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Reactive & Functional Polymers 65 (2005) 121–125

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Poly(acrylamide) grafts on spherical polyvinyl pyridine resin for removal of mercury from aqueous solutions

Erdem Yavuz, Bahire Filiz Senkal *, Niyazi Bicak

İstanbul Technical University, Department of Chemistry, 34469 Maslak-İstanbul, Turkey

Received 22 July 2004; received in revised form 3 December 2004; accepted 6 December 2004
Available online 18 July 2005

Abstract

Poly(acrylamide) is grafted onto cross-linked poly (4-vinyl pyridine) (P4-VP) resin "Reillex 425". Its quaternization with potassium chloroacetate results in cross-linked poly (4-vinyl pyridine) having carboxymethyl pyridinium groups. This resin is grafted with acrylamide after redox initiation through the carboxyl groups with cerium ammonium nitrate.

The resulting resin with 111.7 wt% of poly(acrylamide) grafts is a high capacity (3.36 mmol g^{-1}) mercury specific sorbent.

Experiments performed under identical conditions with some other ions such as Zn(II), Pb(II), Fe(III) and Cd(II) showed that those metal ions are not sorbed by the resin.

Flexible graft chains of poly(acrylamide) provide nearly homogeneous reaction conditions in mercury uptake. Regeneration of the mercury loaded polymer can be achieved by acetic acid treatment.

Keywords: Mercury uptake; Poly(vinyl pyridine) resin; Poly(acrylamide) graft polymer; Redox polymerization

1. Introduction

From different industrial heavy metal wastes, mercury is among those with the greatest impact on environment.

Removal of mercury from aqueous solution is of special importance in waste water treatments and in hydrometallurgical applications. Removal of trace mercury can not be achieved by conventional ion exchangers. Removal of mercury and other toxic metals require more efficient sorbents. Specially designed chelating polymers show excellent metal-uptake capabilities and these have been discussed in many articles and reviews [1,2].

Thio and amide groups have been used in the design of polymeric sorbents for binding mercury ion selectively. The well-known reactivity of thiol

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* Corresponding author.
E-mail address: bsenkal@itu.edu.tr (B.F. Senkal).

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doi:10.1016/j.reactfunctpolym.2004.12.006

[3–6] and thioether [7] compounds toward mercuric ions is the main principle of selective mercury uptake for laboratory or industrial levels of applications. In fact, mercury–thiol interaction is not specific because thiol and thioether functions react also with other metal ions [8].

In our previous studies we have demonstrated that, amide groups provide better selectivity in mercury binding [9]. The mercury–amide linkage is covalent [10] and the reaction takes place even in aqueous solutions at room temperature.

In this study poly(acrylamide) chains were anchored to cross-linked (P4-VP) by graft copolymerization of acrylamide through the carboxyl groups by using Ce(IV). Linear graft chains on cross-linked (P4-VP) are expected to have potential applications due to the combination of resin insolubility and the flexibility of the chains. The flexible side-chains can provide pseudo-homogenous reaction conditions and better accessibility of the functional groups involved.

Quaternary groups are hydrophilic and may balance the lipophilic nature of amido-mercury structures. We, therefore, thought that their presence could facilitate binding of mercuric ions, although their contribution to the hydrophilicity of the resin environment is smaller in comparison to those produced by polyacrylamide chains.

In this work, cross-linked poly (4-vinyl pyridine) was quaternized by chloroacetic acid and acrylamide was grafted by a redox polymerization through the carboxyl groups. Mercury sorption characteristics and regeneration conditions of the resulting resin was studied. Affinity of the resin for some other metal ions such as Cd(II), Pb(II), Fe(III) and Zn(II) was also investigated.

2. Experimental

Materials: poly (4-vinyl pyridine) (P4-VP) beads (Reillex 425) (210–420 μm) (cross-linked with 25% (w/w) commercial divinyl benzene (DVB), 55% of which is a mixture of meta and para isomers) was supplied from Reilly industry Inc., IN, USA.

