

Congo Red Attached Poly(EGDMA–HEMA) Microspheres as Specific Sorbents for Removal of Cadmium Ions

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SYNOPSIS

Poly[ethyleneglycoldimethacrylate (EGDMA)–hydroxyethylmethacrylate (HEMA)] microspheres (150–200 μm in diameter) were produced by suspension copolymerization of EGDMA and HEMA in an aqueous medium. Toluene was included in the formulations in order to produce water-swellable microspheres. Poly(vinyl alcohol) and benzoyl peroxide were used as stabilizer and initiator, respectively. Congo red was chemically attached to the microspheres as a metal chelating ligand for specific adsorption of heavy metal ions. These sorbents were characterized by an optical microscopy and a FTIR. Adsorption/desorption of cadmium (Cd^{2+}) ions from aqueous solutions on these sorbents were investigated in batch equilibrium experiments by using an atomic absorption spectroscopy with a graphite furnace atomizer. The maximum cadmium adsorption on to the dye-attached microspheres (i.e., by complex formation) was about 18.3 mg Cd^{2+} ions/g polymer, which was observed at pH 6.8. While adsorption onto the plain poly(EGDMA–HEMA) microspheres (i.e., nonspecific adsorption) was about 0.93 mg Cd^{2+} ions/g polymer at the same conditions. More than 90% of the adsorbed cadmium was desorbed in 1 h by using 2M NaCl as an eluant. The resorption capacity of the sorbent did not significantly decrease during repeated sorption–desorption cycling. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The selective and quantitative separation of metal ions from aqueous solutions have been extensively investigated by applying several techniques.^{1–3} Among them, approaches where specific sorbents are used have been considered as one of the most promising techniques.^{4–6} Sorbents consist of a ligand (e.g., ion-exchange material or chelating agents), which interacts with the metal ions specifically, and a carrier matrix, which may be an inorganic material (e.g., aluminium oxide, silica, or glass) or polymer microspheres [e.g., polystyrene, cellulose, poly(maleic anhydride), or polymethylmethacrylate].^{7–10}

As carrier matrices, polymer microspheres have attracted the most attention because they may be easily produced in a wide variety of compositions and modified into specific sorbents by introducing

a variety of ligands. Synthetic polymers have almost entirely displaced inorganic carriers in the separation of heavy metal ions.^{11–14} Nonporous or porous polymer microspheres with average diameter of usually more than 100 μm are used in these applications. In order to increase the active surface area available for attachment of the ligands, and for specific adsorption, porous polymeric microspheres are preferentially utilized. There are commercially available polymer based porous sorbents, which exhibit surface areas 100–250 m^2 , or larger, per gram of sorbent.¹⁵ 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, 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 fine pores and, therefore, cannot use the active surface area

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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 a very important issue to achieve both high adsorption rates and high adsorption capacities.

Recently, we have produced water-swella-ble poly[ethylene(1,2-hydroxyoxide)dimethacrylate-hydroxyethylmethacrylate] microspheres with different sizes and swelling abilities.¹⁶ In order to introduce specificity against heavy metal ions, we proposed to covalently attach a new ligand, i.e., Congo red to these microspheres. We studied adsorption-desorption of cadmium ions to these specific sorbents in batch experiments. Results of these initial studies are presented here.

EXPERIMENTAL

Preparation of Dye-Attached Poly(EGDMA-HEMA) Microspheres

Ethyleneglycoldimethacrylate (EGDMA), supplied from Rohm and Haas, Germany, was purified by passing through active alumina. Hydroxyethylmethacrylate (HEMA) was purchased from Sigma Chemical Co., St. Louis, MO, and purified by the same method. Benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVAL; MW: 100,000, 98% hydrolyzed, Aldrich Chemical Co., Milwaukee, WI) were utilized as the initiator and the stabilizer, respectively, without further purification. Toluene (Merck, Germany) was selected as the diluent and used without further purification. Dispersion medium was distilled water.

