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Glycidyl methacrylate based polymer resins with diethylene triamine tetra acetic acid functions for efficient removal of Ca(II) and Mg(II)

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Abstract

Crosslinked terpolymer beads prepared by suspension polymerization of glycidyl methacrylate (GMA) (0.4 mol), methyl methacrylate (MMA) (0.5 mol) and divinyl benzene (DVB) (0.1 mol) mixtures have been modified through epoxy functions in two steps: (i) by treating with excess of diethylene triamine (DETA); and (ii) by subsequent reaction with potassium chloroacetate. The resulting polymer possessing diethylene triamine tetra acetic acid (DTTA) functions (with degree of functionalization DF:1.70 $\text{mmol} \cdot \text{g}^{-1}$) is an efficient sorbent for removal of Ca (II) and Mg (II) ions in ppm levels. Interestingly when the sodium form of the resin is used in relatively high concentrations (0.1 M) sorbed amounts will be 10–45% in excess of the theoretical capacity due to precipitation of the metal hydroxides on polymer particles beside chelation with the metal ions. Having EDTA-like chelating units, the polymer is able to absorb also heavy metal ions such as Fe (III), Zn (II), Cd (II), Pb (II), Ni (II), Cu (II), Co (II) ions. Not having hydrolysable linkages, metal-free resins can be obtained by acid treatment (4 M HCl) without loosing its activity. The resin with DTTA functions seems to be applicable in large scale water softening processes.

Keywords: Chelating polymer; Metal extraction; Water processing; Glycidyl methacrylate; Polymer

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1. Introduction

Removal of inorganic pollutants from water is a tedious process in comparison to organics. Because most of the later can be removed relatively simply by activated carbons without much regard to their origin. Inorganics, however, need to use sorbents which are able to bind to them by forming chemical bonds. Most common materials for their removal are ion-exchangers. Chelating polymers can be regarded as a second generation of inorganic sorbents. These sorb metal ions by coordination yielding chelate complexes and these are efficient even for trace quantities as low as few parts per million (ppm's). In the literature, there are a large number of papers [1–3] and reviews [4,5] dealing with metal sorption and heavy metal uptake using polymer sorbents with chelating groups. Ca (II) and Mg (II) ions are most

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abundant ions in water. Their presence in water causes the widespread use of softeners as detergent additives in laundry. As a result the process imparts additional wastes to the water by softening agents. Especially in steam generators, pretreatment of water by using chelating polymers can be beneficial and cost effective to give Ca (II) and Mg (II) free-water.

The chemistry of calcium reveals that ethylenediamine tetra acetic acid (EDTA) is one of the most important chelating agents. EDTA is a chemically stable compound and able to chelate with many transition metal ions including Ca (II), Mg (II). EDTA is such a powerful chelating agent that even $CaCO_3$ (water-insoluble) becomes soluble on standing in a solution.

Based on these considerations in our previous works we have prepared crosslinked polystyrene sulfonamides with EDTA-like chelating groups. It has been shown that these polymers are very efficient in removal of Ca (II), Mg (II) ions [6] and heavy metal ions [7]. By a similar analogy polymers with carboxymethylated oligoethylene imine pendant groups have been prepared using chloromethylated polystyrene resin for efficient sorption of metal ions [8]. In earlier reports polystyrene with imino diacetic acid functions have been shown to be useful in removal of many metal ions to some extent [9].

In all those studies, the basic requirements such as high chelating ability, inert backbone, regenerability, are established. The only drawback of polystyrene based resins are mechanical disintegration in long-term uses.

To overcome this drawback in the present work we have used glycidyl methacrylate (GMA)–methylmethacrylate (MMA)–divinyl benzene (DVB) terpolymer beads as reactive support.

By incorporation of diethylene triamine (DETA) via ring opening of the epoxide groups and subsequent carboxymethylation with chloro acetic acid, the chelating polymer was obtained. Its chelating ability with Ca (II) and Mg (II) ions and regenerability conditions were investigated.

2. Experimental

2.1. Materials

All the chemicals, Glycidyl methacrylate (GMA) (Fluka), Methyl methacrylate (MMA) (Fluka), Divinyl benzene (DVB) (Aldrich), Diethylene triamine (DETA) (Fluka), Chloroacetic acid (E-Merck) were analytical grade chemicals. They were used as supplied.

