New Dye-Ligand: Procion Red MX-3B Carrying Poly(EGDMA-HEMA) Microbeads for Removal of Copper Ions

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NEW DYE-LIGAND: PROCION RED MX-3B CARRYING POLY(EGDMA-HEMA) MICROBEADS FOR REMOVAL OF COPPER IONS

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ABSTRACT

Procion Red MX-3B-attached poly(ethylene glycol dimethacrylate-hydroxy-ethyl methacrylate [poly(EGDMA-HEMA)] microbeads were prepared for removal of Cu^{2+} ions from aqueous media containing different amounts of Cu^{2+} ions (2-50 ppm). Procion Red MX-3B-attached microbeads were characterized by FTIR, optical microscopy and elemental analysis. Dye-attached microbeads with a swelling ratio of 55% and carrying 8.95 μmol Procion Red MX-3B/g polymer were used in the adsorption-desorption of Cu^{2+} ions. Very high adsorption rates were observed at the beginning of adsorption process and then equilibrium was achieved in about 5-10 minutes. The maximum adsorption of Cu^{2+} ions onto the Procion Red MX-3B-attached poly(EGDMA-HEMA) microbeads (i.e., by chelate formation of Cu^{2+} ions with dye molecules) was about 4.6 mg Cu^{2+} ions/g polymer, which was observed at pH 7.5. Adsorption onto the plain poly(EGDMA-HEMA) microbeads (i.e., non-specific adsorption) was about 0.36 mg Cu^{2+} ions/g polymer under

the same experimental conditions. More than 90% of the adsorbed Cu^{2+} ions was desorbed in 15 minutes by using 0.1 M HNO_3 as an desorption agent.

INTRODUCTION

Heavy metal ions are among the most important toxic pollutants in water sources. The heavy metal pollution is becoming more and more a serious public health problem throughout the world due to rapid industrialization. Removal of precipitation and ion-exchange, but usually with limited success. In the last decade, adsorption has been shown to be an effective and economically feasible alternative method for removal of heavy metal ions [1-3]. Specific polymeric sorbents consist of a metal chelating ligand which interacts with the heavy metal ions specifically, and a carrier matrix which may be an inorganic material (e.g., aluminium oxide, silica, activated carbon or glass) or polymer microbeads (e.g., polystyrene, cellulose, poly(maleic anhydride) or polymethylmethacrylate) [4, 5]. Polymers have almost entirely displaced inorganic carriers, with few exceptions in the separation of heavy metal ions [6, 7].

Recently, we produced poly(ethyleneglycoldimethacrylate-hydroxyethyl methacrylate) microbeads with different swelling abilities as a carrier matrix to prepare specific sorbents [8]. Several dye-ligands were immobilized on these polymeric microbeads and used for removal of heavy metal ions from aqueous media [9-11]. In this article, we attached a new ligand, i.e., Procion Red MX-3B to these microbeads. We now report on the synthesis, characterization and Cu^{2+} adsorption-desorption properties of Procion Red MX-3B-attached poly(EGDMA-HEMA) microbeads.

EXPERIMENTAL

Preparation of Procion Red MX-3B-Attached Microbeads

Ethyleneglycoldimethacrylate (EGDMA) was supplied from Rohm and Haas, Germany and purified by passing through active alumina. Hydroxyethyl-methacrylate (HEMA) was purchased from Sigma Chem. Co., USA., and purified by the same method. Benzoyl peroxide (BPO) and poly(vinyl-alcohol) (PVAL; MW: 100.000, 98% hydrolyzed, Aldrich Chem. Co., USA) were utilized as the initiator and the stabilizer, respectively, without further purification. Toluene (Merck, Germany) was selected as the polymerization diluent and used without further purification. Dispersion medium was distilled water.

Poly(EGDMA-HEMA) microbeads were produced by a modified suspension polymerization method described in detail elsewhere [8]. In order to obtain microbeads 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. 12 ml toluene 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 hours, and then at 90°C for 2 hours. After polymerization, the microbeads were cleaned by following several washing steps with water and ethyl alcohol, and dried in a vacuum oven at 60°C for 48 hours [8].

