Synthesis of a Polyacrylamide Chelating Resin and Applications in Metal Ion Extractions

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SYNOPSIS

A series of differently crosslinked polyacrylamide chelating resins were prepared, using N,N'-methylene-bis-acrylamide as the crosslinking agent. The crosslinked resins were functionalized by the reaction with ethylene diamine to get amino group capacities varying from 4.2 to 1.1 mequiv/g. The maximum adsorption capacities of the lightly crosslinked resin for Fe^{3+}, Fe^{2+}, Ni^{2+}, and Cu^{2+} are 3.62, 4.22, 1.48, and 1.67 mequiv/g, respectively. The adsorbed metal ions can be quantitatively desorbed. The adsorption rate and the influence of pH on the adsorption of metal ions were examined. The resins can be used for the separation between different metal ions as well as the ions in different valence states (e.g., Fe^{3+} and Fe^{2+}). The resin is amenable for continuous process and can be regenerated several times.

INTRODUCTION

Chelating resins have many practical applications in water treatment, environmental protection, chemical analysis, etc. The synthesis and applications of chelating resins have been reviewed recently.[1-6] The chelating sorbents are assumed to form chelate rings in the sorbent phase during the sorption of metals. The possibility of forming chelate rings in the sorbent phase is affected by different factors such as the nature of the chemically active groups capable of complexation, the physical nature of the polymeric matrix, steric factors, sorption conditions, etc.[7,8] A majority of the chelating sorbents reported so far are based on polymeric organic matrices, mostly hydrophobic polymers. Reports on the use of chelating sorbents based on hydrophilic polymers are relatively rare.[9]

This work describes the preparation and applications of a chelating resin based on the hydrophilic polyacrylamide. Resins were prepared by varying the extent of crosslinking, which is expected to change the physical nature of the polymer matrix and thereby alter the formation of chelate rings in the sorbent phase. The resins were prepared by a single-step polymer-analogous reaction of ethylenediamine with polyacrylamide. The sorption behavior of the resin toward various metal ions, the sorption rate, and the influence of various sorption conditions on metal ion adsorption were investigated. The article also presents the results of the effect of the extent of crosslinking of the polymer backbone and the selectivity toward various metal ions.

EXPERIMENTAL

Materials and Methods

Acrylamide and N,N'-methylene-bis-acrylamide (SRL, Bombay) were used after recrystallization. Ethylene diamine (Merck, Germany) was distilled and used. Copper sulfate, nickel sulfate, ferrous ammonium sulfate, and ferric ammonium sulfate (all AR, BDH) were used for preparing standard metal ion solutions. The metal ions were estimated by spectrophotometry using Shimadzu UV-200, UV-visible spectrophotometer, and by atomic absorption spectrometry using varian AA 1275 atomic absorption spectrometer.

Preparation of the Crosslinked Polymers

The crosslinked polymers were prepared by free radical solution polymerization. Ammonium persulfate (200 mg) dissolved in hot (90°C) water (70 mL) was used as the initiator. Mixture of monomers (30 g) was added to the initiator solution and heated at 90°C with stirring for 40 min. The precipitated polymer was filtered, washed with water, methanol, and dried at 60°C.

Functionalization of the Crosslinked Polymer

Excess ethylene diamine (40 mL) was taken in a round-bottomed flask and the crosslinked polymer (20 g) was added with stirring. The mixture was heated at 90°C for 8 h, poured into 200 g of crushed ice, filtered, and washed with water till the washings were free from amine as determined by color reaction with ninhydrine, which detects amino group up to 0.1 μmol/g.[10] The gel was then washed with methanol and dried under vacuum.

The capacities of the resins were determined by adding excess acid (0.05 N) and back titrating against standard alkali (0.05 N NaOH). The resins, powdered and sieved through 800 μm and retained on 400 μm standard sieves were used for further studies.

Complexation with Metals

The amino resin (1 g) was equilibrated with water for 24 h and shaken with different metal salt solutions containing 4.5 mmol of the metal ion for 5 h. The amount of metal left in the solution was determined by spectrophotometric methods or using atomic absorption spectrometer. The course of the complexation reactions was followed by withdrawing aliquots of the reaction mixture at regular intervals of time and estimating the amount of metal ions left in the solution. The adsorbed metal ions were desorbed by treating the resins with diluted HCl, and the amount of desorbed metal ions were also estimated.