Chloroacetic acid (E. Merck), acrylamide (E. Merck) and all the other chemicals used were analytical grade commercial products.

2.1. Quaternization of cross-linked (P4-VP) beads

Quaternization of polymer beads was carried out by reacting the potassium salt of monochloroacetic acid solution, while 18.9 g (0.2 mol) chloroacetic acid was dissolved in 20 ml H_2O. Then 13.8 g (0.1 mol) K_2CO_3 in 25 ml of distilled water was added dropwise to the ice cooled solution of the chloroacetic acid while stirring.

A sample containing 10 g of the P4-VP resin was placed in this solution and the mixture was shaken by means of a continuous shaker for 48 h at room temperature. The mixture was heated to 70 °C for 4 h, filtered and washed with water. The product was filtered washed with excess of water and acetone, respectively. The vacuum-dried sample weighed 14.8 g.

2.2. Estimation of the Carboxyl content

To 40 ml of 0.1 M NaOH solution 0.5 g of the quaternized resin was added and left to stand overnight. The mixture was filtered.

The filtrate was titrated with 0.1 N H_2SO_4 solution. Carboxylic acid content was found as about 2.2 mmol g^{-1} resin, which corresponds to 38.9% of quaternization of the pyridine units.

2.3. Graft copolymerization of acrylamide from carboxylic acid groups

The polymer sample with carboxymethyl pyridinium groups (3 g) was wetted with 5 ml of distilled water and left stand for 2 h. To this mixture, 0.1 g (1.8 mmol) of $Ce(NH_4)_2(NO_3)_6$ in 5 ml of water was added and shaken for 2 min at room temperature. A solution of 9 g (0.126 mol) of acrylamide in 30 ml of distilled water was added to this mixture and shaken for 24 h at room temperature with a 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 6.35 g.

Meanwhile, in order to examine homopolymer formation, 10 ml of filtrate was added to 40 ml of acetone. Evaporation of the solvents in the filtrate gave 21 mg of homopolymer 23.9%.

2.4. Determination of the grafting degree

The degree of grafting was determined by Kjeldahl nitrogen analysis of the graft copolymer sample as follows: 0.2 g of the bead were placed in 20 ml of concentrated H_2SO_4 and boiled for 10 h. The mixture was filtered and diluted to 70 ml with distilled water. The total nitrogen content of the filtrate was assayed by Kjeldahl method, as given in the literature [11]. This analysis gave a nitrogen content 6.88 of a mmol g^{-1}.

2.5. Mercury uptake

The mercury sorption capacity of the grafted polymer was determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous Hg(II) solution (0.1 M).

The mixture was stirred for 24 h and the filtered. The Hg(II) concentrations were determined colorimetrically using diphenyl carbazide [12].

The mercury-loading capacities were calculated from the initial and final Hg(II) contents of the solution. 1 ml volume of the filtrate was used for determination of the residual mercury. Therefore, a 0.0162 M residual Hg (II) concentration in the filtrate indicated 3.36 mmol g^{-1} mercury uptake capacity.

In order to examine the selectivity of Hg binding, sorption capacity measurements were also performed using Cd(II), Pb(II), Zn(II), and Fe(III) ion solutions (0.15 M initial concentrations). Analysis of the residual metal contents of the supernatant solutions were performed by a complexometric titration method using EDTA solution (0.1 M). The data collected are given in Table 1.

2.6. Kinetics of the sorption

In order to estimate efficiency of the sorbent for trace mercury batch kinetic experiments were performed using high diluted Hg(II) solutions (3.683×10^{-3} M). For this purpose the polymeric resin (0.2 g) was wetted with distilled water (1.5 ml) and added to a solution of Hg (100 ml of 0.1 g $HgCl_2$ in 90 ml water). The mixture was stirred magnetic stirring bar and aliquots of the solution (10 ml) were taken at appropriate time intervals for analysis of the residual Hg(II) contents by the method as described above. Fig. 1. shows the data obtained.

