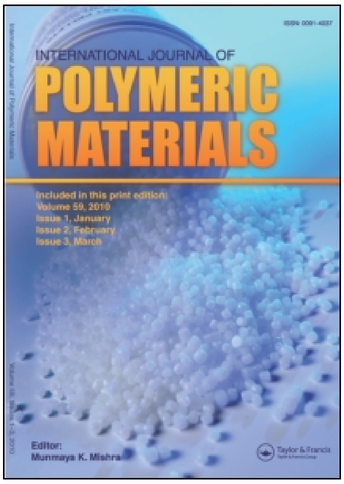

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A Novel Highly Copper(II)-selective Chelating Ion Exchanger Based on Poly(Glycidyl Methacrylate-*co*-ethylene Dimethacrylate) Beads Modified with Aspartic Acid Derivative

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Anchoring the hydroxyaspartic acid onto poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) (poly(GMA-*co*-EDMA)) beads or epoxysuccinic acid onto ammonium-modified poly(GMA-*co*-EDMA) beads resulted in a novel chelating resin, which contained up to 0.37 mmol of the ligand per gram of resin. Batch extraction experiments showed a very high selectivity for Cu^{2+} over Zn^{2+} and Cd^{2+} ions in buffered solutions under competitive conditions.

Keywords: Chelating ion exchanger; Poly(glycidyl methacrylate-*co*-ethylene dimethacrylate); Aspartic acid derivative; Beads; Epoxysuccinic acid; Chelating resin; Cu^{2+}; Zn^{2+}; Cd^{2+}

INTRODUCTION

The need for more highly specific, metal recovery processes in both hydrometallurgical and environmental applications has led to an

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increasing interest in selective ion exchange. In particular the search for 'ion-specific' resins which, under proper operating conditions, are selective for only one ionic species [1,2] has intensified. Important properties of such ion exchangers should include high capacity, high selectivity and fast kinetics [3]. Most of the commercial resins, when tested in wastewater treatment show a high capacity, but a very poor selectivity towards different metal ions. In some cases the kinetics are slow, due to the hydrophobic character of the polymer backbone and chelating groups. Therefore, studies towards the development of resins with improved selectivity and better kinetic performance have been initiated in our laboratory. Recently, some Cu^{2+}-selective chelating ion exchangers based on polystyrene [4] or poly(glycidyl methacrylate-*co*-trimethylpropane trimethacrylate) [2] have been published.

This communication describes the synthesis and metal-ion uptake experiments of a novel, highly Cu^{2+}-selective ion exchange resin based on poly(GMA-*co*-EDMA) containing derivatives of aspartic acid as the chelating ligand. This ion exchanger combines a high selectivity for Cu^{2+} ions with fast exchange kinetics.

EXPERIMENTAL

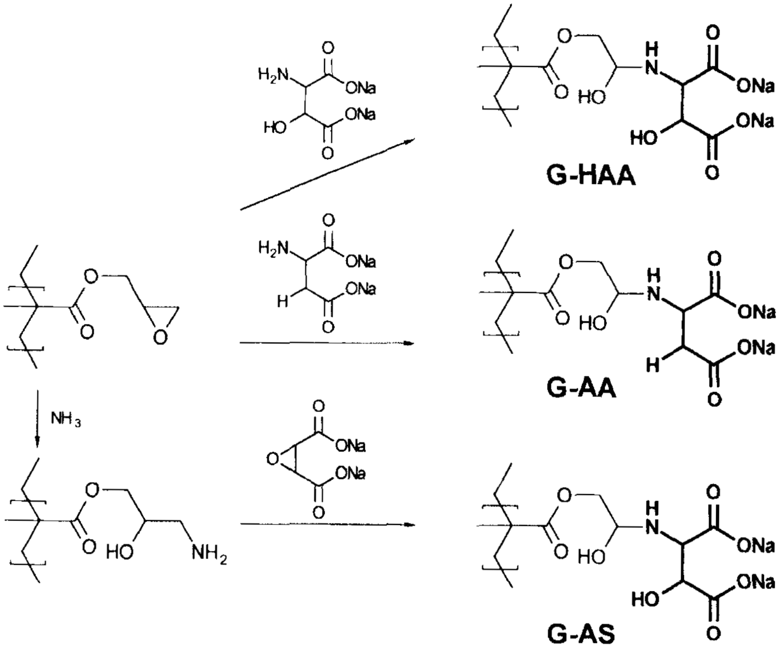
Synthesis of the sodium salt of epoxysuccinic acid [5]. 500 ml of aqueous alkaline (pH 4–5.5) maleic acid (116 g, *i.e.*, 1 mol) solution was stirred at 65°C for 1 h with 6.6 g Na_2WO_4 (used as catalyst) and 145.7 g of 28 wt.% hydrogen peroxide solution. The volume of the reaction mixture was reduced to 300 ml and the product was precipitated by acetone, separated and dried. Yield: 178.4 g; the elemental analysis (calculated values in parenthesis): C 26.3 (27.3), H 1.2 (1.1). ^{1}H-NMR data: δ 3.6; ^{13}C-NMR data: δ 58 (C alifat.), 176 (C=O).

