Metal Chelating Properties of Cibacron Blue F3GA-Derived Poly(EGDMA-HEMA) Microbeads

ADIL DENIZLI,¹ KEMAL KESENCI,² BEKIR SALIH,¹ SERAP ŞENEL,¹ ERHAN PIŞKIN²

¹ Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

² Department of Chemical Engineering, Hacettepe University, Ankara, Turkey

Received 11 November 1997; accepted 20 April 1998

ABSTRACT: Metal chelating properties of Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads have been studied. Poly(EGDMA-HEMA) microbeads were prepared by suspension copolymerization of ethylene glycol dimethacrylate (EGDMA) and hydroxy-ethyl methacrylate (HEMA) by using poly(vinyl alcohol), benzoyl peroxide, and toluene as the stabilizer, the initiator, and the pore-former, respectively. Cibacron Blue F3GA was covalently attached to the microbeads via the nucleophilic substitution reaction between the chloride of its triazine ring and the hydroxyl groups of the HEMA, under alkaline conditions. Microbeads (150–200 μ m in diameter) with a swelling ratio of 55%, and carrying 16.5 μ mol Cibacron Blue F3GA/g polymer were used in the adsorption/desorption studies. Adsorption capacity of the microbeads for the selected metal ions, i.e., Cu(II), Zn(II), Cd(II), Fe(III), and Pb(II) were investigated in aqueous media containing different amounts of these ions (5-200 ppm) and at different pH values (2.0-7.0). The maximum adsorptions of metal ions onto the Cibacron Blue F3GA-derived microbeads were 0.19 mmol/g for Cu(II), 0.34 mmol/g for Zn(II), 0.40 mmol/g for Cd(II), 0.91 mmol/g for Fe(III), and 1.05 mmol/g for Pb(II). Desorption of metal ions were studied by using 0.1 M HNO₃. High desorption ratios (up to 97%) were observed in all cases. Repeated adsorption/desorption operations showed the feasibility of repeated use of this novel sorbent system. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1397-1403, 1999

Keywords: poly(EGDMA-HEMA) microbeads; Cibacron Blue F3GA; metal chelating properties

INTRODUCTION

Rapid industrialization and the increase in population have all contributed to the heavy metal pollution in the eco-system. Toxic heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, due to their accumulation in vital organs and animals. The traditional methods for the removal of heavy metals are filtration, chemical precipitation, reverse osmosis, solvent extraction, electrodeposition, electrodeionization, and membrane techniques.¹ The main limitation of these techniques is their low efficiency in the removal of trace levels of metal ions. The adsorption on polymer sorbents is reported to be the best method for the removal of metal ions in a low concentration such as the ppm level.² Nonspecific sorbents, such as activated carbon, metal oxides, silica, and ionexchange resins have been used.³ But recently, specific sorbents have been considered as one of the most promissing techniques.⁴ Specific sorbents consist of a ligand (e.g., ion-exchange material or chelating agents) that interacts with the

Correspondence to: A. Denizli.

Journal of Applied Polymer Science, Vol. 71, 1397–1403 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/091397-07

metal ions specifically, and a carrier matrix that may be an inorganic material (e.g., aluminium oxide, silica or glass) or polymer microbeads [e.g., polystyrene, chitosan, cellulose, poly(maleic anhydride) or polymethylmethacrylate].^{5–10}

Polymer microbeads have attracted the most attention as adsorbents because they may easily be produced in different compositions, and modified into specific sorbents, by introducing a variety of metal chelating groups. Nonporous or porous polymer microbeads with an average diameter of usually more than 100 μ m are used in these applications. To increase the active surface area available for attachment of the ligands. therefore, porous polymeric microbeads are preferentially utilized for specific adsorption. There are commercially available polymer-based porous sorbents that exhibit surface areas 100–250 m² or even larger per gram of sorbent.¹¹ One of the most critical points in the use of porous sorbents is their pore structure, because the pore diffusion and the surface area in the pores determine adsorption rate and capacity, respectively. Sorbents with highly open pore structures are needed for high adsorption rates. However, the high active surface area of the porous sorbents is mainly due to the fine pores in the matrix, which are not available for large molecules. In other words, large molecules cannot penetrate within these pores and, therefore, cannot use the active surface area there, which means low adsorption capacities for large molecules. As a conclusion, it can be said that the optimization of pore structures of the carrier matrices is very important for achieving both high adsorption rates and adsorption capacities.