2.2. Preparation of GMA–MMA–DVB terpolymer beads

This was obtained by suspension polymerization of GMA (0.4 mol), MMA (0.5 mol), DVB (0.1 mol) mixture in 120 ml toluene using 360 ml of aqueous styrene–maleic acid copolymer salt (1.6 g) as suspension stabilizer according to the previous report [10].

2.3. Modification with diethylene triamine (DETA)

GMA–MMA–DVB terpolymer resin (8 g) was put in 25 ml of DETA in a 100 ml of flask. The mixture was stirred for 24 h at room temperature. While stirring, it was heated at 100°C in a termostated oil bath for 3 h.

After chilling the mixture was poured into 250 ml of distilled water and washed with excess of water (1 l), 25 ml alcohol and dried overnight under vacuum for 24 h. The yield was 9.3 g.

2.4. Determination of amine content

For determination of the amine content, 1 g of the polymer sample was left in contact with 20 ml of HCl (1 M) for 2 h. After filtration, 1 ml of the filtrate was taken and diluted to 10 ml, and the acid content of the solution was determined by titration with 0.1 M NaOH solution in the presence of phenol–phatalein color indicator. A total amine content of the polymer was calculated as 5.2 mmol g^{-1} resin.

2.5. Carboxymethylation of the DETA functions (resin III)

Carboxymethylation of polymer beads was carried out by reacting 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. Stirring was continued until foaming had ceased (for about 2 h). A sample containing 10 g of resin III was placed in this solution and the mixture was shaken by means of a continuous shaker for 48 h at room temperature. Then the mixture was heated to 70°C for 3 h, filtered and washed with water.

The product was dispersed in 100 ml of water, filtered and dried at 50°C under vacuum for 24 h.

The dry weight of the product was 13.86 g. The surface area was found to be 0.624 $m^2\ g^{-1}$ (BET method).

2.6. Determination of the carboxyl content

To 6 ml of 1 M NaOH solution 0.4 g of the resin III sample was added and left to stand overnight. The mixture was filtered and washed with distilled water.

The filtrate and washings were combined and diluted to 50 ml in a volumetric flask. Then, 25 ml of the solution was titrated with 0.1 M HCl solution. The resulting 9.9 ml of the titrand indicates 4.95 mmol g^{-1} carboxyl content. This reveals that 99.8% of the free amino groups of the resin II sample have been carboxymethylated.

2.7. Determination of metal sorption capacities of the resin

Metal sorption capacities of resin III were assigned by analysis of residual metal contents of 50 ml of metal ion solutions in contact with 1 g of resin III samples.

The initial metal concentrations were 0.36 M. In these experiments the sodium form of resin III was used to attain maximum loading capacities. For this purpose, first 0.2 g of the resin samples of each were treated with 10 ml of 2 M NaOH solutions. After 4 h, the bead samples were filtered and washed with excess water. The samples were carefully transfered into bottles containing 25 ml 0.36 M metal ion (Ca (II), Mg (II), Fe (III), Pb (II), Cd (II) and Zn (II)) solutions and left to stand for 24 h. After filtration of the mixtures 5-ml aliquots were used to determine unreacted metal contents of the solutions.

Analysis of the metal ions were performed by titration with 0.01 M EDTA (ethylenediamine tetra acetic acid) solutions as described for each metal ion in the text books (Ref. [11]).

From the differences of the metal contents in the initial and final solutions, the loading capacities of resin III was calculated and are listed in Table 1.

2.8. Kinetics of Ca (II) and Mg (II) sorptions

The kinetics of Ca (II) and Mg (II) ion sorptions were performed by simple batch experiments. Experiments were conducted by interacting 0.35 g of resin III samples with 50 ml of 9.3×10^{-3} M Ca (II) and Mg (II) solutions under stirring.

Then 5-ml aliquots were taken out at appropriate time intervals. Variation of metal concentrations of the solutions were determined by titration with 0.01 M EDTA as described above. The collected data were used to build up Fig. 1.

