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Graft copolymer of acrylamide onto cellulose as mercury selective sorbent

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Abstract

Polyacrylamide grafted onto cellulose has been demonstrated to be a very efficient selective sorbent for removal of mercuric ions from aqueous solutions. The mercury-uptake capacity of the graft polymer is as high as 3.55 mmol/g and sorption is also reasonably fast. Thus, 0.2 g of the graft copolymer is able to extract 50 ppm Hg(II) from 50 ml water completely in 8 min. The Hg(II) sorption is selective and no interferences have been observed in the presence of Ni(II), Co(II), Cd(II), Fe(III), Zn(II) ions in 0.1 M concentrations at pH 6. Regeneration of the loaded polymer without losing its original activity can be achieved using hot acetic acid. The graft copolymer described seems very suitable for removal of large amounts of mercury in hydrometallurgical applications and may also be useful for other water treatments. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymers with ligands capable of coordinating with metal ions have attracted great interest for cleaning up waste water and the recovery of noble metals. Current efforts are at the stage of developing selective chelating species [1]. In some cases selective separation of any desired metal ion from binary or ternary mixtures can be achieved to some extent by controlling the pH or using a masking agent.

A metal oriented post-crosslinking polymerization of vinyl monomers such as 4-vinylpyridine [2] has also been proposed as a route to selective sorbents. However, the success of the selectivity depends strictly on the crosslinking density [3], and in this case diffusion of metal ions into the polymer matrix becomes slower as the crosslinking density increases. For this reason this method seems to be applicable, for the time being, to analytical purposes only and it is not suitable for large scale separations. The best method of achieving selective separation is to use a metal specific ligand, but it has proved impossible to find specific ligands for each metal ion in the periodic table at least, so far.

An exception is the mercury-amide interaction. It is interesting to note that amide compounds are selective reagents for binding mercury. The reaction is reasonably fast even at

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room temperature. The amide nitrogen forms a covalent bond with Hg(II) ions but not with other metal ions. Generally, the amide nitrogen atom lacks sufficient electron donating character due to the adjacent electron withdrawing carbonyl group and it cannot normally form coordination bonds with transition metal ions. Although Cu(II) ion has been reported to form complexes through amide groups in polyamides and polypeptides, generally these complexes form at high pH levels or complexation occurs through amine and amide nitrogens [4]. This makes the amide group potentially unique for selective mercury binding from mixtures of ions. In our previous paper we have demonstrated that crosslinked polyacrylamide is an extremely powerful sorbent for mercury uptake [5] sorbing as high as 3 g Hg(II) per gram of polymer.

Although some polymer-supported thioethers [6-8] and thiols [9] have also been reported as selective reagents to remove mercury, the selectivity is not as high as that of the amide compounds.

In the present study, we report the use of grafted polyacrylamide for mercury uptake. For this purpose acrylamide has been grafted onto cotton cellulose and its Hg(II) sorption characteristics have been investigated.

Since grafted chains of polyacrylamide have much more flexibility, these are expected to show rapid mercury binding ability.

2. Experimental

Hydrophilized commercial cotton (Ipek Pamuk Sanayii, Turkey) was used as the base for all grafting. All the other chemicals were analytical grade products: $Ce(SO_4)_2 \cdot 4H_2O$, acrylamide, acetone and $Hg(CH_3COO)_2$ (all from Merck) and were used as supplied.

2.1. Preparation of the graft copolymer

Grafting of acrylamide onto cellulose was performed by using Ce(IV) sulphate, according

to the procedure described in the literature [10]. A typical procedure is as follows: hydrophilized natural cotton (8 g) was added to distilled water (200 ml) in a 1-l flask. Acrylamide 20 g (0.28 mol) was also dissolved in distilled water (40 ml). While a nitrogen stream was bubbled through the flask, a solution of $Ce(SO_4)_2 \cdot 4H_2O$ (0.5 g, 1.23 mmol) in distilled water (10 ml) and the acrylamide solution were added and the system was flushed again with N2. The flask was closed with a stopper and placed on a shaker for 24 h at room temperature. At the end of this time, the swollen cotton was filtered and transfered into distilled water (1500 ml). After mixing for a while, the washings were decanted. This procedure was repeated six times and the solid product transfered into acetone (100 ml) and agitated with a glass rod for 5 min. Then the acetone was decanted off and the graft polymer was dried in vacuo at 40°C for 24 h.

The dry product weighed 16.8 g. Elemental microanalysis gave C 42.8%, H 6.85% and N 9.70%. Based on the nitrogen content of the product, the degree of grafting was calculated as 106.0%.

2.2. Swelling of the copolymer

A weighed amount of dry sample (0.2 g) was placed in a sintered glass funnel and immersed in water in a beaker. At appropriate time intervals, it was filtered and weighed. Based on the weights in swollen and dry states, w/w_0 were pictured as a function of time, as shown in Fig. 1.