In this study, Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads were prepared, and the metal chelating properties for metal ions including copper, zinc, cadmium, iron, and lead was determined. The effects of initial metal ion concentration, pH, and desorption of metal ions have also been investigated.

EXPERIMENTAL

Preparation of Cibacron Blue F3GA-Derived Microbeads

The poly(EGDMA-HEMA) microbeads were selected as the carrier matrix for the synthesis of affinity sorbent for metal removal. The microbeads were produced by a modified suspension polymerization of the respective comonomers, i.e., ethyleneglycol dimethacrylate (EGDMA, Rohm, Germany) and 2-hydroxyethylmethacrylate (HEMA, Sigma, St. Louis, MO) in an aqueous media as described in our previous articles.^{12–14} Benzoyl peroxide (BPO) and polyvinyl alcohol (PVAL) $(M_n: 100,000, 98\%$ hydrolyzed, Aldrich, Rockford, IL) were used as the initiator and the stabilizer, respectively. Toluene (Merck AG, Darmstadt, Germany) was utilized as the diluent and used as received. The dispersion medium was distilled water. To produce polymeric microbeads of about 150–200 μ m in diameter and with a narrow size distribution, the amounts of EGDMA, HEMA, toluene, water, BPO, and PVAL were 8 mL, 4 mL, 12 mL, 50 mL, 0.06 g, and 0.2 g, respectively. Polymerizations were carried out at an agitation rate of 600 rpm at 65°C for 4 h and at 90°C for 2 h. After cooling, the polymeric microbeads were separated from the polymerization medium by filtration, and the residuals (e.g., unconverted monomer, toluene) were removed by a cleaning procedure given in detail elsewhere.

Cibacron Blue F3GA was used as the affinity ligand that was obtained from Sigma. Three grams of microbeads was magnetically stirred (at 400 rpm) in a sealed reactor at a constant temperature of 80°C for 4 h with 100 mL of the Cibacron Blue F3GA aqueous solution containing 4.0 g NaOH. Under these experimental conditions, a nucleophilic substitution reaction took place between the chlorine containing group of the Cibacron Blue F3GA and the hydroxyl groups of the poly(EGDMA-HEMA) microbeads, with the elimination of hydrochloric acid, resulting in covalent attachment of Cibacron Blue F3GA to the polymer matrix. The initial concentration of the Cibacron Blue F3GA in the medium was 4.0 mg/ mL. After incubation, the Cibacron Blue F3GAderived microbeads were filtered and washed with distilled water and methanol several times until all the physically attached Cibacron Blue F3GA molecules were removed. The modified microbeads were stored at 4°C with 0.02% sodium azide to prevent microbial contamination. The leakage of the Cibacron Blue F3GA from the microbeads was followed by treating the microbeads with adsorption and desorption media for 24 h at room temperature. After this treatment, Cibacron Blue F3GA concentration in the liquid phase was measured spectrophotometrically at 630 nm.

FTIR spectra of the Cibacron Blue F3GA, the underived and Cibacron Blue F3GA-derived microbeads were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry sample (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed in to form a pellet, and the spectrum was then recorded. The amount of Cibacron Blue F3GA immobilized on the microbeads was evaluated by using an elemental analysis instrument (Leco, CHNS-932, USA), by considering the nitrogen and sulfur stoichiometry.