3. Results and discussion

Glycidyl methacrylate (GMA) based crosslinked polymers have advantages over other polymer supports due to ease of functionalization through the epoxide groups involved. Also remarkable resistance of its ester linkage to acid and base hydrolysis is an additional advantage

Table 1
Metal uptake characteristic of the resin III sample

Metal ion	Initial conc. (M)	Loading capacity[a] (mmol g^{-1})	Recovered metal ion[b] (mmol g^{-1})	Capacity per function[c] (mol/mol)
Ca (II)	0.36	1.38	1.375	1.11
Mg (II)	0.367	1.79	1.79	1.44
Fe (III)	0.361	1.51	1.48	1.21
Zn (II)	0.350	1.38	1.38	1.11
Cd (II)	0.356	1.76	1.72	1.42
Pb (II)	0.350	1.8	1.8	1.45

[a] Metal loading from 0.36 M metal ion solutions in 24 h contact times.
[b] In first contact with 4 M HCl solution.
[c] Based on 1.24 mmol g^{-1} DTTA capacity (weight increases of metal sorbed samples have been neglected).

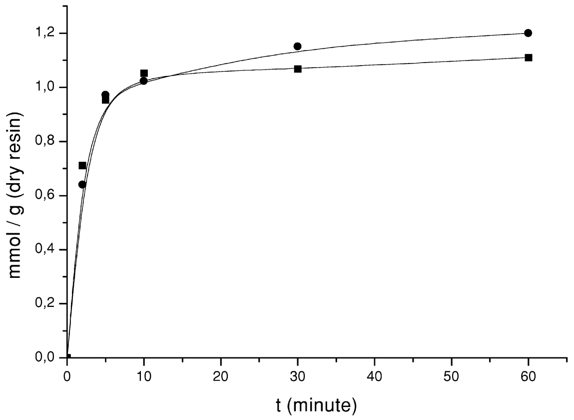


Fig. 1. Sorption-time plots of 0.35 g resin samples with 50 ml 9.3×10^{-3} M Ca (II) ■ and Mg (II) ● ion solutions.

to use as ligand carrying polymer. In the present study GMA copolymer (resin I) was deliberately chosen, instead of its homopolymer, to provide the epoxy groups far apart from each other so that two or more epoxy groups do not react with the other amino groups of the same molecule during its modification. Normally some part of epoxy groups must remain inside the crosslinked polymer matrix. Inevitably these are not accessible in subsequent reaction steps and in analytical determinations. However, a careful analysis of the epoxide functions by pyridine–HCl method gives 3.4 mmol g^{-1} of epoxide function. This is slightly higher than even the theoretical content (3.32 mmol g^{-1}) based on the feed composition. This difference can be ascribed to small reactivity differences of GMA and MMA monomers in their copolymerization [12]. Reaction with excess of diethylene triamine gives a product (resin II) with 5.2 mmol g^{-1} amine functions (Scheme 1). This implies 61.0% conversion of the epoxide functions.

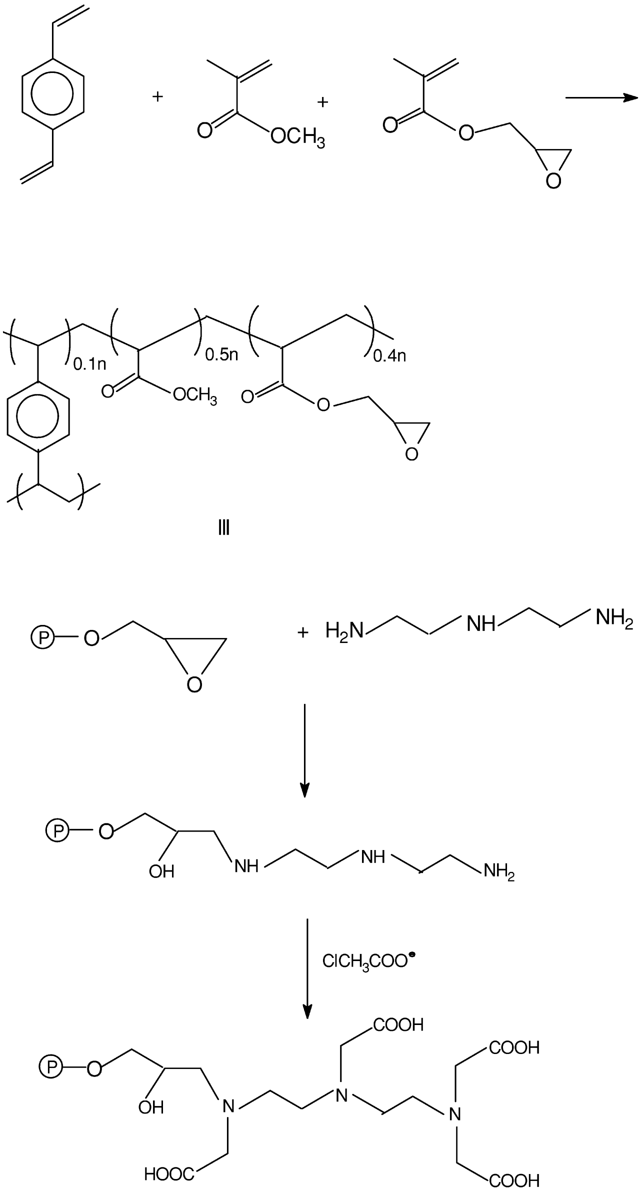
Amino functions of resin II can be carboxymethylated by potassium salt of chloroacetic acid. Determination of its carboxyl functions (4.95 mmol g^{-1}) indicates high yields of transformation (99.8%) in reaction with chloroacetic acid.