The complexation experiments were conducted at different pH values and the selectivity toward different metal ions was also experimented.

RESULTS AND DISCUSSION

Preparation of the Chelating Resin

Crosslinked polyacrylamide gels were prepared using N,N'-methylene-bis-acrylamide as the crosslinking agent. Four types of gels were prepared by varying the crosslink density from 2 to 15 mol % (Table I). When the crosslink density increased from 2 to 15, the rigidity of the gels increased and the extent of swelling in water decreased correspondingly. It has been observed by several authors that the network structure of the polyacrylamide gels is highly dependent on the concentration of acrylamide and NNMBA.[11-13] Results from techniques sensitive to very different properties and mechanical measurements show that polyacrylamide networks are heterogeneous because of the mechanism of polymerization, in which three stages can be distinguished as (i) the network formation that involves 15% of the initial acrylamide and 25% of the initial NNMBA, (ii) the gelation process in which 50% acrylamide and 60% of the tetrafunctional monomer react suddenly, and (iii) the slow crosslinking after gelation.[14]
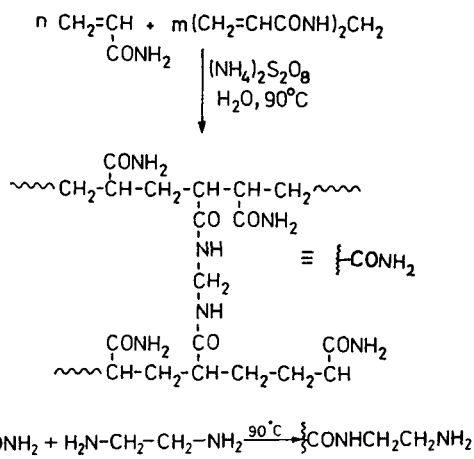
The composition of the polymer formed in each stage is different and therefore microdomains of different structures will be formed. Thus the acrylamide gels prepared using tetrafunctional monomer do have microdomains of different characteristics, and when these gels are functionalized, the resulting functional polymers also have reactive sites with different microenvironments. The typical structure of the gel is shown in Scheme I.

The crosslinked gels are functionalized by reaction with ethylenediamine. Excess ethylene diamine is used, which reduces the chances of further crosslinking. The capacities of the different resins, as determined by titration with standard acid and the extent of swelling are given in Table I. The lightly crosslinked resin is having the highest amine capacity of 4.2 mequiv/g, and the 15% crosslinked resin has a capacity of 1.1 mequiv/g. It can be seen that the extent of swelling is decreasing with increase in crosslinking.

Table I   Capacities and Extent of Swelling of the Amino Resins

Crosslinking (mol %)	Amine Capacity (mequiv/g)	% Weight[a] Increase upon Swelling in Water
2	4.2	425
5	3.0	380
10	1.7	300
15	1.1	285

[a] Equilibrated in water for 24 h.

n CH$_2$=CH + m(CH$_2$=CHCONH)$_2$CH$_2$
   |
   CONH$_2$ $\Big|$ (NH$_4$)$_2$S$_2$O$_8$
                $\Big|$ H$_2$O, 90°C
                $\downarrow$

           CONH$_2$
~~~CH$_2$-CH-CH$_2$-CH-CH-CH$_2$~~~
              | |
              CO   CONH$_2$
              |
              NH $\equiv$ $\Big\}$CONH$_2$
              |
              CH$_2$
              |
              NH
   CONH$_2$ |
      | CO   CONH$_2$
~~~CH-CH$_2$-CH-CH$_2$-CH$_2$-CH

$\Big\}$CONH$_2$ + H$_2$N-CH$_2$-CH$_2$-NH$_2$ $\xrightarrow{90°C}$ $\Big\}$CONHCH$_2$CH$_2$NH$_2$

Scheme 1 Preparation of crosslinked poly[N-(2-amino ethyl) acrylamide].

