been modified in two steps by a reaction with glycine and polyacrylamide has been grafted by a redox polymerization technique. The selectively mercury uptake ability and regeneration conditions of the resulting resin have been investigated.

Experimental

Materials: Inhibitor-free styrene (Fluka) was obtained by re-distillation under vacuum. All other chemicals were analytical grade: Glycine (E.Merck), DVB (Aldrich), Chlorosulfonic acid (Fluka), cerium ammonium nitrate (Aldrich), $HgCl_2$ (E-Merck), Diphenyl carbazide (E-Merck). Colorimetric analyses were performed using a Schimadzu 160 a UV-Vis. Spectrometer.

Crosslinked Poly (styrene-divinyl benzene) beads

Beads were prepared by the suspension polymerization of a mixtured styrene (54 ml, 0.48 mol) and DVB (55 % grade, 10 ml, 0.038 mol) in toluene (60 ml), using gum-arabic as stabilizer, according to a previously described procedure [10]. The beads were sieved and the 420-590 µm size fractions were used for further reactions.

Chlorosulfonation of the beaded polymer

The beaded polymer was chlorosulfonated using chlorosulfonic acid as described in the literature.[11] The degree of chlorosulfonation was determined by analysis of the liberation of chloride ions. For these purpose, a polymer (0.2 g.) sample was added to 10 % NaOH (20 ml) and boiled for 4h. After filtration and neutralization with HNO_3 (5 M), the chlorine content was determined by the mercuric-thiocyanate method [11].This gave a final chlorosulfonation of 4.0 mmol. g^{-1}.

Sulfamidation of the beads

The chlorosulfonated polymer (10 g.) was added portion wise to a stirred solution of glycine (4 g, 0.053 mol) in 2-methyl pyrrolidone (25 ml) at 0 ^{0}C. The mixture was shaken with a continuous shaker for 12 h at room temperature. The reaction content was poured into water (500 ml), filtered and washed with excess water. The product was dried under vacuum at 40°C for 24 h. The yield was 12 g. The sulfonamide content was determined according to the literature [10] and found to be 3.38 mmol.g^{-1}.

Graft copolymerization of acrylamide from carboxylic acid groups

The carboxylic acid containing polymer (3.0 g) was wetted with 5 ml of distilled water and left stand for 3h. To this mixture, 0.1 g. (1.8 mmol) of $Ce(NH_4)_2(NO_3)_6$ in 5 ml of distilled water was added and shaken for 5 minute at room temperature. A solution of 9 g (0.126 mol) of acrylamide in 30 ml of distilled water was added to the mixture and shaken for 24h at room temperature with continuous shaker. The reaction contents were poured into water (500 ml), the resin filtered off and washed with excess water. The yield of crude product was 6.6 g.

Meanwhile, in order to examine homopolymer formation, 15 mL of filtrate was added to 50 mL acetone. About 28 mg of dry sample implies a 20 % of homopolymer yield.

Determination of the degree of grafting

The degree of the grafting was determined by Kjeldahl nitrogen analysis of the graft polymer sample as follows: 0.5 g.of were 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 total nitrogen content of the filtrate was assayed by the Kjeldahl method, as given in the literature [12]. This analysis gave nitrogen content of a 9.5 $mmol.g^{-1}$.

Swelling of the graft polymer

Due to hydrophilic poly (acrylamide) brushes, the bead polymer was expected to show water absorbence. Swelling of the polymeric beads was determined by determining the mass increase of the polymeric sample (0.1 g) soaked in distilled water in a crucible. After contact for 24 h, the increase in mass of the filtered sample (0.123 g) indicated a 23 % (w/w) water sorption.