In the carboxymethylation step, the use of potassium salt of chloroacetic acid is crucial to attain high conversions. Direct reaction with chloroacetic acid yields always low substitution degrees (i.e. 16%) even in prolonged reaction periods.

Regarding the high transformation yield in the last modification step, each pendant chelating unit might be considered as a heptadentate ligand.

3.1. Metal uptake by resin III

The constitution of resin III reveals a 1.24 mmol g^{-1} of ligand content. Low molecular-weight analogue of the ligand, EDTA is a hexadentate ligand and shows 1:1 l/M complexation with metal ions. With seven ligating groups the pendant ligand on the polymer is



Scheme 1.

expected to exhibit 1:1 l/M complexation similarly. This assumption implies a maximum metal sorption capacity around 1.25 mmol gram^{-1} of the chelating resin.

In order to examine maximal metal binding capacities of resin III its sodium form has been used to attain the most favourable chelating conditions. In these experiments buffer solutions have not been used to obey practical conditions. Because, the use of buffer solutions is not practical in processing tap water when large quantities are in question.

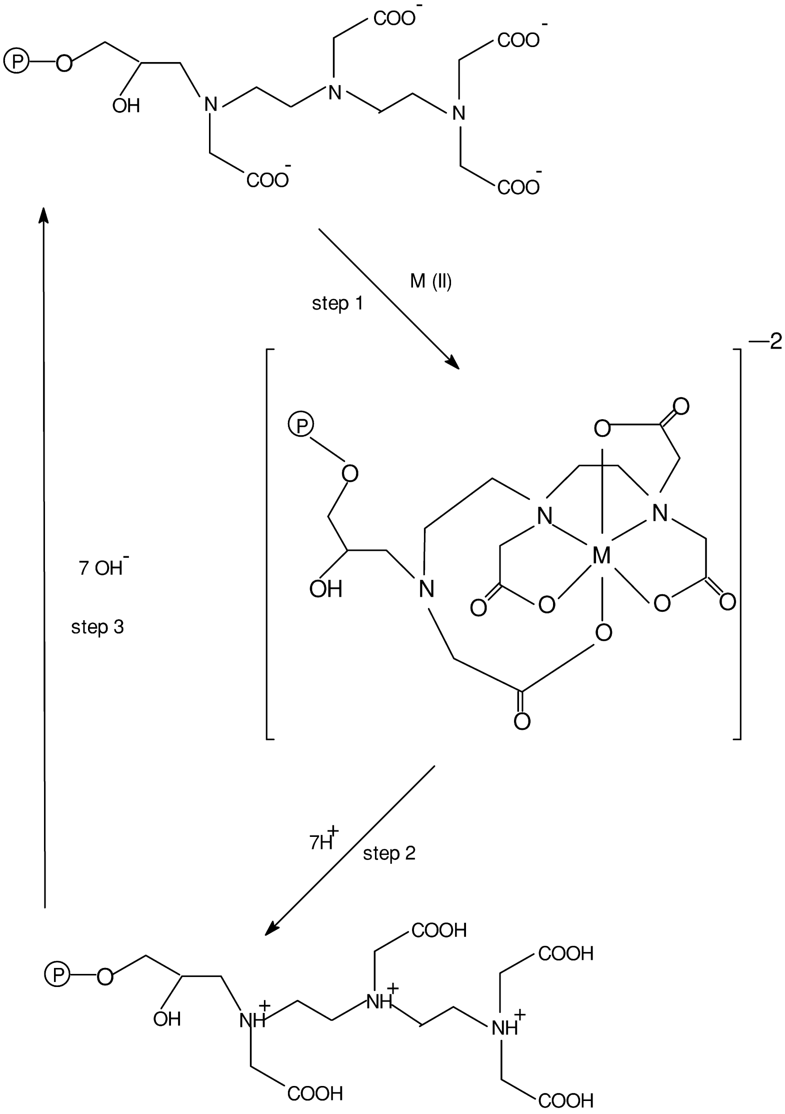
When resin III is contacted with distilled water (1 g resin with 100 ml water) the pH of the solution becomes 9.5 due to hydrolysis of the amino and carboylate groups on the resin.

