

Adsorption of Ni²⁺ from Aqueous Solutions by Novel Polyethyleneimine-Attached Poly(*p*-chloromethylstyrene) Beads

RIDVAN SAY,¹ ALI TUNCEL,² ADIL DENIZLI³

¹ Department of Chemistry, Anadolu University, Eskişehir, Turkey

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

³ Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

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ABSTRACT: In this study Ni²⁺ adsorption properties of polyethyleneimine (PEI)-attached poly(*p*-chloromethylstyrene) (PCMS) beads were investigated. Spherical beads with an average size of 186 μm were obtained by the suspension polymerization of *p*-chloromethylstyrene conducted in an aqueous dispersion medium. Owing to the reasonably rough character of the bead surface, PCMS beads had a specific surface area of 14.1 m²/g. PEI chains could be covalently attached onto the PCMS beads with equilibrium binding capacities up to 208 mg PEI/g beads, via a direct chemical reaction between the amine and chloro-methyl groups. After PEI adsorption with 10% (w/w) initial PEI concentration, free amino content of PEI-attached PCMS beads was determined as 0.91 mEq/g. PEI-attached PCMS beads were utilized as adsorbents in the adsorption/desorption of Ni²⁺ ions from synthetic solutions. The adsorption process was fast; 90% of adsorption occurred within 90 min, and equilibrium was reached at around 2 h. Adsorption capacity was obtained to be 78.2 mg/g at a pH of about 6.0. The chelating beads can be easily regenerated by 0.1 M HNO₃ with higher effectiveness. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2467–2473, 2002

Key words: water purification; polyethyleneimine; heavy metal removal; Ni(II); adsorption

INTRODUCTION

The role of heavy metal ions in environmental issues has become increasingly more prominent in recent years as ecological awareness has achieved global proportions.¹ Nickel is one of the heavy metals present in raw wastewater streams from industries such as nonferrous metals min-

eral processing, paint formulation, porcelain enameling, and steam-electric power plants.^{2–4} A number of technologies have been used to remove Ni from wastewater streams, such as adsorption onto activated carbon,⁵ filtration of precipitate,⁶ and by crystallization in the form of nickel carbonate.⁷ Cost-effective alternative technologies or adsorbents for the treatment of metal-containing wastewaters are needed. Recently, chelating polymers have found widespread applications in the enrichment and removal of heavy metals from a variety of matrices.^{8–18} Several criteria are important in the design of chelating polymers with

Correspondence to: A. Denizli (denizli@hacettepe.edu.tr).

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substantial stability for the selective removal of heavy metal ions: specific and fast complexation of the metal ions as well as the reusability of the chelating polymeric ligands. A large number of chelating polymers incorporating a variety of ligands (e.g., imino-diacetate, amidoxim, phosphoric acid, amine, dithiocarbamate, oxime, reactive textile dyes) have been prepared, and their analytical properties investigated.^{14–20} Recently, PEI-attached polymer matrix has been reported in a series of recent publications.^{21–23} The idea of using PEI chains by these researchers stems from the fact that polyethyleneimine is very reactive with different chemical substances including metal ions. The higher flexibility and durability of these complexing ligand as well as significantly lower material and manufacturing costs are also very important.

In this study, a chelating bead system using, PEI-attached PCMS beads was prepared by suspension polymerization of CMS and EGDMA monomers in the presence of an initiator (azobisisobutyronitrile, AIBN). Adsorption/desorption of Ni²⁺ from aqueous media were studied. Here we present preparation of these novel PEI-attached chelating beads, and potential for their use in Ni²⁺ adsorption/desorption.

EXPERIMENTAL

Materials

The monomer, 4-chloromethylstyrene (CMS; Aldrich, Milwaukee, WI) and the crosslinker ethylenglycoldimethacrylate (EGDMA; Aldrich) were used without further purification. Cyclohexane (BDH, Poole, UK) was selected as the diluent. Azobisisobutyronitrile (AIBN; BDH) was crystallized from methanol and used as the initiator. Polyvinyl alcohol (PVA, M_r : 85,000–146,000, 87–89% hydrolyzed, Aldrich) was the stabilizer. Linear PEI sample (molecular structure: H₃C—CH₂—NH—[CH₂—CH₂—NH]_n—CH₂—CH₂—NH₂) with high molecular mass (M_r : 25,000 Da; Aldrich) were used as received. All other chemicals were of reagent grade, and were purchased from Merck AG (Darmstadt, Germany). All water used in the experiments was purified using a Barnstead (Dubuque, IA) ROpure LP[®] reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure[®] organic/colloid removal and ion exchange packed-bed system. The resulting

purified water (deionized water) has a specific conductivity of 18 megaohm/cm¹.