Hg uptake experiments

The Hg sorption capacity of the grafted beads was determined as follows. To the grafted polymeric resin (0.2 g) in water (5 ml) was added a Hg (II) solution (20 ml , 0.15 M). The mixture was left to stirring for 24 h and then filtered. A sample (1 ml) of the supernatant solution was transferred to a volumetric flask and diluted to 10 ml with water. The residual Hg content of the solution was assayed using a colorimetric method as described in the literature [13]. Analysis of the supernatant in contact with resin indicated a Hg (II) concentration of 0.074 M in the final solution, which corresponds to a mercury loading capacity of 5.75 $mmol.g^{-1}$.

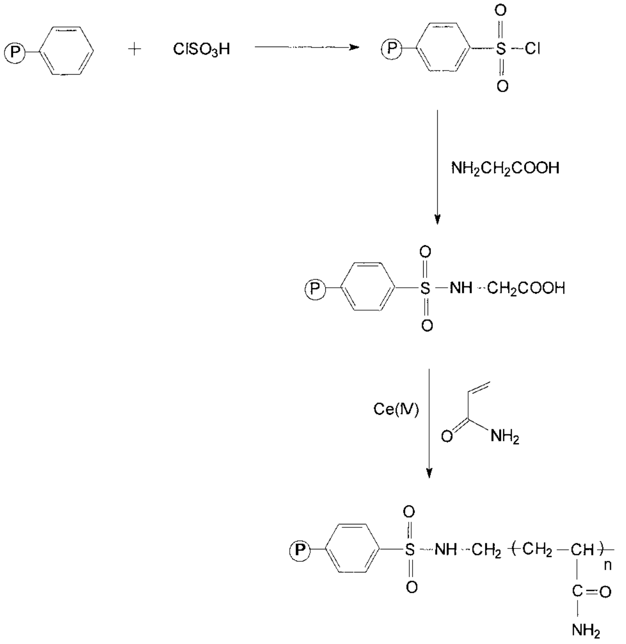
Kinetics of Hg sorption

Batch kinetic experiments were performed with very dilute Hg solutions (66 ppm). For this purpose the polymer resin sample (0.1 g) was wetted with distilled water (5ml) and added to a solution of Hg (90 mL of 0.01g $HgCl_2$ in 100 mL water). The mixture was stirred magnetically and aliquots of the solutions (10 ml) were taken at appropriate time intervals for analysis of the residual Hg content by the method described above Fig.1. below summarizes the data obtained.

Results and Discussion

Crosslinked poly (styrene-DVB-g-poly (acrylamide) was prepared successfully by grafting from glycine sulfonamidated styrene-divinylbenzene (420-590 μm), the latter being obtained via stepwise modifications shown in Scheme 1.

Chloride analysis of the product in the first step (4 mmol g^{-1}) revealed a degree of chlorosulfonation of ~ 70%. The second step was performed with essentially quantitative conversion of the chlorosulfonyl groups when excess glycine in NMP was used. The sulfonamide content was found to be 3.38 mmol g^{-1}; This amount is almost equal to the theoretical value of 4.0 mmol $g^{-1,}$ corresponding to 98 % conversion in the second step. Finally, poly (acrylamide) brushes were anchored to the bead surface by graft polymerization of acrylamide from carboxylic acid groups on the crosslinked support.



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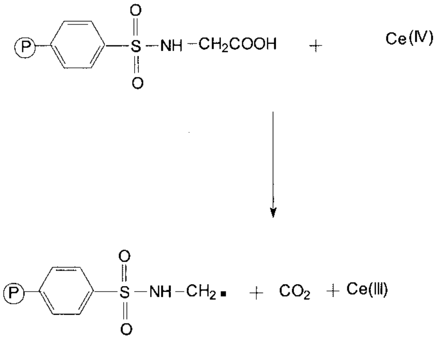
Grafting

Grafting from carboxylic acid group by redox interaction with $Ce(NH_4)_2(NO_3)_6$ is a very complicated process because homopolymer formation is a side reaction.

For fast initiation, the reactivity of the reducing groups on the surfaces is of prime importance in grafting using the Ce(IV) method (Scheme 2).