Swella-ble poly(EGDMA-HEMA) microspheres were produced by a modified suspension polymerization method described in detail elsewhere.¹⁶ In order to obtain poly(EGDMA-HEMA) microspheres with an average diameter of 150–200 μm , the following procedure was applied: the dispersion medium was prepared by dissolving 0.2 g of PVAL within 50 mL of distilled water. Toluene (12 mL) was mixed with 8 mL of EGDMA and 4 mL of HEMA, then 0.06 g of BPO was dissolved in this mixture. This monomer phase was then transferred into the dispersion medium placed in a magnetically stirred (at a constant stirring rate of 600 rpm) glass polymerization reactor (100 mL), which was in a thermostatic water bath. The reactor was flushed by bubbling nitrogen and then was sealed. Polymerization was conducted, first at 65°C for 4 h, and then at 90°C for 2 h. After polymerization, the microspheres were cleaned by following several wash-

ing steps with water and ethyl alcohol, and dried in a vacuum oven at 60°C for 48 h.¹⁶

For dye attachment to the poly(EGDMA-HEMA) microspheres, 10 mL of the aqueous solution containing 300 mg of Congo red (BDH Ltd., UK) was poured into 90 mL of the suspension of the poly(EGDMA-HEMA) microspheres in distilled water (containing 3.0 g of the microspheres), and then 4.0 g of NaOH was added. The medium was heated in a sealed reactor for 4 h at a stirring rate of 400 rpm, and at a constant temperature of 80°C. The dye-attached poly(EGDMA-HEMA) microspheres were filtered and washed with distilled water and methanol several times until all the unbound dye was removed.

Characterization of Dye-Attached Poly(EGDMA-HEMA) Microspheres

In order to determine swellability of the poly(EGDMA-HEMA) microspheres, first the apparent volume of the dry microspheres (10 g) was measured within a cylindrical glass tube (100 mL). Then water was added into the tube, and the microspheres were allowed to swell at room temperature for 24 h (i.e., the predetermined equilibrium swelling time) with occasional shaking, and then the volume of the swollen microspheres was measured. The equilibrium swelling ratio of the poly(EGDMA-HEMA) microspheres were calculated by using the following expression:

$$\text{Equilibrium Swelling Ratio} = V_{\text{wet}}/V_{\text{dry}} \quad (1)$$

where V_{wet} and V_{dry} are volumes of the microspheres before and after swelling, respectively.

The optical micrographs were taken with the dry (nonswollen) and swollen microspheres under an optical microscope (Nikon, Alphapot YS, Japan) equipped with a dark-field phase-contrast attachment. The average size and standard deviation were determined by measuring the size of 100–300 microspheres on the optical micrographs.

FTIR spectra of the dye (i.e., Congo red), plain, and dye-attached poly(EGDMA-HEMA) microspheres were obtained by using a FTIR spectrophotometer (Shimadzu, FTIR 8000 Series, Japan). The microspheres (0.1 g) and KBr (0.1 g, IR Grade, Merck, Germany) were thoroughly mixed and this mixture was pressed to form a tablet, and the spectrum was recorded.

Adsorption-Desorption Studies

Adsorption of Cd^{2+} ions from aqueous solutions was investigated in batch experiments. Effects of the initial cadmium concentration and pH of the medium on the adsorption rate and capacity were studied. A 20 mL of aqueous solutions containing different amounts of Cd^{2+} ions (in the range of 1–200 ppm) were treated with the sorbents (i.e., the plain and the dye-attached poly(EGDMA-HEMA) microspheres) at different pH (in the range of 1.5–8.0) (adjusted with universal buffer solution) at room temperature, in the flasks agitated magnetically at an agitation speed of 600 rpm. After adsorption, the polymeric microspheres were separated from the polymerization medium by filtration. The concentrations of the Cd^{2+} ions in the aqueous phases after the desired treatment periods were measured by using an Atomic Absorption Spectrophotometer (GBC 932 AA, Australia). The amount of adsorption per unit mass of the microspheres were evaluated by using the following expression:

$$Q = [(C_0 - C) \cdot V] / m \quad (2)$$

Here, Q is the amount of Cd^{2+} ions adsorbed onto unit mass of the microspheres (mg/g); C_0 and C are the concentrations of the Cd^{2+} ions in the initial solution and in the aqueous phase after treatment for certain period of time, respectively (mg/mL); V is the volume of the aqueous phase (mL); and m is the amount of poly(EGDMA-HEMA) microspheres used (g).