Preparation of PCMS Beads

A modified version of suspension polymerization method proposed by Nonaka et al.²⁴ was used for the preparation of spherical PCMS beads. A typical preparation procedure was exemplified below. Continuous medium was prepared by dissolving PVA (100 mg) in the distilled-deionized water (50 mL). For the preparation of dispersed phase, CMS (2.5 mL), EGDMA (0.75 mL), and cyclohexane (3.6 mL) were mixed, and AIBN (60 mg) was dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (300 rpm), in a sealed-cylindrical, Pyrex polymerization reactor. The reactor content was heated to polymerization temperature (i.e., 78°C) within 40 min, and the polymerization was conducted for 8 h with a 300 rpm stirring rate at 78°C. Final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 4°C.

Characterization of PCMS Beads

Surface morphology of PCMS beads were observed in a scanning electron microscope (JEOL, JEM 1200 EX, Tokyo, Japan). PCMS beads were dried at room temperature and coated with a thin layer of gold (about 100 Å) in vacuum and photographed in the electron microscope with 800× magnification. The specific surface areas of the PCMS and the PEI-attached PCMS beads were determined in BET apparatus. The average size and size distribution of the PCMS beads were determined by screen analysis performed by using Tyler Standard Sieves.

PEI Attachment onto PCMS Beads

The following procedure was applied for the covalent attachment of PEI onto the PCMS beads. Dry PCMS beads (approximately 1.0 g) were put into an aqueous solution (30 mL) containing 10% (w/w) PEI (pH 10.6). The medium was shaken at 120 cpm for 6 h at 55°C. The preliminary experiments showed that PEI adsorption equilibrium was attained within this period. To find the equilibrium PEI adsorption capacity of PCMS beads, final PEI concentration (i.e., after completion of adsorption period) was determined by the poten-

tiometric titration of a sample (5 mL) withdrawn from adsorption medium with 0.1 M standard HCl solution. Equilibrium PEI adsorption capacity (Q , mg PEI/g beads) was calculated based on eq. (1), where, C_o and C_f (mg/mL) are the initial and final PEI concentrations in the adsorption medium, respectively. V (mL) and M (g) are the volume of the adsorption medium and the amount of PCMS beads, respectively.

$$Q = (C_o - C_f) \cdot V/M \quad (1)$$

PEI-attached PCMS beads were extensively washed with distilled water to remove any physical adsorption PEI from the beads. To determine the leakage of PEI, washing solutions were collected and analyzed by the same procedure. Then the amount of PEI released per gram of particle was determined. This value was subtracted from the equilibrium adsorption capacity (Q) to calculate the covalently bound PEI onto the bead surface. Approximately 10–25% (w/w) of the PEI present on the bead surface was released by the washing. The reported PEI binding capacities were calculated based on the covalently attached amount of PEI onto per gram of PCMS beads.

Free amino contents of PEI-attached PCMS beads were determined by potentiometric titration. For this purpose, PEI-attached PCMS beads (approximately 1.0 g) were treated with 0.1 M HCl solution (100 mL) for 6 h at a 120 cpm shaking rate. After consumption of HCl by the free amine groups of beads, the final HCl concentration in the aqueous medium was determined by a potentiometric titration with a 48 mM NaOH solution.

Ni²⁺ Adsorption/Desorption Studies

Adsorption of Ni²⁺ ions from aqueous solutions was investigated in batch experiments. Effects of the initial Ni²⁺ concentration and pH of the medium on the adsorption rate and capacity were studied. Aliquots (20 mL) of aqueous solutions containing different amounts of Ni²⁺ ions (in the range of 5–500 mg/L) were treated with the PEI-attached PCMS beads at different pH (in the range of 2.0–7.0) (adjusted with HCl–NaOH) at room temperature, in the flasks stirred magnetically at 100 rpm. Nitrate salt was used as the source of Ni²⁺ ions. The concentration of the Ni²⁺ ions in the aqueous phase, after the desired treatment periods was measured by using a graphite furnace atomic absorption spectrophotometer

(AAS 5EA, Carl Zeiss Technology, Zeiss Analytical Systems, Germany). The instrument response was periodically checked with known Ni²⁺ solution standards. The experiments were performed in replicates of three, and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples to determine the margin of error. The amount of adsorption per unit mass of the beads was evaluated by using the concentration difference.