For dye attachment to the microbeads, 10 ml of the aqueous solution containing 300 mg of Procion Red MX-3B (Sigma, USA) was poured into 90 ml of the suspension of the microbeads in distilled water (containing 3.0 g of the microbeads), and then 4.0 g of NaOH was added. The medium was heated in a sealed reactor for 4 hours at a stirring rate of 400 rpm, and at a constant temperature of 80°C. Under these experimental conditions, a chemical reaction took place between the chlorine containining group of the Procion Red MX-3B and the hydroxyl groups of the HEMA monomer, with the elimination of HCl, resulting in covalent attachment of Procion Red MX-3B onto the poly(EGDMA-HEMA) microbeads. Any remaining chlorine atoms in the dye-attached microbeads due to the dichlorotriazinyl dye Procion Red MX-3B structure, after covalent immobilization, was converted to amino groups by treating with 2 M NH_4Cl at pH 8.5 for 24 hours at room temperature. The dye-attached microbeads were filtered, and washed with distilled water and methanol several times until all the unbound dye was removed.

Characterization of Procion Red MX-3B-Attached Microbeads

For determination of swelling degree of microbeads, first the apparent volume of the dry microbeads (10 g) was measured within a cylindirical glass tube (100 ml). Then, water was added into the tube, and the microbeads were allowed to swell at room temperature for 24 hours (i.e., the predetermined equilibrium swelling time) with occasional shaking, and then the volume of the swollen microbeads was measured. The equilibrium swelling ratio of the microbeads were calculated by using the following expression:

$$\text{Equilibrium Swelling Ratio} = V_{wet} / V_{dry} \tag{1}$$

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

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

FTIR spectra of the plain poly(EGDMA-HEMA) microbeads and Procion Red MX-3B-attached poly(EGDMA-HEMA) microbeads were obtained by using a FTIR spectrophotometer (Shimadzu, FTIR 8000 Series, Japan). The microbeads (0.1 g) and KBr (0.1 g, IR Grade, Merck, Germany) were thorougly mixed and this mixture was pressed to form a pellet, and the FTIR spectrum was recorded.

Adsorption/Desorption Studies

Adsorption of Cu^{2+} ions from aqueous solutions was investigated in batch experiments. Effects of the initial Cu^{2+} concentration and pH of the medium on the adsorption rate and capacity were studied. A 20 ml of aqueous solutions containing different amounts of Cu^{2+} ions (in the range of 2-50 ppm) were treated with the 100 mg of sorbents (i.e., the plain and the dye-attached poly(EGDMA-HEMA) micro-beads) at different pH (in the range of 2.0-7.5) (adjusted with HCl-NaOH) at room temperature, in the flasks agitated magnetically at an agitation speed of 100 rpm. The concentration of the Cu^{2+} ions in the aqueous phase after the desired treatment periods was measured by using a graphite furnace atomic absorption spectrophoto-meter (AAS, GBC 932 AA, Australia). All instrumental conditions were optimized for maximum sensitivity as described by the manufacturer. For each metal solution sample, the mean of 10 AAS measurements was recorded. The amount of adsorp-tion per unit mass of the microbeads were evaluated by using the following expres-sion.

$$Q = [(C_0-C) . V] / m \qquad (2)$$

Here, Q is the amount of Cu^{2+} ions adsorbed onto unit mass of the microbeads (mg/g); C_0 and C are the concentrations of the Cu^{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) microbeads used (g).

Desorption of Cu^{2+} ions was sudied in 0.1 M HNO_3. The microbeads loaded Cu^{2+} ions were placed in this desorption medium and stirred (at a stirring

rate of 100 rpm) for 15 minutes at room temperature. The final concentration of Cu^{2+} ions in the aqueous phase was determined by using a graphite furnace atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of Cu^{2+} ions adsorbed on the microbeads and the final concentration of Cu^{2+} ions in the desorption medium, by using the following expression.

$$\text{Desorption Ratio} = \frac{\text{amount of } Cu^{2+} \text{ ions desorbed to the elution medium}}{\text{amount of } Cu^{2+} \text{ ions adsorbed on the microbeads}} \times 100 \qquad (3)$$

RESULTS AND DISCUSSION

Characteristics of Procion Red MX-3B-Attached Microbeads

The hydrophilic poly(EGDMA-HEMA) microbeads are a crosslinked structure. They do not dissolve in aqueous media, but do swell, depending on the degree of crosslinking. 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 μm. It should be noted that these dye-attached microbeads are suitable for packed-bed or fluidized-bed column applications.