Table 1
Metal uptake characteristics of the poly (acrylamide) grafted beads

Metal ion	Initial concentration (M)	Resin capacity (mmol g^{-1})	Recovered metal (mmol g^{-1})
Hg(II)	0.10	3.36	3.20
Hg(II)	0.05	3.12	3.01
Hg(II)	0.025	3.45	3.25
Cd(II)	0.15	0.19	–
Pb(II)	0.15	0.20	–
Zn(II)	0.15	0.18	–
Fe(III)	0.15	0.77	–

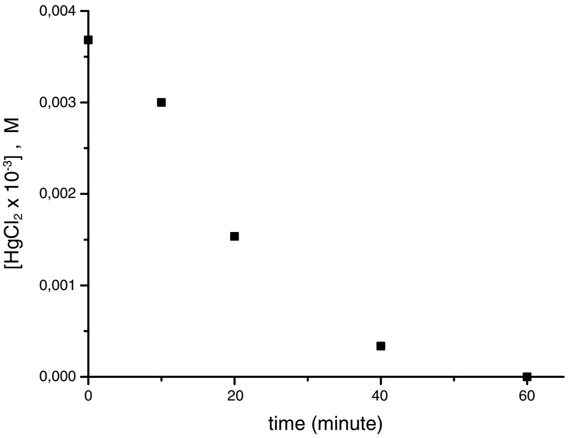
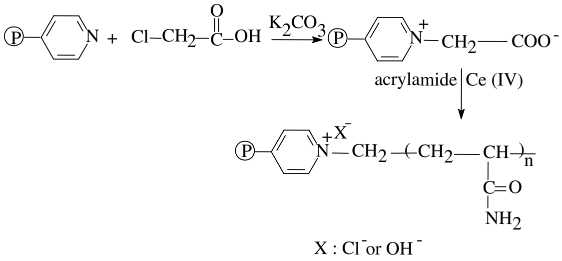


Fig. 1. Concentration–time plot of 90 mL $HgCl_2$ solution (initial concentration 3.683×10^{-3} M) while contacting with 0.2 g of polymer sample.

3. Results and discussion

Cross-linked polyvinylpyridine–graft–polyacrylamide was prepared successfully by grafting from quaternized P4-VP- (210–420 μm). Quaternization was performed with chloroacetic acid. At the end of reaction carboxylic acid content of the product was found as 2.2 mmol g^{-1}. Finally, poly (acrylamide) brushes were anchored to the bead surface by graft polymerization of acrylamide



Scheme 1.

from carboxylic acid groups on the cross-linked support (Scheme 1).

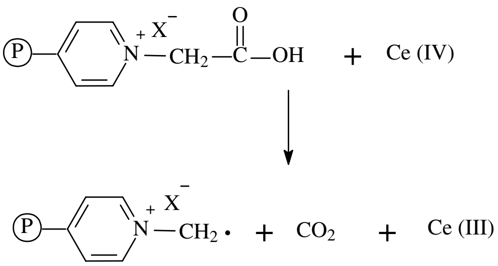
3.1. Grafting

Grafting from carboxylic acid group by redox interaction with cerium ammonium nitrate is a very complicated process due to homopolymer formation as 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).

This requirement is fulfilled by the acid functionality, as described in the literature [13].

The grafting degree depends on the reaction conditions and still possesses a high tendency to form homopolymers. More likely, chain transfer to the solvent is responsible for the homopolymer formation [14].

Our experiences showed that pretreatment of the polymeric beads with a Ce(IV) solution for at least 2 min. prior to the addition to the acrylamide is suitable to suppress homopolymer formation. By this way, we obtained mass increases (111.7%) in 24 h at room temperature.



Scheme 2.