Desorption of Ni²⁺ ions was studied in 0.1 M HNO₃ solution. The PEI-attached PCMS loaded with Ni²⁺ ions were placed in this desorption medium and stirred (at a stirring rate of 100 rpm) for 3 h at room temperature. The final concentration of Ni²⁺ ions in the aqueous phase was determined by using a graphite furnace atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of Ni²⁺ ions adsorbed on the beads and the final concentration of Ni²⁺ ions in the desorption medium, by using the following expression:

Desorption ratio

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

To evaluate the reusability of the PEI-attached PCMS beads, adsorption–desorption cycles were repeated 10 times by using the same affinity beads.

RESULTS AND DISCUSSION

Characterization of PCMS Beads

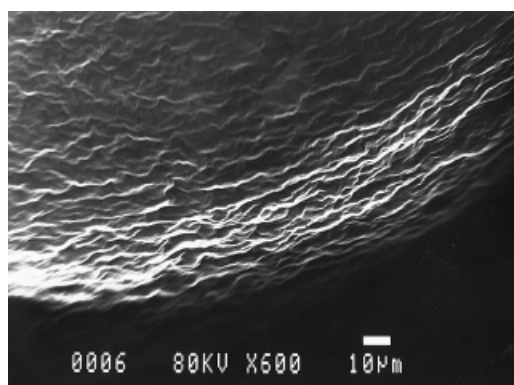
The suspension polymerization procedure provided crosslinked PCMS beads in the spherical form. Surface morphology of PCMS beads were exemplified by the electron micrographs in Figure 1. As seen in Figure 1(A), PCMS beads had a reasonably rough surface. However, the surface of the PCMS beads contained no macropores. A typical electron micrograph of PEI-attached PCMS beads prepared with the initial PEI concentration of 10% is given in Figure 1(B). It should be noted that surface morphology of PEI-attached PCMS

beads was different than that of plain PCMS beads. The roughness of bead surface observed in Figure 1(A) disappeared with the attachment of PEI. The specific surface area of the unmodified PCMS beads was found to be $14.1 \text{ m}^2/\text{g}$. The specific surface area of the PEI-attached-PCMS beads was also measured, and was obtained as $13.5 \text{ m}^2/\text{g}$. Free amino ($-\text{NH}_2$) content of PEI-attached PCMS beads was also determined as 0.91 mEq/g .

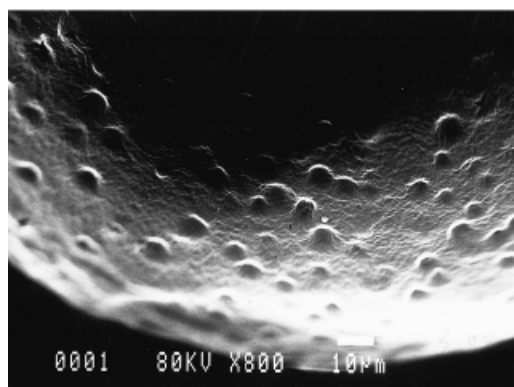
Ni^{2+} Adsorption Studies

Equilibrium Adsorption Time

Figure 2 shows the adsorption rate of Ni^{2+} on PEI-attached PCMS beads. The adsorption of Ni^{2+} ions on the PCMS beads was low, about 0.64 mg/g . There are no chelating functional groups on the plain PCMS beads; therefore, this adsorption



(A)



(B)

Figure 1 The electron micrographs showing (A) surface morphology of PCMS beads (magnification: $560\times$) and (B) PEI-attached PCMS beads prepared with the initial of 10% (magnification $560\times$).

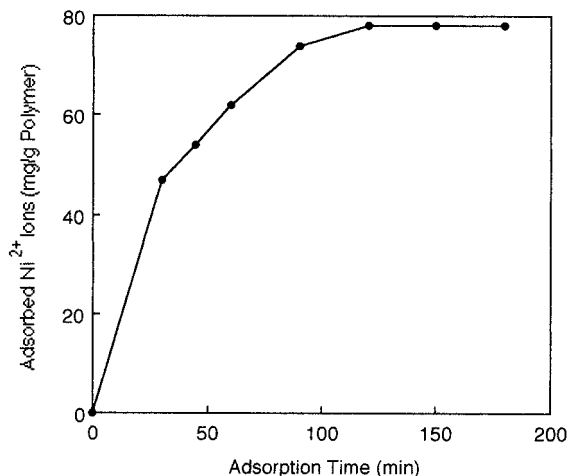


Figure 2 Adsorption rates of Ni^{2+} ions on the PEI-attached PCMS beads; initial concentration: 500 mg/L ; temperature: 20°C and $\text{pH: } 7.0$.