The dry poly(EGDMA-HEMA) 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 [9]. However, the opacity of the microbeads significantly decreases and the color of the microbeads become light blue, when the microbeads are swollen in water. After the Procion Red MX-3B attachment, the size of the swollen microbeads did not change, but the color became dark red, which is a clear indication of the incorporation of the Procion Red MX-3B molecules in the structure of the microbeads. Procion Red MX-3B was covalently coupled to the microbeads via the nucleophilic substitution reaction between the chloride atoms of its triazine ring and the hydroxyl groups of the HEMA, under alkaline conditions.

Elemental analysis of the plain and Procion Red MX-3B-attached poly(EGDMA-HEMA) microbeads were performed, and the attachment of the Procion Red MX-3B was found as 8.95 μmol/g. Procion Red MX-3B leakage was also investigated. There was no Procion Red MX-3B leakage in any of the Cu^{2+} adsorption and desorption media. This shows that the washing procedure was sufficient for removal of physically adsorbed Procion Red MX-3B molecules from the polymeric matrix.
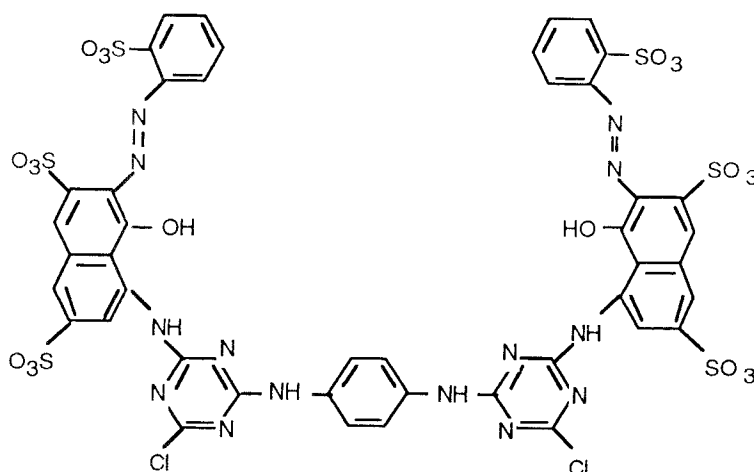
Figure 1. Chemical Structure of Procion Red MX-3B.