Desorption of Cd^{2+} ions was studied in buffer solutions containing 2M NaCl at pH 7.0. The microspheres carrying Cd^{2+} ions were placed in this desorption medium and stirred (at a stirring rate of 600 rpm) for 2 h at room temperature. The final cadmium concentration in the aqueous phase was determined by using an Atomic Absorption Spectrophotometer. In order to prevent interference of NaCl during the atomic absorption measurements, 4000 ppm NH_4NO_3 matrix modifier was added to the sample solution (1:1 ratio). The desorption ratio was calculated from the amount of Cd^{2+} ions adsorbed on the microspheres and the final cadmium concentration in the desorption medium, by using the following expression:

Desorption Ratio

$$= \frac{\text{amount of } \text{Cd}^{2+} \text{ ions desorbed to the elution medium}}{\text{amount of } \text{Cd}^{2+} \text{ ions adsorbed on the microspheres}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Characteristics of Dye-Attached Poly(EGDMA-HEMA) Microspheres

The poly(EGDMA-HEMA) matrix prepared in this study is a crosslinked hydrophilic network, i.e., an hydrogel. Therefore, the matrix does not dissolve in aqueous media, but swells, depending on the degree of crosslinking and on the hydrophilicity of the matrix.¹⁶ The equilibrium swelling ratio of the microspheres produced with the recipe given in the previous section was obtained as 55% by using the expression given in eq. (1). Note that the swollen particles are strong durable enough due to a highly crosslinked structure, therefore suitable for fixed-bed or fluidized-bed applications.

The dry poly(EGDMA-HEMA) microspheres 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 microspheres significantly decreased and the color of the microspheres became light blue when the microspheres were allowed to swell due to water uptake. After the attachment of the dye (i.e., Congo red) the size of the swollen microspheres did not change but the color became light red, which is a clear indication of the incorporation of the dye molecules in the structure of the poly(EGDMA-HEMA) microspheres. Figure 1 gives a representative picture of Congo red attached poly(EGDMA-HEMA) microspheres.

In order to show incorporation of Congo red within the poly(EGDMA-HEMA) microspheres, FTIR spectra of the plain and dye-attached microspheres were taken (Fig. 2). The bands observed at 1075 cm^{-1} , 1155 cm^{-1} , 1280 cm^{-1} , and 3570 cm^{-1} represent symmetric stretching of S=O, asymmetric stretching of S=O, aromatic C-N vibration, and N-H and SO_3H groups, respectively, as also pointed out on the chemical structure of Congo red given in Figure 3. These bands may be considered as another indication of the presence of Congo red within the poly(EGDMA-HEMA) microspheres.

Adsorption-Desorption of Cadmium Ions Adsorption Rate

Figure 4 shows adsorption rates of Cd^{2+} ions onto the dye-attached poly(EGDMA-HEMA) microspheres from aqueous solutions containing different amounts of Cd^{2+} ions (in the range of 1–200 ppm) at a constant pH of 6.8. Note that the ordinate values on this figure were calculated by using the expression