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This requirement is fulfilled by the acid functionality, as described in the literature[14].The grafting degree depends on the reaction conditions and still possesses a high tendency to form homopolymers. Most likely, chain transfer to the solvent is responsible for the homopolymer formation [15].

Therefore, we have known that pretreatment of the bead polymer particles with a Ce(IV) solution for at least 3 min prior to the addition to the acrylamide is suitable to suppress homopolymer formation . This way, we obtained high mass increases (220%) in 24 h. at room temperature. Under this condition, homopolymer is isolated by precipitation in acetone indicates a free polymer yield of 20% as by-product.

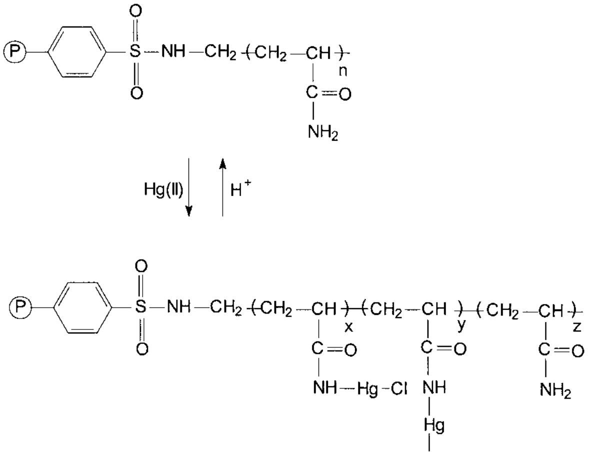
A longer interaction period with Ce (IV), prior to the addition of the monomer, causes the consumption of vast amounts of the initiator groups for direct oxidation and the degree of grafting falls sharply to low values. Initiation through carboxylic acid functions is believed to proceed via CO_2 elimination as described in the literature [16].

Kjeldehal nitrogen analysis of the graft polymer gave 9.5 mmol nitrogen / g of polymer. This indicates 216 % grafting, which is very close to the value of 9.68 mmol.g^{-1} found by mass increase.

Hg Uptake

The resulting beaded polymer with poly (acryl amide) grafts was expected to show the characteristics of semi homogenous reaction conditions. Flexible poly (acrylamide) graft chains should offer the opportunity for rapid interaction with aqueous Hg (II) solutions to form mercury-amide linkages. In accordance with the previous study,[15] the mercury binding process occurs via simultaneous proton releasing as it was inferred by increase in pH of the mercury solutions while interacting.

There exist possible reaction sites, one sulfonamide group and carbon amide groups, available for the mercury binding. Mercury binding via carbonamide groups can occur in principle either by formation of monoamide or diamide Hg structures, which provide a means of capturing Hg^{2+} from aqueous solution (Scheme 3).



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Aqueous solutions of $HgCl_2$ were used in Hg sorption experiments. The sorption capacity of the grafted beads was assessed by analysis of the excess Hg^{2+} in the supernatant solutions. The overall Hg^{2+} uptake capacity from 0.15 M $HgCl_2$ solution was high, (5.75 $mmol.g^{-1}$).

In 0.05- 0.15 M initial mercury concentration range loading capacity of the polymer did not change practically. There is no limitation of diffusion inside the polymer particles, since the reactive sites are

located on flexible poly (acrylamide) chains outside the particle surface. Also, the mercury binding takes place as if under homogenous conditions. (Table 1).

Table 1. Mercury sorption characteristic of the resin.

initial conc., ($mol.L^{-1}$)	sorbed Hg ($mmol.g^{-1}$)	mass increase (%)	stripping Hg, ($mmol.g^{-1}$)
0.15	5.75	88.0	5.52
0.10	5.63	80.0	5.60
0.05	5.76	85.0	5.70

Since, in ordinary conditions the amide group is not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the amide nitrogen; the separation of Hg^{2+} is expected to be highly selective.