Adsorption Studies

Adsorption of Cu(II), Zn(II), Cd(II), Fe(III), and Pb(II) from the single metal ions aqueous solutions was investigated in batch adsorption-equilibrium experiments. Effects of the initial concentration of metal ions and pH of the medium on the adsorption capacity were studied. Twenty milliliters of aqueous metal ion solutions with different concentrations (in the range of 5-200 ppm) were treated with the underived and Cibacron Blue F3GA-derived microbeads (200 mg) at different pH (in the range of 2.0-7.0, adjusted with universal buffer solution, citric acid-potassium dihydrogen phosphate-boric acid-diethylbarbituric acid). The flasks were magnetically stirred at an agitation speed of 600 rpm at room temperature. Nitrate salts were used as the source of metal ions. After the predetermined adsorption time, the microbeads were separated from the adsorption medium, and the residual concentration of the metal ions in the aqueous phase was measured by using a graphite furnace atomic absorption spectrophotometer (GBC 932 AA, Australia). All instrumental conditions were optimized for maximum sensitivity as described by the manufacturer. For each sample, the mean of 10 AAS measurements were recorded. Adsorption values (mg/g) were calculated as the difference in initial and final metal ion concentrations. To eliminate contamination, all glassware and plasticware were washed with RBS detergent (Pierce, Rockford, IL) and rinsed with deionized water.

Desorption of metal ions was performed in 0.1 $M \text{ HNO}_3$. The microbeads loaded metal ions were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final metal ion concentration in the aqueous phase was determined by using an atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of metal ions adsorbed on the microbeads and the final metal ions concentration in the desorption medium, by using the following equation.

Desorption ratio

$$= \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \quad (1)$$
on the microbeads

To test the reusability of the Cibacron Blue F3GA-derived microbeads, adsorption-desorption cycles were repeated five times by using the same polymer matrix.

RESULTS AND DISCUSSION

The poly(EGDMA-HEMA) microbeads are crosslinked hydrogels. They do not dissolve in aqueous media, but do swell, depending on the degree of crosslinking (i.e., EGDMA amount). The equilibrium swelling ratio (the ratio of the volumes of the microbeads before and after swelling) of the microbeads is 55%. These swollen microbeads have an average diameter within the range of 150–200 μ m. It should be noted that these microbeads are suitable for packed-bed column applications.

The dry microbeads are opaque (white in color), which is an indication of the porosity in the matrix, as a result of the diluent (i.e., toluene) used in the polymerizations.¹⁶ However, the opacity of the microbeads significantly decreases and the color of the microbeads becomes light blue when the microbeads are swollen in water. After the Cibacron Blue F3GA derivatization the size of the swollen microbeads did not change, but the color became dark blue, which is a clear indication of the incorporation of the dye molecules in the structure of the microbeads. Cibacron Blue F3GA was covalently coupled to the microbeads via the nucleophilic reaction between the chloride of its triazine ring and the hydroxyl groups of the HEMA, under basic conditions.^{16–18}

Elemental analysis of the underived and Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads were obtained, and Cibacron Blue attachment F3GA was found as 16.5 μ mol/g. Cibacron Blue F3GA leakage was also investigated. There was no Cibacron Blue F3GA leakage in any of the metal adsorption and desorption media. This shows that the washing procedure was sufficient for removal of physically adsorbed Cibacron Blue F3GA molecules from the polymer matrix.

To explain the nature of the interaction between the Cibacron Blue F3GA and the poly-



Figure 1 Chemical structure of Cibacron Blue F3GA.