To explain the nature of the interaction between the Procion Red MX-3B and the poly(EGDMA-HEMA) microbeads, FTIR spectra of plain poly(EGDMA-HEMA), Procion Red MX-3B, and Procion Red MX-3B-attached poly(EGDMA-HEMA) were obtained. As shown in Figure 2, FTIR spectra of both poly(EGDMA-HEMA) and poly(EGDMA-HEMA)-Procion Red MX-3B 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 3400 cm^{-1}, 1670 cm^{-1} and 640 cm^{-1} and characteristic N-H stretching, N-H bending (scissoring) and S-O stretching, respectively observed also in Procion Red MX-3B (Figure 1). Procion Red MX-3B-attached poly(EGDMA-HEMA) spectrum has a sharp shoulder absorption band at about 3400 cm^{-1} and interpreted as the N-H absorption. These absorption bands at 1070 cm^{-1}, 1170 cm^{-1} and 1280 cm^{-1} represent symmetric stretching of S=O, asymmetric stretching of S=O and aromatic C-N vibration, respectively, are due to Procion Red MX-3B bonded to poly(EGDMA-HEMA). The band at 1670 cm^{-1} shows C=N stretching band in the structure of triazine ring. These bands, however, do not appear, because plain poly(EGDMA-HEMA) also has some absorption bands in the same region. Thus, absorption bands of plain poly(EGDMA-HEMA) overlap with those of the Procion Red MX-3B at around these wave-numbers. For dye attached-poly(EGDMA-HEMA) absorption band intensities in this region are higher than those of plain
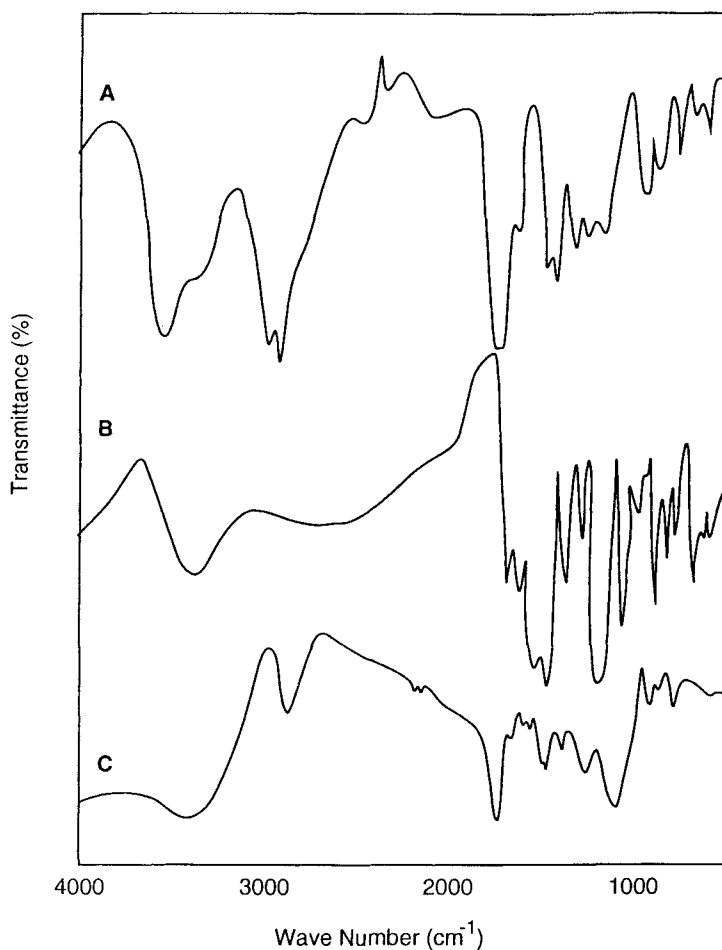
Figure 2. FTIR Spectra of (A) poly(EGDMA-HEMA); (B) Procion Red MX-3B;(C) Procion Red MX-3B-attached poly(EGDMA-HEMA) microbeads.

poly(EGDMA-HEMA), but the intensity increase is quite small because of the low concentration of Procion Red MX-3B on polymeric surface. On the other hand, hydrogen bonded alcohol O-H stretching band intensity of plain poly(EGDMA-HEMA) is higher than that of poly(EGDMA-HEMA)-Procion Red MX-3B micro-beads. The reason for the loss of the -OH groups is as a result of the nucleophilic substitution reaction between -OH groups of poly(EGDMA-HEMA) and -Cl groups of Procion Red MX-3B.
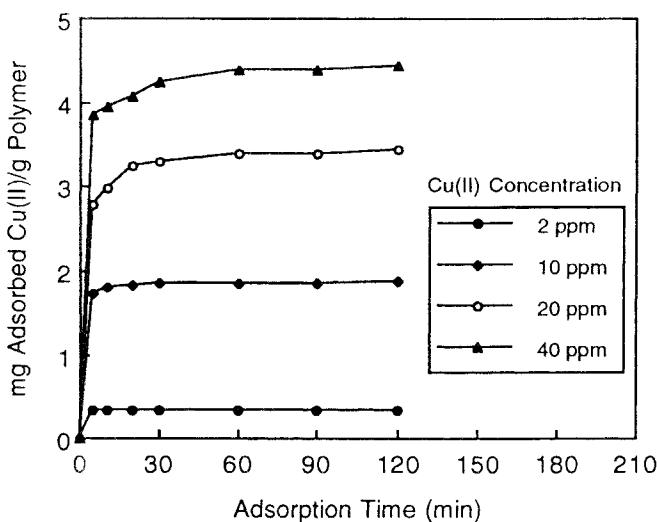
Figure 3. Adsorption rates of Cu^{2+} ions on the Procion Red MX-3B-attached poly(EGDMA-HEMA) microbeads.