To probe the degree of selectivity of the Hg^{2+}, the sorption experiments were repeated with other potentially contaminating ions. In particular, 0.15 M single metal ion solutions of Cd (II), Zn (II), Pb(II) were examined. Very small sorption capacities between 0.06-0.1 $mmol.g^{-1}$) were observed. Those small quantities are likely in experimental error limits. Therefore, overall the results clearly indicate that Hg sorption is extremely selective.

Batch kinetic sorption experiments from highly dilute (66 ppm) Hg (II) solutions indicate relatively fast binding of Hg (II) (Fig 1). The uptake obeys second order kinetics ($k= 63\ M^{-1}.s^{-1}$ with a correlation factor of 0.989) as in the case of many metal complexations involving solid surfaces (Fig.2).

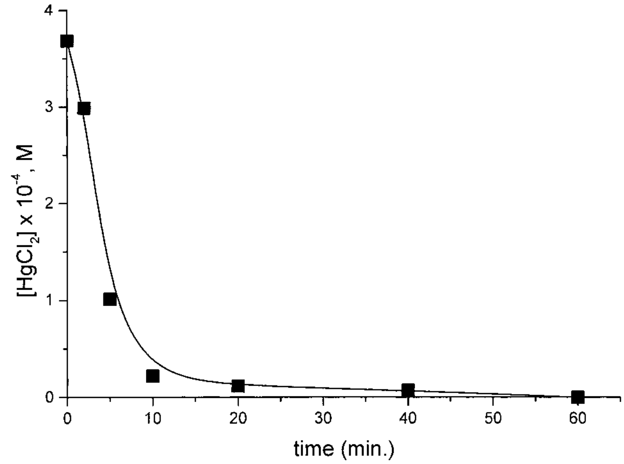

Figure 1. Concentration-time plot of 100 mL $HgCl_2$ solution (initial concentration $3.7x10^{-4}$ M) while contacting with 0.2 g. of polymer sample.

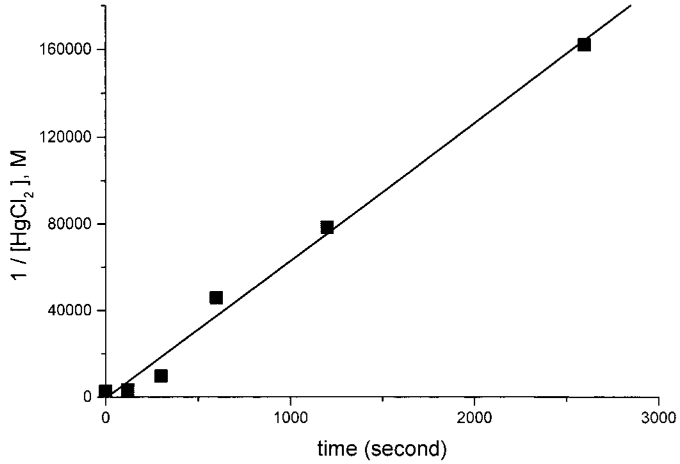

Figure 2. Second order kinetic plot for sorption of mercury from 100 mL $HgCl_2$ solution (initial concentration $3.7x10^{-4}$ M) while contacting with 0.2 g. of polymer sample.

Splitting of the Sorbed Mercury

Regeneration of the polymer sorbent can be achieved by acid treatment, but the use of mineral acids is not advisable because strong acids may cause hydrolysis of the amide groups in the graft chains. To avoid such hydrolysis, we have found that acetic acid is the most suitable one for splitting of the mercury. When mercury loaded samples were heated to 80 ^{0}C in acetic acid .5.52 mmol mercury re-extracted into the acid per gram of the polymer. This amount indicates an almost quantitative elution of the sorbed mercury.

In conclusion, polyacrylamide can be grafted efficiently onto spherical bead polymers by redox initiation of acrylamide from supported carboxylic acid groups with Ce(IV). The resulting graft polymer resin is highly effective and selective for Hg sorption and the resin format makes the material of interest as a column packing material for industrials use.

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