2.3. Mercury uptake

The mercury sorption capacity of the grafted polymer was determined by mixing the sample (0.65 g) with 50 ml aqueous Hg(II) solution (0.08 M).The concentration of Hg(II) in the solution was measured colorimetrically using diphenyl carbazide [11]. The mercury loading capacities were calculated from the initial and final Hg(II) contents of the solution.



Fig. 1. Swelling ratio (w/w_0) of the graft copolymer in distilled water versus time.

More specifically, a graft polymer sample (0.65 g) was added to distilled water (50 ml) in a 250-ml flask and shaken for 15 min, a solution of mercuric acetate (1.274 g, 4 mmol) in distilled water (50 ml) was added and the mixture was stirred for 2 h at room temperature and filtered. A 1-ml volume of the filtrate was used for the determination of the residual mercury. This inspection indicated that final concentration of the mercury solution was 0.034 M. The results obtained are shown in Table 1.

Mercuric nitrate can also be used. However, in that case during the mercury binding, HNO₃ release may cause hydrolysis of the amide groups. Because of this fact mercuric acetate was chosen as the mercuric ion source.

2.4. Mercury uptake under competitive conditions

In order to determination the selectivity of the mercury uptake the above experiment was repeated separately in the presence of 0.1 M $Cd(NO_3)_2$, $Zn(CH_3COO)_2$, Ni(II) and $Fe(CH_3COO)_3$ in the Hg(II) solutions.

In order to check any possible interaction of the graft copolymer with these competitive ions each of the latter solutions (0.1 M) was contacted with a copolymer sample in the absence of Hg(II). The metal contents of the resultant solutions were determined by conventional EDTA titration methods [11]. No differences were observed in the initial and final concentrations of the competition metal ion solutions. Thereafter the same experiments were repeated in the presence of Hg(II). In each experiment $Hg(CH_{3}COO)_{2}$ (6.37 g, 20 mmol) and 25 mmol of one of the metal salts were dissolved in water and mixed with 50 ml of sodium acetate-acetic acid buffer solution (pH 6.2) and diluted to 250 ml. A sample of the solution (50 ml) was interacted with the graft copolymer (0.2 g) for 2 h at room temperature. The polymer samples were filtered and dried.

Since the diphenyl carbazide colorimetric method is not applicable in the presence of other metal ions, the amounts of the mercury sorbed was determined by analysis of the acid leaching solutions. For this purpose, the Hg(II) was desorbed from each loaded sample by acetic acid treatment as described in Section 3.4. The mercury content of each acetic acid solution was then assayed colorimetrically.

Table 1Mercury sorption capacities of some polyamides

Polymer	Amide content (mmol/g)	Mercury loading capacity	Amide/Hg(II) (mol/mol)	Desorption ^a (mmol/g)
Polyacrylamide graft copolymer	6.92	3.55	1.95	2.52
Natural wool	_	0.41	_	-
Nylon 66	9.43	0.09	67.4	-

^a Based on the mercury loaded copolymer sample.

From these experiments the mercury sorption capacities were found to be 3.54, 3.55, 3.55, 3.56 and 3.55 mmol/g in the presence of Zn(II), Cd(II), Ni(II), Co(II) and Fe(III) ions, respectively.

2.5. Kinetics of the mercury uptake

In order to test the efficiency of the graft copolymer for trace quantities, kinetic experiments were conducted with aqueous Hg(II) solution at 50 ppm concentration. Batch kinetic experiments were performed as follows: a copolymer sample (0.5 g) was chopped into small pieces (2-3 mm) and put into distilled water (50 ml) in a 250-ml flask. After stirring for 15 min, $Hg(CH_3COO)_2$ solution (50 ml of $0.5 \cdot 10^{-3}$ M) was added to the flask to yield a Hg(II) concentration of 50 ppm. While stirring with a magnetic stirrer, 5-ml aliquots of supernatant were taken at appropriate time intervals and these were transfered into volumetric flasks through filter paper. The mercury concentrations were analysed as before.

The same experiment was repeated at different pH values adjusted using buffered solutions (NaOAc-AcOH for pH 6.2 and 3.3), so that the total volume was 100 ml. The concentrationtime plots of the mercury solutions are shown in Fig. 2.



Fig. 2. Concentration-time plots of 100 ml mercuric acetate solution (50 ppm) contacting with 0.5 g of the graft polymer at different pH values.

2.6. Regeneration of the used polymer and recovery of the sorbed mercury

Desorption of mercury from the copolymer loaded samples was performed simply by boiling in acetic acid. Thus a mercury loaded copolymer sample (0.5 g) was placed in a 50-ml of flask fitted with a reflux condenser. Acetic acid (20 ml) was added to the flask and refluxed for 30 min. After cooling the mixture was filtered and 5 ml of the filtrate was taken out for mercury colorimetric analysis. The amount of mercury recovered is shown in Table 1.