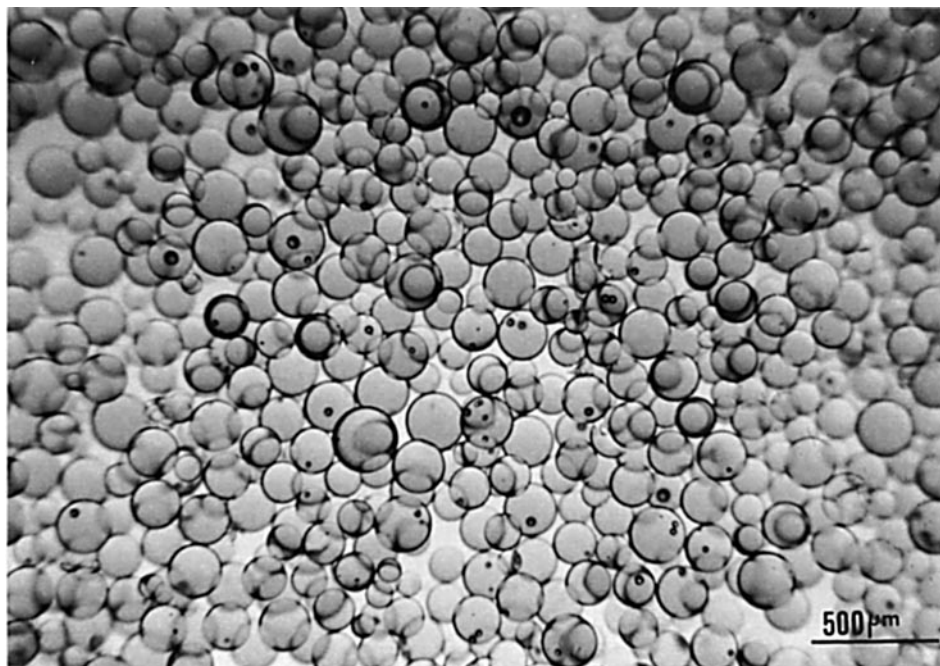


Figure 1 A representative optical photograph of the Congo red attached poly(EGDMA-HEMA) microspheres.

given in eq. (2). As seen here, high adsorption rates are observed at the beginning, and then plateau values (i.e., adsorption equilibrium) are gradually reached within 15–90 min. Adsorption of Cd^{2+} ions was quite fast, especially when the Cd^{2+} ion concentration was high. This may be due to high driving force, which is the Cd^{2+} ion concentration difference between the liquid (i.e., adsorption medium) and the solid (i.e., the microspheres) phases, in the case of high Cd^{2+} ion concentration.

Several experimental data on the adsorption kinetics of cadmium by various sorbents have shown

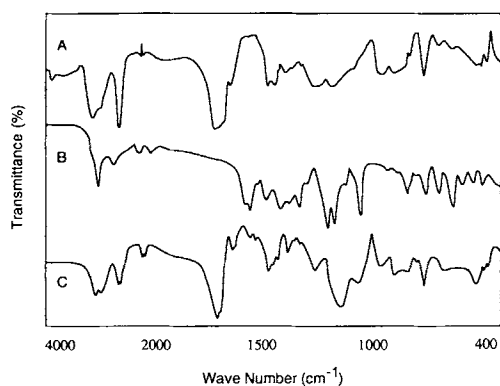


Figure 2 FTIR spectra: (A) Plain poly(EGDMA-HEMA); (B) Congo red; (C) dye-attached poly(EGDMA-HEMA).

a wide range of adsorption rates. For example, recently, Reed and Matsumoto have considered 6 h as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent.^{3,17} Konishi et al. have investigated recovery of zinc, cadmium, and lanthanum by biopolymer gel particles of alginic acid. In their recent article they reported very high adsorption/desorption rates for lanthanum by alginic acid, in which equilibrium was achieved in about 60–90 min.¹⁸ Note that in such an adsorption process there are several parameters that determine the adsorption rate, such as agitation (or flow) rate in the aqueous phase, sorbent structural properties (e.g., size, porosity, surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, chelate-formation rate, and, of course, existence of other ions that may compete with the ions of interest for the active adsorption sites. All individual experimental study

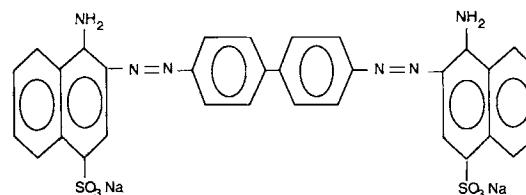


Figure 3 Chemical structure of Congo red.

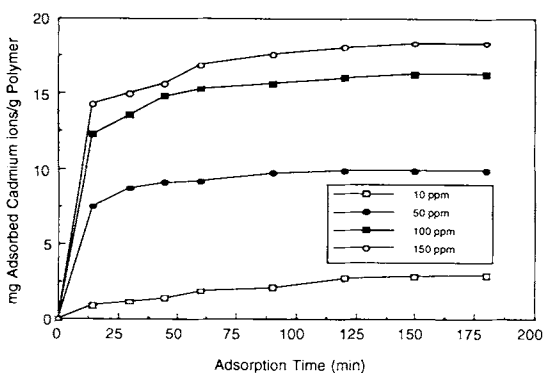


Figure 4 Adsorption rate curves of Cd^{2+} ions on poly(EGDMA-HEMA) microspheres at pH 6.8.

published in the literature has been performed at different conditions. Therefore, it can be concluded that it is almost impossible to compare the adsorption rates reported.