During metal sorptions pH's of the aqueous solutions gradually reduce and retain a 7.6–8.4 range in all experiments after 3 h.

Obviously non-bonding electrons of the amino groups are blocked by chelation with the metal ions and these do not ionize readily. Also ionization of carboxylates takes place to a lesser extent upon bonding with multivalent metal ions. In other words ionization of amino and carboxyl functions in the resin structure have been suppressed by chelation and the pH of the solutions reduced accordingly.

From Table 1 it is clearly seen that almost in all cases the capacities are somewhat higher than the estimated capacity.

The exceeding amounts can be ascribed to precipitation of metal hydroxides on polymer particles in contact with the sodium form of the resin, as has been proven in our previous study [10]. Because hydroxyl ion concentration nearby the ligating sites must be high enough to precipitate metal hydroxides in the microdomain. In other words, due to hydrolysis of amino and carboxilate groups, the pH around



Scheme 2.

the ligating groups must be higher than the critical pH values of the metal hydroxides.

3.2. Kinetics of Ca (II) and Mg (II) ion uptakes

In order to examine efficiency of the resin for trace quantities the kinetics of Ca(II) and Mg (II) uptakes have been followed using 100 ppm initial metal concentrations.

Since the metal sorption is a diffusion controlled process in nature, kinetics of metal sorption would be closely related to the stirring rates. Nevertheless to have an information about the sorption kinetics, experiments have been conducted at moderate stirring rates (350–400 rev. min^{-1}).

Fig. 1 shows that Ca(II) and Mg(II) concentrations fall down to about 1 ppm levels in 10 min of contact times. Corresponding loading curves are reminescent of Langmuir type of sorption profiles and obey second order kinetics with $k_{\mathrm{Ca}} = (1.63 \pm 0.12) \times 10^{-2}$ M^{-1} s^{-1} and $k_{\mathrm{Mg}} = (3.75 \pm 0.20) \times 10^{-2}$ $\mathrm{M}^{-1}\mathrm{s}^{-1}$ rate constants.

3.3. Regeneration of the resin

Sorbed metal ions can be split off almost completely by acid treatment (4 M HCl). More than 96% of sorbed metal ions are recovered in acid leaching process (Table 1).

Since the amino groups are converted into their HCl form in acid treatment (step 2 in Scheme 2), the metal-free resin is regenerated simply by following washing with NaOH solution (step 3). In this step the amino groups are restored and the carboxyl groups are ionized to give carboxylate anions. The overall result is regeneration of the resin to use in the next cycle.

In conclusion, glycidyl methacrylate based polymers with diethylenetriamine tetra acetic acid (DTTA) functions can be used successfully in removal of various metal ions including Ca(II) and Mg(II) ions. Like EDTA, the DTTA functions on the resin serves high complexing abilities with the metal ions studied. For instance based on 1.8 mmol g^{-1} sorption capacity one can deduce that 1 kg of the dry resin (resin III) can clean up to 600 l of water with 300 mg l^{-1} $\mathrm{CaCO_3}$ hardness, in each regeneration step. The metal sorption rates are rapid enough. On account of regenerability of the resin and chemical stability of the ligating groups as well as the backbone, resin III presented seems to be a promising candidate for large scale applications.

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