(EGDMA-HEMA) microbeads, FTIR spectra of underived poly(EGDMA-HEMA), Cibacron Blue F3GA, and Cibacron Blue F3GA-derived poly-(EGDMA-HEMA) were obtained. As shown in Figure 2, FTIR spectra of both poly(EGDMA-HEMA) and poly(EGDMA-HEMA)-Cibacron Blue F3GA have the characteristic stretching vibration band of hydrogen-bonded alcohol, O-H, around 3500 cm^{-1} . The FTIR spectra of dye attached poly(EGDMA-HEMA) has some absorption bands different than those of poly(EGDMA-HEMA). These are at 3375 cm^{-1} , 1520 cm^{-1} , and 650 cm^{-1} and characteristic N-H stretching, N-H bending (scissoring), and S-O stretching, respectively observed also in Cibacron Blue F3GA (Fig. 1). Cibacron Blue F3GA-derived poly(EGDMA-HEMA) spectrum has a sharp shoulder absorption band at about 3380 cm⁻¹ and interpreted as the N—H absorption. The bands at 1075 cm⁻¹, 1160 cm⁻¹, and 1280 cm^{-1} represent symmetric stretching of S=0, asymmetric stretching of S=O and aromatic C-N vibration, respectively, are due to Cibacron Blue F3GA bonded to poly(EGDMA-HEMA). The band at 1650 cm^{-1} shows a C=N stretching band in the structure of the triazine ring. These bands, however, do not appear, because underived poly-(EGDMA-HEMA) also has some absorption bands in the same region. Thus, absorption bands of underived poly(EGDMA-HEMA) overlap with those of the Cibacron Blue F3GA at around these wavenumbers. For dye derived-poly(EGDMA-HEMA) absorption band intensities in this region are higher than those of poly(EGDMA-HEMA), but the intensity increase is quite small because of the low concentration of Cibacron Blue F3GA on the polymeric surface. On the other hand, the hydrogen-bonded alcohol O-H stretching band intensity of underived poly(EGDMA-HEMA) is higher than that of poly(EGDMA-HEMA)-Cibacron Blue F3GA microbeads.

Adsorption Isotherm

Figure 3 shows the Cu(II), Zn(II), Cd(II), Fe(III), and Pb(II) adsorption curves of the Cibacron Blue

F3GA-derived poly(EGDMA-HEMA) microbeads. The amount of metal ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased first with the initial concentration of metal ions then reached a plateau value that represents saturation of the active points (which are available for specific metal ions) on the microbeads. Adsorption of Zn(II), Cd(II), and Pb(II) ions reached saturation at a higher bulk concentrations, i.e., at about 100 ppm, whereas Cu(II) and Fe(III) adsorption reached saturation at lower concentrations, i.e., about 30 ppm. The binding capacities of the Cibacron Blue F3GAderived poly(EGDMA-HEMA) microbeads are 0.19, 0.34, 0.40, 0.91, and 1.05 mmol per gram of the polymer for Cu(II), Zn(II), Cd(II), Fe(III), and Pb(II), respectively. It appears that the Cibacron Blue F3GA-derived microbeads have the strongest affinity for Pb(II) ions. The affinity order of metal ions is as follows: Pb(II) > Fe(III) > Cd(II) $> \operatorname{Zn}(\operatorname{II}) > \operatorname{Cu}(\operatorname{II}).$

The nonspecific adsorptions of metal ions on the underived poly(EGDMA-HEMA) microbeads were very low, about 5.6 μ mol Cu(II), 8.3 μ mol for Cd(II), 6.1 μ mol Zn(II), 19.6 μ mol Fe(III), and 59.3 μ mol for Pb(II) per gram of the polymer. The underived poly(EGDMA-HEMA) microbeads do



Figure 2 FTIR spectra of (A) poly(EGDMA-HEMA); (B) Cibacron Blue F3GA; (C) Cibacron Blue F3GAderived poly(EGDMA-HEMA) microbeads.

not contain metal chelating groups. Preferred coordination structure and preferred coordinating ligand atoms may be utilized for this nonspecific adsorption. For example, metal ions may interact with oxygen atoms as the ligand.¹⁹ Diffusion of metal ions into the pores of the microbeads may also contribute to this nonspecific adsorption.