Adsorption/Desorption of Copper(II) Ions

Adsorption Rate

Figure 3 shows the adsorption rates of Cu^{2+} ions onto the dye-attached microbeads from aqueous solutions containing different amounts of Cu^{2+} ions (in the range of 2-50 ppm) at constant pH of 7.0. Note that the ordinate values on this figure were calculated by using the expression given in Equation 2. As seen here, very high adsorption rates are observed at the beginning of adsorption process, and then plateau values (i.e., adsorption equilibrium) are completely reached in about 5-10 minutes. Adsorption of Cu^{2+} ions was rather fast, especially when the Cu^{2+} ion concentration was high. This is probably due to a high driving force for mass transfer, which is the Cu^{2+} ion concentration difference between the liquid (i.e., adsorption medium) and the solid (i.e., the microbeads) phases, in the case of high Cu^{2+} ion concentration.

Several experimental data on the adsorption kinetics of heavy metal ions by various sorbents have shown a wide range of adsorption rates. For example, recently, Reed and Matsumoto have considered 6 hours as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent [12]. Konishi *et al.* have investigated recovery of zinc, cadmium, and lanthanum by biopolymer gel particles of alginic acid. In their recent paper, they
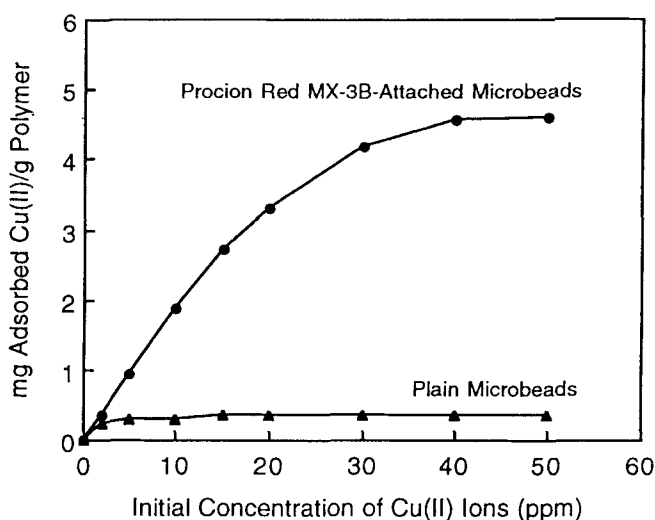
Figure 4. Adsorption capacity of Cu^{2+} ions on the Procion Red MX-3B-attached poly(EGDMA-HEMA) microbeads; medium pH: 7.0.

reported very high adsorption/desorption rates for lanthanum by alginic acid, in which equilibrium was achieved in about 60-90 minutes [13]. Note that in such an adsorption process, there are several parameters which determine the adsorption rate, such as stirring rate in the aqueous phase or flow-rate in columns system, sorbent structural properties (e.g., size, porosity, swelling degree, surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius, coordination complex number), initial concentration of metal ions, chelate-formation rate, and of course existence of other heavy metal ions which may compete with the ions of interest for the active adsorption sites. All individual experimental studies published in the literature have been performed at different conditions. Therefore, it can be concluded that it is almost impossible to compare the adsorption rates reported.

Adsorption Capacity

Figure 4 shows the effects of initial concentration of Cu^{2+} ions onto the adsorption capacity of the dye-attached microbeads. Note that this graph was obtained by using the plateau values (corresponding the equilibrium time of 120 minutes) given in Figure 3. The amount of Cu^{2+} ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased first with the initial concentration of Cu^{2+} ions then reached a plateau value at about an initial Cu^{2+} ions concentration of

40 ppm, which represents saturation of the active binding points (which are available for Cu^{2+} ions) on the microbeads. The maximum adsorption capacity of the Procion Red MX-3B-attached microbeads is 4.6 mg Cu^{2+}/g polymer.