Adsorption Capacity

Figure 5 shows effects of initial concentration of Cd^{2+} ions onto the adsorption capacity of the dye-attached poly(EGDMA-HEMA). Note that this graph was obtained by using the plateau values (corresponding the equilibrium time of 90 min) given in Figure 4. The amount of Cd^{2+} ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased first with the initial concentration of Cd^{2+} ions then reached a plateau value (18.3 mg Cd^{2+} /g polymer) at about an initial Cd^{2+} ions concentrations of 125 ppm, which represents saturation of the active points (which are available for Cd^{2+} ions) on the microspheres. The maximum adsorption capacity of the Congo red attached poly(EGDMA-HEMA) microspheres is 18.3 mg Cd^{2+} /g polymer.

Some previous data on the sorption equilibria of cadmium for aqueous solutions by natural and synthetic polymers have been compared by Konishi et al.¹⁸ These data and other reported values^{3,5,17,19,20} were, again, in a very wide range (4.8–96.3 mg cadmium/g sorbent), in which initial concentration of the cadmium in solution was in the range of 0.056–2.81 mg/L. The extend of adsorption increased by the initial metal ion concentration as expected, similar to our data shown in Figure 4.

Effect of pH

It is well known that cadmium adsorption both on nonspecific and specific sorbents is pH dependent.^{3,5,17,19,20} In the absence of complexing agents,

the hydrolysis and precipitation of the metal ion are affected by the concentration and form of soluble metal species. The solubility of cadmium is governed by hydroxide or carbonate concentration. As discussed in detail by Boomhover²¹ and Reed and Matsumoto,³ hydrolysis of cadmium becomes significant at approximately pH 8. The theoretical and experimental precipitation curves indicate that precipitation begins above this pH, which also depends on the concentration of cadmium in the medium. Therefore, in our study, in order to establish the effect of pH on the adsorption of Cd^{2+} ions onto the dye-attached poly(EGDMA-HEMA) microspheres, we repeated the batch equilibrium studies at different pH in the range of 1.5–8.0. In this group of experiments the initial concentration of Cd^{2+} ions and the adsorption equilibrium time (i.e., time to reach the plateau, as seen in Fig. 4) were 125 ppm and 90 min, respectively. Figure 6 shows both nonspecific adsorption (i.e., adsorption onto the plain poly(EGDMA-HEMA) microspheres) and the specific adsorption (i.e., adsorption by chelating with the Congo red molecules attached on the poly(EGDMA-HEMA) microspheres) of Cd^{2+} ions.

As seen in Figure 6, adsorption of cadmium increased with pH and reached almost a plateau value around pH 6.8. The nonspecific adsorption of Cd^{2+} ions was low, about 0.93 mg Cd^{2+} /g polymer. There is neither ion-exchange nor complex forming groups onto the plain poly(EGDMA-HEMA) microspheres. This adsorption may be due to diffusion of Cd^{2+} ions into the swollen matrix of the microspheres, while the specific adsorption of Cd^{2+} ions, which was pH dependent, was much higher (up to 18.3 mg Cd^{2+} /g polymer) than nonspecific adsorption. High adsorption at basic pH values implies that Cd^{2+} ions interact with Congo red not only through the nitrogen atoms

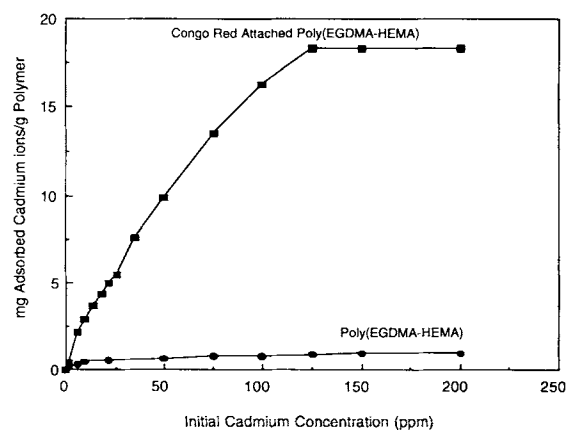


Figure 5 Cd^{2+} ions adsorption capacity of dye-attached poly(EGDMA-HEMA) microspheres at pH 6.8.