3. Results and discussion

The reaction of Hg(II) ions with amides can be depicted as shown in Scheme 1: a covalent bond is formed between the mercury and amide nitrogen atoms in aqueous solution. Generally mercurated amides are insoluble in water and the reaction is common to all primary and secondary amide compounds. The reaction also forms the basis of one of the most common reaction of proteins in which addition of few drops of Hg(II) solution added to an aqueous solution of protein, causes instantaneous precipitation of the biomacromolecule. Apparently this reaction involves crosslinking by mercuric ions via the amide groups.

In aqueous solution anion exchange can take place and the counter anion may be hydroxyl as well.

3.1. Synthesis of polyacrylamide-g-cellulose

To exploit the above reaction in removing mercuric ions from aqueous solutions we have



prepared cellulose-g-polyacrylamide. The degree of grafting was chosen deliberately high to attain high mercury binding capacities. The graft copolymer swells rapidly in water and swelling equilibrium is established in about 30 min as shown in Fig. 1. No further volume expansion occurs with prolonged contact times. The rapid swelling can be ascribed to the mobility of the linear polyacrylamide chains attached to the hydrophilic cellulose. The percentage of grafting was calculated based on the nitrogen content and was found to be 106%.

Using the weight increase indicates 115% of grafting. Taking into account a water content of 4.35% (from the elemental microanalytical data) this corresponds to 108% grafting, which is close to that calculated from the weight increase. If the cotton is assumed to be pure cellulose, according to the microanalytical data there would be 2.68 mol of acrylamide units per each glucose unit of the cellulose. This corresponds to an amide content in the copolymer of 6.92 mmol/g.



Fig. 3. FT-IR spectra of (a) polyacrylamide-g-cellulose, (b) mercury loaded copolymer.

3.2. Mercury sorption capacity

As expected, the mercury binding capacity of the graft copolymer is high (3.55 mmol/g) and after a contact time of 1 h, 1 g of the sample weighed 1.893 g. Hence the molar ratio of the amide content to the sorbed mercury is 6.92/3.55=1.95. At first glance it seems therefore that each mercuric ion binds to two amide groups. But this is inconsistent with the weight increase, since 3.55 mol of mercuric ion would give rise to a weight increase of 0.71 g. which is less than that observed. This indicates that some portion of the sorbed mercury is bonded as acetoxymercury (Scheme 2). The bonding modes of the sorbed mercury can be estimated roughly as follows:

x + y + z = 6.92 mmol/g (from amide balance)

where x refers to the non-bonded amide content in mmol/g, y to the mmol of amide bonded as -CO-NH-HgOAc and z represents the mmol of amide groups bonded to mercury as -CO-NH-Hg-NH-CO-.

Since 3. 55 mmol of mercury is being sorbed

y + z/2 = 3.55 mmol/g (mercury balance

from loading experiment)

By neglecting the low water content (4.35%) of the graft polymer another equation can be written based on the mass balance on loading

$$(y258 + z198/2) \cdot 10^{-3} = 0.893$$

Here 258 and 198 are the weight increases due to incorporation of HgOOCCH₃ and Hg, respectively. Solution of the above equations gives x = 2.98, y = 3.17, z = 0.76 mmol/g

This rough estimation reveals that $\sim 40.0\%$ of amide groups remain unchanged and $\sim 45.0\%$ bind mercury in the monoacetate form. The remaining portion, $\sim 10.0\%$ bind mercury from both sides. Hence overall $\sim 60.0\%$ of the amide groups are involved in the mercury sorption.

The presence of the acetatomercuric group in the loaded polymer is confirmed by the FT-IR spectra (Fig. 3b). The strong band observed at

 1600 cm^{-1} can be assigned to the C=O stretching vibration of the acetate group. Although the N–H plane bending vibration is also observed at the same frequency, after the mercury sorption this band becomes stronger. In contrast the C=O stretching vibration of the amide group appears at 1670 cm^{-1} . This band is broadened with those of the N-H plane bending vibrations at about 1600 cm^{-1} (Fig. 3a). Due to the flexibility of the linear polyacrylamide chains grafted, all the amide groups may be expected be involved in mercury bonding. However, since doublebinding of mercury effectively introduces crosslinks, less than 100% use of amide groups is probably more realistic. In addition to this steric hindrance the hydrophilic-lipophilic balance may bring a limitation. Generally low-molecular-weight mercury-amide compounds are hydrophobic in nature and they are not soluble in water. So in the present case mercury-binding may continues only up to a critical point which is determined by the level of hydrophobicity induced. Beyond this point amide groups may remain unreacted simply because of inaccessibility.