Comparison with Related Literature

A wide variety of sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Shreedhara-Murthy and Ryan found 4.8-27 mg Cu(II)/g removal by cellulose-dithiocarbamate resins [14]. Roozemond *et al.* showed 0.3-31.9 mg Cu(II)/g with pyrazole-containing poly(styrene-divinyl-benzene) sorbents [15]. Liu *et al.* achieved 16.5 mg Cu(II)/g adsorption capacity with N-hydroxymethyl thioamide resin [16]. Hudson and Matejka investigated the length of pendants groups (i.e. ethylene diamine, triethylene tetramine and penta-ethylene hexamine) 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 [17]. They reported 15.2 mg/g adsorption capacity. Sag and Kutsal have used Zoogloea ramigera and Rhizopus arrhizus micro-organisms for heavy metal adsorption [18,19]. The maximum amounts of adsorption capacities achieved were 35 mg Cu(II) and 28.6 mg Cu(II) per gram dry weight of microorganisms for Zoogloea ramigera and Rhizopus arrhizus, respectively. Shambhu *et al.* immobilized polyamines (i.e., ethylene diamine, diethylene triamine and triethylene tetramine) onto polystyrene and reached an adsorption value of 33 mg Cu(II)/g polymer [20]. Janus *et al.* used poly(vinyl amine) sorbent for copper adsorption and reported an adsorption capacity of 0.5 mg Cu(II)/g [21]. Khalfaoui *et al.* achieved an adsorption capacity of 0.04 mg Cu(II)/g on raw charcoal [22]. Denizli *et al.* used Alkali Blue 6B-immobilized poly(EGDMA-HEMA) sorbents, in which the maximum adsorption capacities were 2.9 mg Cu(II)/g [9]. Marzal *et al.* immobilized ethylene diamine and hexamethylene diamine by glow-discharge method and obtained 5.3 mg Cu(II)/g for EDA and 6.8 mg Cu(II)/g for HMDA-plasma treatment [23]. From the results obtained in this study, we may conclude that the new polymeric sorbent presented in this communication is promising for the adsorption from aqueous media.

Effect of pH

It is well-kown that heavy metal adsorption both on non-specific and specific sorbents is pH dependent [5-7]. 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 copper is governed by hydroxide or carbonate concentration. As discussed in detail by Boomhover [24] and Reed and
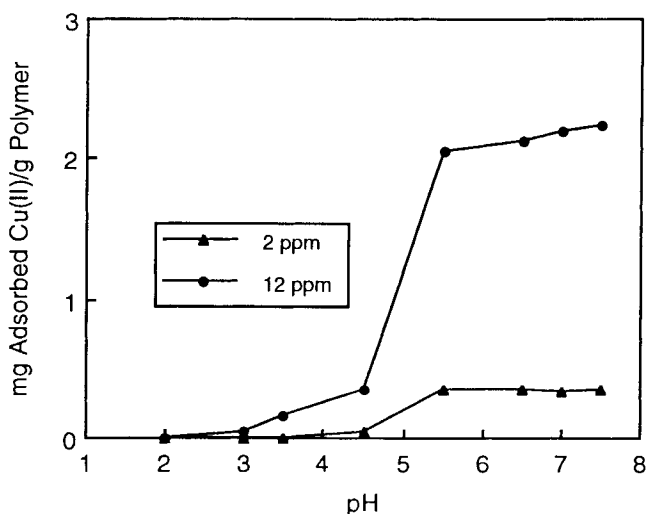
Figure 5. Effect of pH on adsorption of Cu^{2+} ions on the Procion Red MX-3B - attached poly(EGDMA-HEMA) microbeads.

Matsumoto [25], hydrolysis of copper becomes significant at approximately pH 8.0. The theoretical and experimental precipitation curves indicate that precipitation begins above this pH, which also depends on the concentration of copper in the medium. Therefore, in our study, in order to establish the effect of pH on the adsorption of Cu^{2+} ions onto the Procion Red MX-3B-attached microbeads, we repeated the batch equilibrium studies at different pH in the range of 2.0-7.5. In this group of experiments, the initial concentration of Cu^{2+} ions and the adsorption equilibrium time (i.e., time to reach the plateau, as seen in Figure 3) were 40 ppm and 120 minutes, respectively. Figure 5 shows both nonspecific adsorption (i.e., adsorption onto the plain poly(EGDMA-HEMA) microbeads) and the specific adsorption (i.e., adsorption by chelating with the Procion Red MX-3B molecules attached on the poly(EGDMA-HEMA) microbeads) of Cu^{2+} ions.