In the literature, different affinity sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Shreedhara-Murthy and Ryan found 0.03-0.13 mmol Cd(II)/g and 0.08-0.42 mmol Cu(II)/g removal by cellulose-dithiocarbamate resins.²⁰ Roozemond showed 0.36 mmol Cd(II)/g and 0.50 mmol Cu(II)/g with pyrazole-containing poly(styrenedivinyl-benzene) sorbents.²¹ Konishi et al. reported 0.04-0.86 mmol Cd(II)/g with alginic acid gels.²² Liu et al. achieved 0.45 mmol Pb(II)/g and 0.26 mmol Cu(II)/g adsorption capacities with Nhydroxymethyl thioamide resin.²³ Maeda et al. presented 1.39 mmol Cu(II)/g with aminomethyl phosphonic acid containing methylmethacrylate/ divinyl benzene copolymer beads.²⁴ Hudson and Matejka investigated the length of pendants groups on Cu(II) ions adsorption onto poly(styrene-divinyl-benzene) copolymer beads and concluded that the type of pendent groups is important in the adsorption of heavy metal ions.²⁵ They reported adsorption capacities between 0.23-0.73 mmol/g. Sağ and Kutsal have used Zoogloea ramigera micro-organisms for heavy metal adsorption.²⁶ The maximum amounts of adsorption capacities achieved were 0.55 mmol Cu(II) and 0.41 mmol Pb(II)/g dry weight of micro-organisms. Shambhu et al. immobilized polyamines (i.e., ethylene diamine, diethylene triamine, and triethylene tetramine) onto polystyrene and reached an adsorption value of 0.52 mmol Cu(II)/g polymer.²⁷ Janus et al. used poly(vinyl amine) sorbent for copper adsorption and reported an adsorption capacity of 7.86 µmol Cu(II)/g.²⁸ Khalfaoui et al. achieved an adsorption capacity of 0.62 µmol Cu(II)/g on raw charcoal.²⁹ Denizli et al. used Alkali Blue 6B-attached P(EGDMA-HEMA) sorbents, in which the maximum adsorption capacities were 0.036 mmol Cu(II)/g, 0.048. mmol Cd(II)/g, 0.63 mmol Zn(II)/g, and 0.60 mmol Pb(II)/g.14 Denizli et al. immobilized ethylene diamine and hexamethylene diamine onto polyhydroxyethylmethacrylate microspheres by a glow-discharge method and obtained 0.11 mmol Cu(II)/g and 0.84 mmol Pb(II)/g for HMDA treatment.^{30,31} Bıçak et al. reported 2.43 mmol Cu(II)/g by using sorbents based on *p*-dichloromethyl benzene.³² Dev and Rao reported 0.46 mmol Cu(II)/g,



Figure 3 Adsorption capacity of Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads for metal ions; pH: 6.7.

0.46 mmol Cd(II)/g, and 0.39 mmol Pb(II)/g adsorption capacity for polystyrene–vinylbenzene macroreticular resin functionalized with bis-(N,N'-salicylidene)1,3-propanediamine.³³ From the data that we obtained in this study, we may conclude that the Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads is promising for the removal of metal ions from aqueous media.

Effect of pH on Metal Binding

Metal ion adsorption on specific sorbents is pH dependent. In the absence of metal chelating groups, the precipitation of the metal ions are affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by hydroxide or carbonate concentration. As discussed in detail by Reed and Matsumoto,³⁴ precipitation of metal ions becomes significant at approximately pH 8.5, pH 6.5, pH 7.0, and pH 7.5 for Cd(II), Cu(II), Zn(II), and Pb(II), respectively. The theoretical and experimental precipitation curves indicate that precipitation begins above these pHs, which also depends on the concentration of metal ions in the medium. Therefore, in our study, to establish the effect of pH on the adsorption of metal ions onto the Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads, we repeated the batch equilibrium studies at different pH in the range of 2.0–7.0. In this group of experiments, the initial concentration of metal ions was 30 ppm for all ions. Figure 4 shows the pH effect. The adsorption capacities of the Cibacron Blue F3GA-derived poly(EGDMA-HEMA)