Synthesis of the sodium salt of hydroxyaspartic acid [6]. 160 ml of 25% aqueous ammonia was stirred at 50°C for 32 h with 11 g of sodium salt of epoxysuccinic acid. The volume of the reaction mixture was reduced until the crystallization of the product. Yield: 11.3 g; the elemental analysis (calculated values for 0.8-M hydrate in parenthesis): C 21.7 (21.7), H 3.0 (3.0), N 6.1 (6.3); ^{1}H-NMR data: δ 3.8 (CH—NH_2), 4.4 (CH—OH); ^{13}C-NMR data: 60 (CH—NH_2), 75 (CH—OH), 175 and 179 (C=O).

Poly(GMA-*co*-EDMA) beads were prepared by suspension polymerization using a mixture of glycidyl methacrylate (GMA) and ethylene dimethacrylate (EDMA) (3 : 2 v/v) with a mixture of cyclohexanol and 1-dodecanol (9 : 1 v/v) as a porogen (monomers: porogens 2 : 3 v/v) as described earlier [7]. Bead size fraction 12–20 μm was used for further reactions. The BET surface area of the beads in the dry state was 69 m^2/g and the pore volume was 1.4 cm^3/g.

The resin G-A was prepared from poly(GMA-*co*-EDMA) beads (50 g) by heating them in an excess (400 ml) of 25 wt.% ammonia at 50°C for 28 h. The resulting product was washed in a column with water until pH 7, followed with 200 ml of methanol, 200 ml of acetone, dried in vacuum over P_2O_5. The elemental analysis (calculated values in parenthesis are for 60% conversion of oxirane to amino groups): C 57.1 (57.7), H 7.3 (7.4), N 2.95 (2.96).

The resins G-HAA, G-AA or G-AS were prepared according to Scheme 1. A mixture of 5 g of poly(GMA-*co*-EDMA) suspended in



SCHEME 1 Immobilization of chelating ligands on poly(GMA-co-EDMA) beads.

28 ml water for 16 h and sodium salt of hydroxyaspartic acid (8.15 g, *i.e.*, two molar excess with regard to oxirane groups), or sodium salt of aspartic acid (5.62 g, *i.e.*, two molar excess with regard to oxirane groups), and 35 mg of cetyltrimethylammonium bromide used as a catalyst was heated at 90°C for 1, 2, 5, 10 and 21 h. The resin was filtered and purified in a column by thorough washing with water, followed by conditioning with 0.5 N-HCl. The resin was washed with water until neutral pH and dried *in vacuum* for 48 h. The reaction of the aminoderivative of poly(GMA-*co*-EDMA) (sample G-A) with sodium salt of epoxysuccinic acid was performed under the same conditions as described above, resulting in G-AS resin. The resulting resins were characterized by elemental analysis and the degree of conversion of the oxirane (or amino) groups was determined as a best fit between the results of elemental analysis and those calculated from chemical formulas corresponding to various reaction conversions.

Batch metal-uptake experiments with resins under competitive and noncompetitive conditions were performed with standard 0.2 M-$CuSO_4$ solution and with standard 0.2 M-metal chloride solutions of Zn^{2+} and Cd^{2+} in buffer solution NaOAcHOAc (pH 5) at room temperature for 24 h. For the competitive experiments, batches of 0.2 g of resin in H^+ form were used, together with a mixture of 60 ml of buffer and 60 ml standard MCl_2 solution. Samples for metal analysis were prepared by elution of the loaded resin in column by 0.5 N-HCl. The metal contents of the resulting solutions were determined by AAS spectroscopy in acetylene-air flame using Varian Spectra apparatus. For the non-competitive experiments, batches of 0.2 g of resin its H^+ form were contacted with an aqueous solution containing 20 ml of each of the standard MCl_2 solution and 60 ml of buffer. The resin was transferred into a column, washed with an excess of water and the metal ion was eluted with 0.1 N-HCl.