may be due to diffusion of Ni^{2+} ions into the swollen matrix and weak interactions between Ni^{2+} ions and carbonyl groups on the surface of the PCMS beads. But high adsorption capacity (78.2 mg/g) was achieved with PEI-attached PCMS beads due to the incorporation of PEI chains into the polymer structure. Short adsorption equilibrium time is observed with the PEI-attached PCMS beads at the beginning of adsorption, plateau value (showing adsorption equilibrium) is gradually reached within 150 min. This fast adsorption equilibrium time is probably due to high complexation rate (i.e., high affinity) between Ni^{2+} ions and PEI chains in the bead structure.

Experimental data on the adsorption kinetics of heavy metal ions by various adsorbent systems in membrane and bead form have shown a wide range of adsorption rates. For example, Reed and Matsumoto²⁵ have considered 6 h as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent. Marchese et al.²⁶ have investigated separation of cobalt, nickel, and copper ions with alanine liquid membranes, and they reported that equilibrium was achieved in about 4–5 h. Shreedhara-Murthy and Ryan²⁷ have investigated mercury, copper, cadmium, lead, and uranium adsorption on cellulose-dithio-carbamate resins and reported that the adsorption rates were very slow. Egawa²⁸ has studied uranium adsorption on polyacrylo-nitrile fibers containing amidoxime groups and reported a 7-h equilibrium adsorption time. Teramoto et al.²⁹ reported that a spiral type sup-

ported liquid membrane reached steady state at about 4 h. Roozmond et al.³⁰ studied copper and cadmium uptake by 3,5-dimethyl-1-hydroxymethyl pyrazole attached *p*-amino-methyl substituted poly(styrene-*co*-divinylbenzene) chelating polymer. They showed that adsorption was rather slow, and took 2 days for the resin to reach equilibrium. Ebraheem and Hamdi³¹ studied the adsorption of various divalent ions including Ni(II), Cu(II), Zn(II), and Cd(II) on phenol formaldehyde polymer containing poly(salicylaldoxime 3,5-diylmethylene), and reported a 10-h equilibrium adsorption time. Latha et al.³² studied ethylenediamine-functionalized polyacrylamide resin for extraction of several metal ions such as Fe(III), Fe(II), Cu(II), and Ni(II), and they reported that the complexation reaction proceeded very slowly (equilibrium time 5 h). Several criteria are important in the design of chelating polymers with substantial stability for the selective adsorption of metal ions: specific and fast binding of the metal ions as well as the recyclability of the chelating polymeric adsorbents. All these experimental studies reported here have been carried out at different conditions. Therefore, it can be concluded that it is too difficult to compare the adsorption rates reported. However, the adsorption rates obtained with the affinity beads produced by us seem to be very satisfactory.

Adsorption Capacities

Effects of Initial Concentration of Ni²⁺ Ions

Figure 3 shows the adsorption isotherms of Ni²⁺ ions onto the PCMS and PEI-attached PCMS beads. The amount of Ni²⁺ ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased first with the initial concentration of Ni²⁺ ions then reached a plateau value at about an initial Ni²⁺ ions concentration of 300 mg/L, which represents saturation of the active binding imine sites (which are available for chelation for Ni²⁺ ions) on the PEI-attached PCMS beads. The maximum adsorption capacity of the PEI-attached PCMS beads is 78.2 mg Ni²⁺/g.

Natural and synthetic adsorbents used in heavy metal removal from aqueous solutions and real wastewaters are in particulate form in most of the cases. Yu and Kaewsarn² used a pretreated biomass of macroalga *Durvillaea potatorum* for Ni²⁺ adsorption and they obtained 66.3 mg/g. George et al.¹¹ investigated metal ion complexation behavior of glycine functions supported on divinylbenzene and *N,N'*-methylenebisacrylam-

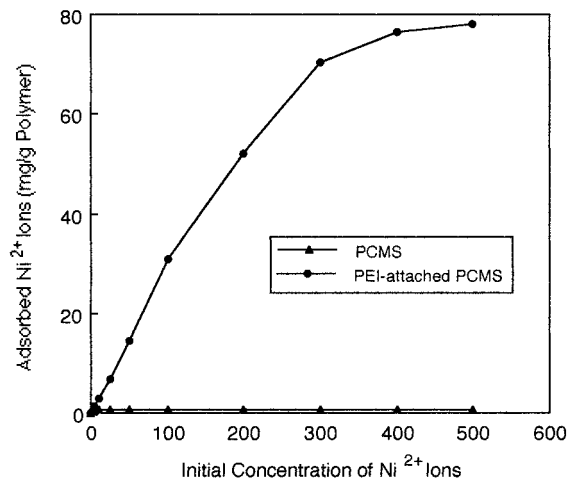


Figure 3 Adsorption capacity of Ni²⁺ ions on the PCMS and PEI-attached PCMS beads; pH: 7.0. Temperature: 20°C.