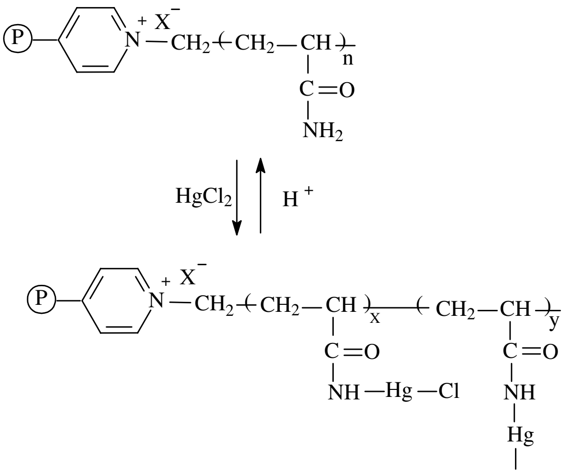
The homopolymer in solution was precipitated in acetone to indicate free polymer formation. The homopolymer yield was 21.0 mg yield of (23.9%). Kjeldahl nitrogen analysis of the graft polymer gave 6.88 mmol nitrogen per gram of the resin of the polymer. By assuming each Ce(IV) atom involves in initiation, this value corresponds to 21.8 repeat units per initiation site.

3.2. Hg uptake

The resulting beaded polymer with poly (acrylamide) grafts was expected to show the characteristics of semi homogenous reaction conditions. Flexibility poly (acrylamide) graft chains and hydrophilicity of the quaternary groups offer opportunity for rapid interaction with aqueous Hg(II) solutions to form mercury–amide linkages.

Mercury binding via carbonamide groups in principle can occur either by formation of monoamide or diamide mercury structures, which provide a means of capturing Hg^{2+} from aqueous solution (Scheme 3).

Aqueous solutions of $HgCl_2$ were used in mercury sorption experiments. The sorption capacity of the poly (acrylamide) grafted beads was analyzed by the determination of the excess mercury ions in the supernatant solutions. The mercury sorption capacity of the grafted resin from 0.1 M $HgCl_2$ solution was found as 3.36 mmol g^{-1}.



Scheme 3.

In 0.025–0.1 M of initial mercury concentration range loading capacity of the polymer did not change. Practically, there is no limitation of diffusion inside the polymer particles, because the reactive sites are located on flexible poly (acrylamide) chains. Also, the mercury binding takes place as if under homogenous conditions (Table 1).

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 mercury ions is expected to be highly selective. To prove the selectivity of the mercury sorption, experiments were repeated with other metal ions. In particular, 0.15 M single metal ion solutions of Cd(II), Zn(II), Pb(II) and Fe(III) were examined. Small sorptions (0.18–0.77 mmol g^{-1}) were detected. Overall the results clearly indicate that mercury sorption can be considered as selective.

Batch kinetic sorption experiments from highly dilute Hg(II) solutions (3.683×10^{-3} M) indicate relatively fast binding of mercury (Fig. 1).

The curve in Fig. 1 indicates a second order kinetics ($k = 1.17\ M^{-1}\ s^{-1}$ with a correlation factor of 0.983).

This result omits small change of surface area of the particles due to mechanical disintegration while stirring with magnetic bar.

3.3. Desorption of the sorbed mercury

The use of a mineral acid for back extraction of the sorbed mercury is not suitable, because amide group itself is susceptible to hydrolysis. To avoid amide hydrolysis mercury desorptions were carried out by acetic acid. As it might be expected hot acetic acid does not cause hydrolysis, transamidation with acetic acid, is also not favoured due to volatility of the acetic acid. 60–65% of the sorbed mercury is desorbed by the first treatment with hot acetic acid for 1 h. While a second treatment results in a almost complete desorption of the remaining mercury. After washing with excess of water, polymeric resin becomes mercury-free. When the mercury-loading experiment was repeated with regenerated polymer, its loading capacity was exactly the same.

4. Conclusion

Graft copolymerization of acrylamide from carboxyl groups can be carried out using Ce(IV). The resulting material is a high capacity mercury sorbent. Since sorptions of the foreign ions are lower than that of mercury, the resin is highly mercury selective.

Regenerability of this material with acetic acid makes it attractive for large scale applications.

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