As seen in Figure 5, adsorption of Cu^{2+} ions increased with increasing pH and then reached almost a plateau value around pH 5.5. It should be noted that the non-specific adsorption of Cu^{2+} ions was low, about 0.36 mg Cu^{2+}/g polymer. There is neither ion-exchange nor chelate forming groups onto the plain polY(EGDMA-HEMA) microbeads. This non-specific adsorption of Cu^{2+} ions may be due to diffusion of Cu^{2+} ions into the pores of the swollen matrix of the microbeads. While the specific adsorption of Cu^{2+} ions, which was pH dependent,
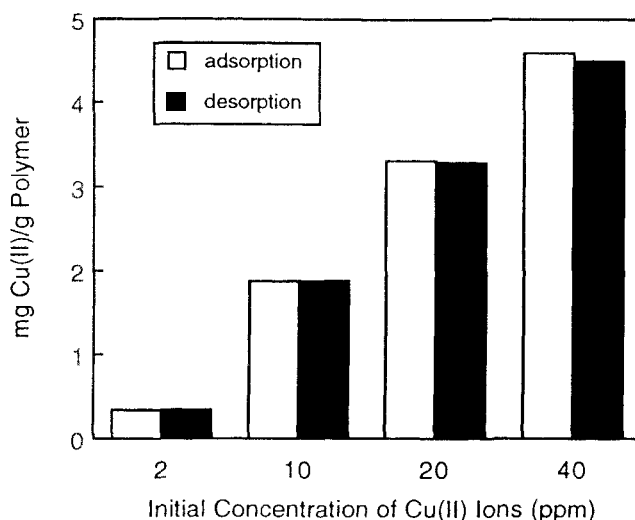
Figure 6. Adsorption-Desorption of Cu^{2+} ions. Adsorption medium pH : 7.0. Desorption medium : 0.1 M HNO_3, pH: 1.0

was much higher (up to 2.24 mg Cu^{2+}/g polymer) then non-specific adsorption. Cu^{2+} adsorption around pH 2.0-4.0 was very low, maybe due to protonation of the functional groups on the Procion Red MX-3B structure. High adsorption at basic pH values implies that Cu^{2+} ions interact with Procion Red MX-3B not only through the nitrogen and oxygen atoms (see Figure 1) by chelating, but also through -SO_3H groups by cation-exchange, which are unprotonated at high pH.

Desorption

Desorption of the adsorbed Cu^{2+} ions from the Procion Red MX-3B-attached microbeads was also studied in a batch experimental set-up. The dye-attached microbeads loaded (at pH: 7.0) with different amounts of Cu^{2+} ions were placed within the desorption medium containing 1 M HNO_3 and the amount of Cu^{2+} ions desorbed in 15 minutes was measured. The desorption ratio was then calculated by using the expression given in Equation 3. Figure 6 shows the results of desorption studies. As seen in this table, desorption ratio was very high (up to 99%) with the desorption system and conditions used. It is obvious that chelate forming interactions between the attached Procion Red MX-3B molecules and Cu^{2+} ions are weaker with decreasing pH.

CONCLUSION

Poly(EGDMA-HEMA) microbeads containing 8.95 μmol Procion Red MX-3B/g polymer were used for adsorption/desorption of Cu^{2+} ions from aqueous solution under different experimental conditions. Very high adsorption rates are observed at the beginning of adsorption process, and then plateau values (i.e., adsorption equilibrium) are gradually reached in about 5-10 minutes. Maximum Cu^{2+} adsorption capacity of Procion Red MX3B microbeads was 4.6 mg/g. Adsorption amounts of Cu^{2+} ions increased with increasing pH and reached almost a plateau value around pH 5.5. Desorption was performed by using 0.1 M HNO_3 and very high desorption ratios were achieved up to 99%. From the results presented in this paper, it can be concluded that the Procion Red MX-3B-attached microbeads may effectively (means with high adsorption rates and capacities) be used for removal of Cu^{2+} ions from aqueous solutions. Our studies related to adsorption/desorption of other heavy metal ions (e.g., Cd^{2+}, Pb^{2+}, Hg^{2+}, Zn^{2+}) are still under investigation.

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