Chelation Experiments with Metal Ions

Poly[N-(2-aminoethyl)acrylamide]s function as efficient chelating sorbents for different metal ions. Chelation experiments were done with 1 g of resin (5% crosslink density and 3.0 mequiv amino group capacity) and 4.52 mmol each of Cu^{2+}, Ni^{2+}, Fe^{2+}, and Fe^{3+} ions. The results are given in Table II. From the quantities of metal ions left in solution after 5 h of shaking with the resin, the amount of metal ions adsorbed was calculated. The maximum chelation has taken place with Fe^{3+} (4.22 mequiv/ g) and the minimum with Ni^{2+} (1.48 mequiv/g). Fe^{2+} and Cu^{2+} fall in between (3.62 and 1.67 mequiv/ g, respectively). From this table it can be noted that the metal ions are quantitatively desorbed when the chelated resins were treated with dilute HCl.

In order to investigate whether complete removal of metal ions is possible by these resins, solutions containing 0.5, 1.0, and 1.5 mmol of Cu^{2+} were

shaken with 1 g of the resin. It was found that the solutions were free of Cu^{2+} after 5 h. The course of the complexation reactions of the different metal ions with the resins was followed by measuring the metal ion concentration left in solution at regular intervals of time. The amount of different metal ions adsorbed with time is shown in Figure 1. From the figure it can be noted that 90–95% of the complexation is completed in the initial phase itself. Thereafter, the reaction proceeds very slowly. This data indicates the suitability of the resin in continuous process.

Effect of pH

The chelation of metal ions with the resin is highly dependent on pH. By adjusting the pH values, selectivity can be achieved for different metal ions. The effect of pH on the chelation of Cu^{2+} is illustrated in Figure 2. Thus these resins can be used for concentration or removal of Cu^{2+} from water at pH value around 4.5 and can be desorbed by washing with an acid solution of pH less than 2. The effect of pH on the chelation of Fe^{3+} and Fe^{2+} is shown in Table III. It can be seen from Table III that by lowering the pH, Fe^{3+} can be preferentially adsorbed. It may be possible to selectively remove Fe^{3+} from a mixture containing Fe^{2+} and Fe^{3+} by carefully adjusting the pH and other reaction conditions.

Table II   Chelation Experiments with Different Metal Ions Using the 5% Crosslinked Resin[a]

Metal Ion	Amount of Metal Ions Left in Solution (mmol)	Amount of Metal Ions Adsorbed (mmol)	Amount of Metal Ions Desorbed[b] (mmol)
Cu^{2+}	2.85	1.67	1.66
Fe^{2+}	0.90	3.62	3.60
Fe^{3+}	0.30	4.22	4.14
Ni^{2+}	3.04	1.48	1.47

[a] Using 4.52 mmol of the metal ion and 1 g resin.
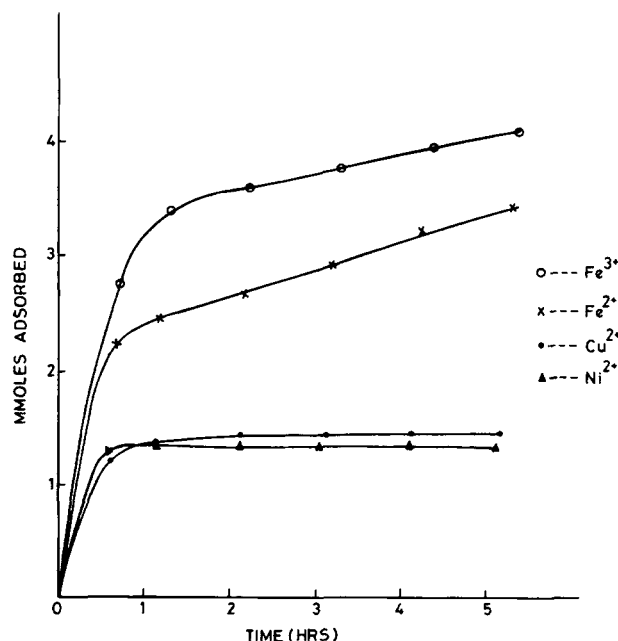[b] By washing with 0.5 N HCl.