Figure 4 Effect of pH on adsorption of metal ions on Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads.

microbeads are 0.19, 0.098, 0.23, 0.68, and 0.91 mmol per gram of the polymer for Cu(II), Zn(II), Cd(II), Pb(II), and Fe(III), respectively. It appears that the Cibacron Blue F3GA-derived microbeads had the strongest affinity for Fe(III) ions at low concentration (i.e., 30 ppm). The affinity order of metal ions is as follows: Fe(III) > Pb(II) > Cd(II) > Cu(II) > Cu(II) > Zn(II).

Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads exhibited a low affinity for heavy metal ions in acidic conditions (pH < 4), a somewhat higher affinity between pH 5 and 7. The difference in adsorption behavior of Fe(III) compared to Pb(II), Cd(II), Zn(II), and Cu(II) can be explained by the different affinity of heavy metal ions for the donor atoms (i.e., oxygen and nitrogen) in the dye-ligand Cibacron Blue F3GA. A difference in coordination behavior is also most probably the case for the attached Cibacron Blue F3GA ligand resulting in a relatively high adsorption of Fe(III) ions at high pH under noncompetitive adsorption conditions.

Desorption and Repeated Use

Desorption of the adsorbed metal ions from the Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads was also studied in a batch experimental setup. The dye-derived microbeads carrying the maximum amounts of the respective metal ions were placed within the desorption medium containing 0.1 M HNO₃, and the amount of metal ions desorbed in 2 h was measured. The desorption ratio was then calculated by using the

expression given in eq. (1). Desorption ratios were very high (up to 97%) with the desorption agent and conditions used for all metal ions.

To obtain the reusability of the Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads, the adsorption-desorption cycle was repeated five times by using the same sorbent. As shown in Figure 5, the adsorption capacity of the sorbent for all metal ions did not significantly change during the repeated adsorption-desorption operations.

CONCLUSION

Poly(EGDMA-HEMA) microbeads having a swelling ratio of 55% were prepared by suspension method. An affinity dye ligand, i.e., Cibacron Blue F3GA was then immobilized in these microbeads with a concentration of 16.5 μ mol/g polymer. Adsorption/desorption of Cu(II), Zn(II), Cd(II), Fe(III), and Pb(II) from aqueous media on these microbeads led to the following conclusions: the metal adsorption is rapid, and adsorption equilibria were reached in about 30 min. Adsorption capacities of these affinity microbeads from their single metal ions solutions were 0.19 mmol/g for Cu(II), 0.34 mmol/g for Zn(II), 0.40 mmol/g for Cd(II), 0.91 mmol/g for Fe(III), and 1.05 mmol/g for Pb(II). Cibacron Blue F3GA-derived poly(EGDMA-HEMA) microbeads exhibit the following metal ion affinity sequence: Pb(II) > Fe(III) > Cd(II) > Zn(II) > Cu(II). Adsorbed metal ions were easily desorbed by using



Figure 5 Repeated use of the Cibacron Blue F3GAderived poly(EGDMA-HEMA) microbeads. Initial concentrations of metal ions: 200 ppm for Zn(II), Cd(II) and Pb(II); 30 ppm for Cu(II) and 50 ppm for Fe(III).

0.1 M HNO₃. Consecutive adsorption and desorption showed the feasibility of this novel affinity microbead for metal adsorption.