The reaction seems to be general for all amide compounds and so all polymers carrying amide groups might be expected to be useful for selective mercuric ion sorption. However, natural wool and nylon-66 do not provide high reactivity towards Hg(II) ions in water. Under the same conditions used for the copolymer studies mercury loading capacities of these polymers were found to be 0.24 and 0.09 mmol/g, respectively (Table 1). On balance it seems that the very low hydrophilicity of these polymers makes access very restricted, with concomitant low mercury sorption .

3.3. Kinetics of mercury sorption

The sorption kinetics were investigated by following the variation with time of the Hg(II) concentration of the aqueous solution contacted with the graft copolymer. A steep decline is observed in mercury concentration of the reacting solution. The data in Fig. 2 also show that at

pH 6.2, this material is quite efficient for removal of trace quantities of Hg(II) with all the mercury at 50 ppm concentration being completely removed in about 8 min. At pH 3.3 the mercury sorption is somewhat slower. When a mercuric ion solution is contacted with the graft copolymer without buffer solution, the pH goes from 6.1 to 4.4 depending on the concentration and amount of sorbent. This confirms that the mercury binding process proceeds simultaneously with deprotonation of the amide groups.

Since the mercury linkage proceeds with deprotonation of the amide simultaneous groups, variation in pH of the solution should give information about the level of mercury uptake. But the use of mercuric acetate results in formation of a weak acid, acetic acid. Clearcut evidence can be derived when HgCl₂ is used. In this case, HCl is released instead. To observe the pH change, in a separate experiment, 50 mg of the polymer sample was interacted with 0.172 g HgCl₂ in 50 ml water. After 30 min the pH was measured which corresponds to $2 \cdot 10^{-3}$ M of hydrogen ion concentration. This leads to 0.25 mmol of hydrogen ion in 50 ml solution. Whereas in 50 mg of sample there are 0.346 mmol amide groups. Since y = 3.71mmol/g and z = 0.76 mmol/g, at maximum loading in a 50 mg sample $3.17 \cdot 0.05 = 0.1585$ mmol mercury must be bonded as the monohalide form, whereas $0.76 \cdot 0.05 = 0.038$ mmol mercury must be bonded as the diamido form.

The corresponding amount of protons released during the process amounts to $0.1585 + 2 \cdot 0.038 = 0.1658$ mmol.

This result approximately matches with the result predicted from pH measurement. On the other hand, pH 2.6 can be regarded as lower limit of the mercury binding processes.

As a consequence the mercury sorption and desorption of the graft copolymer can be depicted as shown in Scheme 2.

3.4. Recycling of the polymeric sorbent and recovery of the mercury

Mercury-amide linkages are known to hydro-



Scheme 2.

lyse on treating with mineral acids. Use of a mineral acid for extraction of the sorbed mercury is therefore not suitable. To avoid this hydrolysis of the amide groups we have found that the use of hot acetic acid is very suitable for desorption of the sorbed mercury. As it might be expected hot acetic acid does not cause hydrolysis and a second side reaction, transamidation involving the acetic acid, is also not favoured due to volatility of the acetic acid. 68-72% of the sorbed mercury is desorbed by a first treatment with hot acetic acid for 30 min. While a second treatment results in a complete desorption of the remaining mercury. After washing with excess water, the copolymer is available for re-use. When the mercury-loading experiment was repeated with regenerated polymer the observed loading capacity was exactly the same. Further prolonged recycling experiments are required however to establish longterm stability.

3.5. Competitive mercury sorption

In order to determine possible interference from foreign ions on the mercury uptake, we first treated the polymeric sorbent with each of the transition metal ions; Fe(III), Ni(II), Co(II), Cd(II) and Zn(II) separately. No sorption was observed from 0.1 M metal ion solutions whose concentrations were followed by EDTA complexation methods. Secondly the same mercury sorption experiments were repeated with mercuric ions in 0.1 M concentrations of each of the above metal ions. The washed and dried samples of copolymer were subjected to desorption with acetic acid and the amounts of mercury released were determined as before.

No significant deviation in the mercury uptakes were observed in the presence of the above metal ions.

Hence, these experiments show that the mercury uptake by the polymeric sorbent is strictly selective and the transition metal ions studied do not interfere with this sorption.

4. Conclusions

The graft copolymer of acrylamide with cellulose cotton is useful for the highly selective separation of mercuric ions from neutral aqueous solutions in the presence of various transition metal ions. Due to the high mercury sorption capacity and recycling ability, sorbents of this type offer considerable technological potential in hydrometallurgy.

Since the reaction is also rapid and the sorbent is efficient for trace quantities of mercury, these materials may also be of interest for the treatment of drinking and waste waters.

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