The eluent was treated with ammonia until formation of ammocomplex $[Cu(HN_3)_x]^{2+}$ and the amount of metal ion in solution was determined by titration with chelatone 3 using murexide indicator for the determination of Cu^{2+} and using eriochrome black T indicator for Cd^{2+} and Zn^{2+}.

RESULTS AND DISCUSSION

The chelating ion-exchange resins were synthesized from poly(GMA-*co*-EDMA) beads according to Scheme 1 in the presence of cetyltrimethylammonium bromide phase-transfer catalyst. The degree of conversion of oxirane groups after reaction with hydroxyaspartic acid for 21 h was calculated to be 14%, corresponding to a ligand concentration of 0.37 mmol/g of G-HAA resin. Slightly lower conversion (10%) was achieved in the reaction of poly(GMA-*co*-EDMA) with aspartic acid resulting in G-AA resin. In G-AS resin, the monitoring of the reaction conversion was somewhat complicated by the fact that the starting G-A resin, in contrast to poly(GMA-*co*-EDMA), contained nitrogen. Nevertheless, the reaction conversion of amino to succinic acid groups was estimated to 30%. It is interesting to note that in the absence of a catalyst the reactions proceeded only slowly and with very low conversion. Such behavior is often observed in cross-linked resins, where solvent that is very favorable for a given reaction, may be essentially non-solvent for the polymeric matrix [8]. In the case of poly(GMA-*co*-EDMA) the reaction proceeded in water which is a poor solvent for the matrix.

As shown in Figure 1, the uptake of copper by chelating resins increased with reaction time. Since Cu^{2+} uptake did not significantly change after 21 h reaction, in the following the data for resins synthesized only at this reaction time are discussed.

Table I shows the metal-ion uptake capacities of the resins under both noncompetitive and competitive conditions. Uptake experiments with metal ions of Cu^{2+}, Zn^{2+} and Cd^{2+} were performed in buffered solutions. The behavior of G-A, G-AS and G-HAA resins showed that under both conditions the uptake of Cu^{2+} was highest of all three metal ions. Only G-HAA resin retains under non-competitive conditions also Zn^{2+} ions. The lowest metal uptake capacity (not exceeding 0.10 mmol Cu^{2+}/g) was found in G-AA resin. The G-A, G-AS and G-HAA resins retained ca. 0.4–0.5 mmol Cu^{2+}/g under non-competitive conditions and 0.3–0.4 mmol Cu^{2+}/g under competitive conditions. The maximum uptake capacity for Cu^{2+} found in G-A resin for noncompetitive conditions was 0.53 mmol/g. The uptake capacity of G-HAA resin for Cu^{2+} under the same

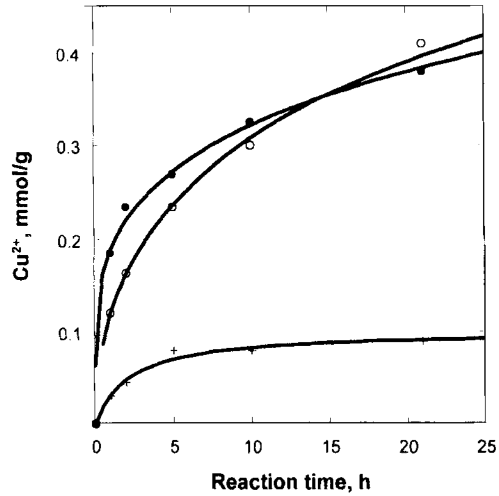


FIGURE 1 Effect of reaction time on the uptake of copper (II) ions: o G-AS; • G-HAA; + G-AA.