Figure 1 Complexation of different metal ions with the 5% crosslinked amino resin.
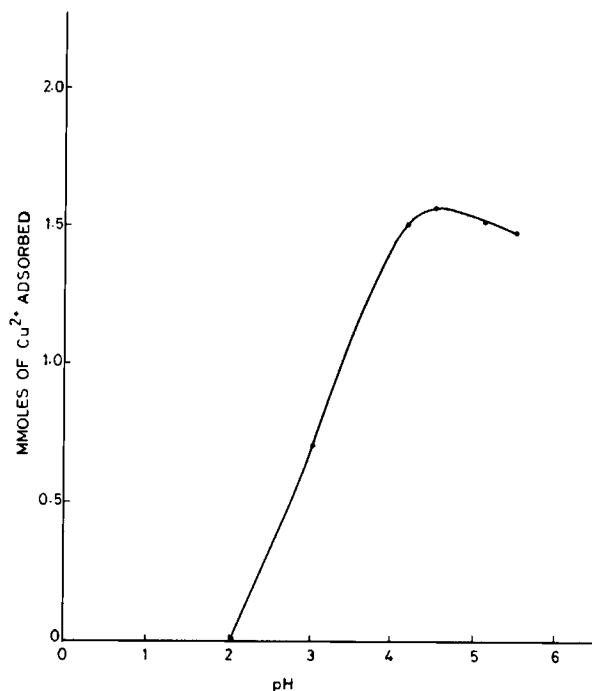
Figure 2   Effect of pH on the adsorption of Cu^{2+}.

Separation of different metal ions is possible using these resins. Thus when a solution containing Cu^{2+} and Fe^{3+} was treated with the 5% crosslinked resin, at pH 1–2, the resulting solution was free from Fe^{3+}. Separation between Fe^{2+} and Fe^{3+} and Cu^{2+} and Ni^{2+} is also possible using these resins.

Effect of the Extent of Crosslinking

In order to investigate the effect of the extent of crosslinking on the complexation reactions of poly[N-(2-aminoethyl)acrylamide]s, the complexation with Cu^{2+} is taken as a model reaction. For these experiments, 5 mmol of Cu^{2+} solution was shaken with resins containing 2 mmol of amino groups. The amine capacity of 15% crosslinked resin is very low and hence not used. After regular inter-

Table III   Effect of pH on the Chelation of Fe^{2+} and Fe^{3+}

pH	Fe^{3+} Adsorbed (mmol)	Fe^{2+} Adsorbed (mmol)	$\dfrac{Fe^{3+} \text{ Adsorbed}}{Fe^{2+} \text{ Adsorbed}}$
2	3.58	2.98	1.2
1	3.42	2.16	1.6

Table IV   Effect of the Extent of Crosslinking on the Chelation of Cu^{2+}[a]

| Crosslinking (mol %) | Amount of Cu^{2+} Adsorbed (mmol) at Intervals (h) | | | |
	1	2	3	4
2	2.39	2.42	2.75	2.84
5	2.75	2.85	2.95	3.08
10	2.69	2.69	2.75	2.85

[a] Using 5 mmol of Cu^{2+} and resin containing 2 mmol of amino group.

vals of time, the amount of Cu^{2+} left in solution was estimated. The results are given in Table IV. It can be seen that the amount of Cu^{2+} chelated is maximum for the 5% crosslinked resin. At 5% crosslinking the microenvironments around the functional group may be optimum for chelation with Cu^{2+} ions. The change in hydrophilicity of the polymer backbone, brought about by the introduction of crosslinks, may also be optimum for complexation at 5% crosslinking. Similar effects of the extent of crosslinking on the reactivity of functional groups immobilized on polyacrylamide supports are reported.[15–17]

The chelation experiments discussed so far are also possible in a column, suggesting the possibilities of continuous operation and automation. Some pilot experiments were done in a column. It was found that the chelation efficiency is greater in a column than in a batch process. Thus, the maximum amount of Cu^{2+} chelated for the 5% crosslinked resin was 1.67 mmol/g in a batch process, whereas in a column the maximum capacity was 2.21 mmol/g.

The resins once used can be regenerated to the original form and thus can be used many times. The resins chelated with Cu^{2+} were washed with 0.1 N HCl to desorb the metal and the same resins were treated with a fresh solution of Cu^{2+}. After half a dozen sorption/desorption experiments there was no detectable loss in the complexing ability of the resins.

Polyacrylamides crosslinked with optimum quantities of NNMBA and reacted with excess ethylenediamine can be used for efficient and selective separation of different metal ions at optimum experimental conditions. The resins can be regenerated and recycled and the metal ions can be quantitatively recovered. It is also amenable for continuous column process.

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