REFERENCES

- 1. Streat, M., Ed., Ion Exchange for Industry; Ellis Horwood Ltd.: Chichester, 1988.
- Weltrowski, M.; Martel, B.; Morcellet, M. J Appl Polym Sci 1996, 59, 647.
- Reed, B. E.; Matsumoto, M. R. Sep Sci Technol 1993, 28, 2179.
- Hunt, S. In Immobilisation of Ions by Bio-Sorption; Ecclos, H.; Hunt, S., Eds.; Ellis Horwood: Chichester, 1986.
- 5. Brajter, K.; Dabek-Zlotorzynska, E. Talanta 1990, 37, 613.
- Kantipuly, C.; Katragadda, S.; Chow, A.; Goser, H. D. Talanta 1990, 37, 491.
- Hwang, D. C.; Damodaran, S. J Appl Polym Sci 1997, 64, 891.
- Brajter, K.; Dabek-Zlotorzynska, E. Analyst 1988, 113, 1571.
- Kabay, N.; Egawa, H. Sep Sci Technol 1985, 28, 1985.
- Ito, Y.; Saegusa, T. J Macromol Sci Chem 1978, A13, 503.
- Kaczvisky, J. R.; Fritz, J. S.; Walker, D. D.; Ebra, H. Radioanal Nucl Chem 1985; 91, 349.
- Salih, B.; Denizli, A.; Pişkin, E. Sep Sci Technol 1996, 31, 715.
- Kesenci, K.; Tuncel, A.; Pişkin, E. React Funct Polym 1995, 31, 137.
- Denizli, A.; Salih, B.; Pişkin, E. React Funct Polym 1995, 29, 11.
- Denizli, A.; Rad, A. Y.; Pişkin, E. J Chromatogr B 1995, 668, 13.

- Denizli, A.; Salih, B.; Pişkin, E. J Chromatogr A 1996, 731, 57.
- Salih, B.; Denizli, A.; Tuncel, A.; Engin, B.; Pişkin, E. J Appl Polym Sci 1996, 60, 871.
- Denizli, A.; Salih, B.; Pişkin, E. J Macromol Sci Part A 1997, A34, 1353.
- 19. Ochiai, E. J Chem Educ 1995, 72, 479.
- 20. Shreedhara-Murthy, R. S.; Ryan, D. E. Anal Chim Acta 1982, 140, 163.
- Roozemond, D. A.; Hond, F. D.; Veldhuis, J. B. J.; Strasdeit, H.; Driessen, W. L. Eur Polym J 1998, 24, 867.
- Konishi, Y.; Asai, S. S.; Midoh, Y.; Oku, M. Sep Sci Technol 1993, 28, 1691.
- Liu, C. Y.; Chang, H. T.; Hu, C. C. Inorg Chim Acta 1990, 172, 151.
- Maeda, H.; Egawa, H. J Appl Polym Sci 1987, 33, 1275.
- Hudson, M. J.; Matejka, Z. Sep Sci Technol 1990, 25, 1417.
- 26. Sağ, Y.; Kutsal, T. Chem Eng J 1995, 60, 181.
- Shambhu, M. B.; Theodorakis, M. C.; Digenis, G. A. J Polym Sci Polym Chem Ed 1977, 15, 525.
- Janus, L.; Morcellet, J.; Delporte, M.; Morcellet, M. Eur Polym J 1992, 28, 1185.
- 29. Khalfaoui, B.; Meniai, A. H.; Borja, R. J Chem Tech Biotechnol 1995, 64, 153.
- Denizli, A.; Salih, B.; Pişkin, E. J Chromatogr A 1997, 773, 169.
- Denizli, A.; Salih, B.; Pişkin, E. In Plasma Processing of Polymers; Agostino, R.; Favia, P.; Fraccassi, F., Eds.; Kluwer Academic Publishers: The Netherlands, 1997, p. 423.
- 32. Bıçak, N.; Koza, G.; Atay, T. J Appl Polym Sci 1996, 61, 799.
- 33. Dev, K.; Rao, G. N. Talanta 1996, 43, 451.
- Reed, B. E.; Nonavinakere, S. K. Sep Sci Technol 1992, 27, 1985.