TABLE I Metal uptake by the chelating ion exchange resins

Sample	*Degree of conversion* %	*Ligand* *mmol/g*	*Non-competitive conditions* *Cu^{2+}* *mmol/g*	*Zn^{2+}* *mmol/g*	*Cd^{2+}* *mmol/g*	*Competitive conditions* *Cu^{2+}* *mmol/g*	*Zn^{2+}* *mmol/g*	*Cd^{2+}* *mmol/g*
G-A	60	2.11	0.53	0.01	0	0.38	0.001	0.001
G-AS	30	0.18[a]	0.41	0.03	0.03	0.33	0.0002	0.00005
G-HAA	14	0.37	0.38	0.21	0.02	0.32	0.0003	0.00004
G-AA	10	0.31	0.09	0.05	0.03	0.10	0.0003	0.00003

[a] Succinic acid groups.

conditions was 0.38 mmol/g which indicates that all of the ligands are chelating.

The metal-ion uptake experiments conducted under competitive conditions indicated that the resins were highly selective for Cu^{2+} over the other metal ions (Tab. I). In spite of the highest capacity of the G-A resin for Cu^{2+} (0.38 mmol/g), the selectivity of this resin was lower than the selectivity of G-AS and G-HAA resin. The uptake capacity for Cu^{2+} in G-AS and G-HAA resin was ca. 0.33 mmol/g. The uptake capacities for Zn^{2+} and Cd^{2+} at pH 6 were very much lower, *i.e.*, ca. 0.003 and 0.005 mmol/g, respectively. The selectivities for Cu^{2+} over Zn^{2+} and Cd^{2+} were thus very high at pH 6 and were higher than that have been found for polyGMA-bimam [2] and other types of ion exchangers, *viz.* those with polystyrene or silica backbones [4, 9]. The lower selectivity of G-A resin found in metal uptake experiments indicated the importance of the hydroxy group of G-AS and G-HAA resins for the formation of metal-ligand complexes. The overall metal-uptake capacity of the resin G-HAA at pH 6 under competitive conditions was 0.32 mmol/g, which indicated that 86% of the ligands in the resin were occupied by metal Cu^{2+} ions, in good agreement with the results obtained in the non-competitive uptake experiments. The high ligand occupation for Cu^{2+} found in these experiments most probably indicates the formation of 1 : 1 Cu^{2+}-ligand complex on the polymer. In these complexes the aspartic ligand probably acts as a tetradentate donor ligand.

The loading capacity of the ion-exchange resins G-HAA for Cu^{2+} remained the same after several cycles of consecutive loading with the 0.2 M-$CuSO_4$ stock solution at pH 6 and stripping with 0.1 M-HCl, indicating that the resin structure, backbone with ligand, is chemically and mechanically stable when treated with strong acid.

In summary, we have demonstrated that the novel chelating ion-exchange resin poly(GMA-*co*-EDMA) modified with hydroxyaspartic acid, has a very high selectivity towards Cu^{2+} ions in the presence of other divalent transition metal ions.

References

[1] Sarzanini, C., Mentasti, E. and Porta, V., *Ion Exchange for Industry*, Ed. Streat, M., Ellis Horwood, Chichester, 1988, p. 189.

[2] van Berkel, P. M., Driessen, W. L., Kodhaas, G. J. A. A., Reedijk, J. and Sherrington, D. C. (1995). *J. Chem. Soc., Chem. Commun.*, **147**.

[3] *Ion Exchange Advances*, Ed. Slater, M. J., Elsevier, London, 1992.

[4] Sahni, S. K., Driessen, W. L. and Reedijk, J. (1988). *Inorg. Chim. Acta*, **154**, 141.

[5] Payne, G. B. and Williams, P. H. (1959). *J. Org. Chem.*, **24**, 54.

[6] Kaneko, T. and Katsura, H. (1963). *Bull. Chem. Soc. Jpn.*, **36**, 899.

[7] Horák, D., Pelzbauer, Z., Bleha, M., Ilavský, M., Švec, F. and Kálal, J. (1981). *J. Appl. Polym. Sci.*, **26**, 411.

[8] Sherrington, D. C., Reaction of Polymers, In: *Encyclopedia of Polymer Science and Engineering*, Eds. Mark, H. F., Bikales, N. M., Overberger, Ch. G. and Mendes, G., Vol. 14, Wiley, New York, 1988, p. 133.

[9] van Berkel, P. M., Verweij, P. D., Driessen, W. L. and Reedijk, J. (1992). *Eur. Polym. J.*, **28**, 747.