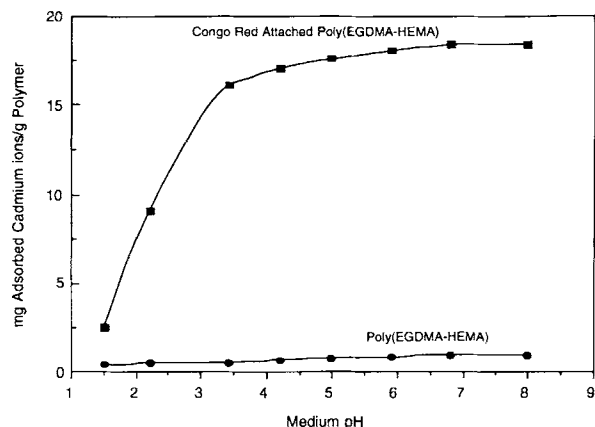


Figure 6 Effect of pH on adsorption of Cd^{2+} ions on plain and dye-attached poly(EGDMA-HEMA) (initial cadmium concentration: 125 ppm).

(see Fig. 3) by chelating, but also through $-\text{SO}_3\text{H}$ groups by cation exchange, which are unprotonated at high pH.

Desorption

Desorption of the adsorbed Cd^{2+} ions from the Congo red attached poly(EGDMA-HEMA) microspheres was also studied in a batch experimental setup. The dye-attached microspheres, loaded (at pH: 6.8) with different amounts of Cd^{2+} ions, were placed within the desorption medium containing 2 M NaCl at pH 7.0 and the amount of Cd^{2+} ions desorbed in 2 h was measured. The desorption ratio was then calculated by using the expression given in eq. (3). Table I summarizes the results of desorption studies. As seen in this table recovery (or desorption ratio) was very high (up to 93%) with the eluant system and conditions used.

Repeated Use

In order to obtain the reusability of the Congo red attached poly(EGDMA-HEMA) microspheres, the

Table I Desorption of Cd^{2+} Ions

Initial Cd^{2+} Ion Conc. (ppm)	Desorption Ratio (%)
5	92.0 \pm 0.4
25	92.5 \pm 0.5
50	91.6 \pm 0.3
100	93.4 \pm 0.4
150	92.6 \pm 0.4

Adsorption medium pH: 6.8. Desorption medium: 2 M NaCl, pH: 7.0

Table II Sorption-Desorption Cycles for Cd^{2+} Ions

Cycle No.	Adsorption (mg Cd^{2+} /g polymer)	Desorption Ratio (%)
1	18.3 \pm 0.5	92.6 \pm 0.4
2	18.2 \pm 0.4	94.5 \pm 0.5
3	18.0 \pm 0.4	93.6 \pm 0.5
4	17.9 \pm 0.5	94.1 \pm 0.3
5	17.8 \pm 0.4	92.7 \pm 0.2

Initial Cd^{2+} ions loading: 18.3 mg Cd^{2+} /g polymer. Adsorption at pH: 6.8 for 2 h, and desorption at pH: 7.0 for 2 h with 2M NaCl.

sorption-desorption cycle was repeated five times by using the same sorbent. An initial amount of Cd^{2+} ions loaded on the dye-attached microspheres was 18.3 mg Cd^{2+} /g polymer. In each cycle, adsorption was achieved at pH: 6.8 in 2 h, and desorption was performed at pH 7.0 in 2 h by using 2 M NaCl. Table II gives the results of these studies. As seen here, resorption capacity of the sorbent did not significantly decrease during repeated sorption-desorption cycling.

CONCLUSION

From the data presented here it can be concluded that the Congo red attached poly(EGDMA-HEMA) microspheres may effectively (means with high adsorption rates and capacities, and repeatedly) be used for removal of Cd^{2+} ions from aqueous solutions. Our studies related to competitive adsorption-desorption of other heavy metal ions are still under investigation.

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Received August 1, 1995

Accepted November 10, 1995