ide-crosslinked polyamide, and they reported around 2.5 mEq Ni²⁺/g polymer. Navarro et al.²¹ achieved very high adsorption capacity (188–329 mg Hg²⁺/g) using porous cellulose carrier modified with polyethyleneimine. Delacour et al.²² prepared a series of polyethyleneimine coated silica gels for removal of Pb²⁺ and Hg²⁺, and they obtained high heavy metal adsorption capacities around 300 mg/g. Bahrami et al.²³ used polyethyleneimine containing sol gels for the removal of Cd²⁺ ions, and they reported approximately 30 mg Cd²⁺/g polymer. Holan and Volesky³³ reported the use of marine alga, *Sargassum fluitans*, for nickel biosorption, and they obtained a maximum uptake of 135 mg/g for a relatively high equilibrium concentration of about 1900 mg/L. Studies on continuous nickel removal using columns of immobilized, nonfilamentous fungus, *Saccharomyces cerevisiae*, are also found in the literature with a saturation uptake of about 3 mg/g.³⁴ Rivas et al.³⁵ investigated metal ion binding properties of poly(*n*-vinylimidazole) hydrogels and they found 2.75 mEq Ni²⁺/g polymer. Becker et al.³⁶ reported 57 mg Ni²⁺/g adsorption capacity by chitosan. The maximum amounts of Ni²⁺ adsorption capacity achieved in this study was 78.2 mg/g. Comparing these data it seems that the adsorption capacities achieved with the novel PEI-attached beads are satisfactory.

Effects of pH

Heavy metal adsorption both on nonspecific and specific adsorbents is pH dependent. In the ab-

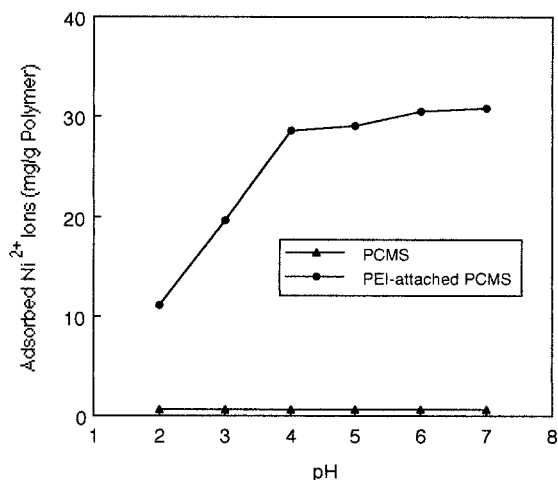


Figure 4 Effect of pH on adsorption of Ni^{2+} ions on the PCMS and PEI-attached PCMS beads: initial concentration of metal ions: 100 mg/L; temperature: 20°C.

sence 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 Ni^{2+} is governed by hydroxide or carbonate concentration. Hydrolysis of Ni^{2+} becomes significant at approximately pH 8.5. The theoretical and experimental precipitation curves indicate that precipitation begins above this pH, which also depends on the concentration of Ni^{2+} in the medium. Therefore, in our study, to establish the effect of pH on the adsorption of Ni^{2+} ions onto the plain PCMS and PEI-attached PCMS beads, 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 Ni^{2+} ions and the adsorption equilibrium time were 200 mg/L and 150 min, respectively. Figure 4 shows the specific adsorption (i.e., adsorption by chelating with the PEI chains incorporated in the PCMS beads) of Ni^{2+} ions.

As seen in Figure 4, adsorption of Ni^{2+} ions increased with increasing pH and then reached almost a plateau value around pH 5.0. At strongly acidic pH, adsorption is very low. This can be explained by the fact that, at this pH, most of amine functions are protonated. Then cationic repulsion can occur between nickel ionic species (such as Ni^{2+} and NiNO_3^+) and protonated PEI units. In mildly acidic pH 4–6 and pH 7.0, PEI-attached PCMS beads are effective for removal of Ni(II) ions from aqueous solutions.

It should be noted that the nonspecific adsorption of Ni^{2+} ions was low, about 0.64 mg Ni^{2+} /g. There is neither ion exchange nor chelate forming

groups in the plain PCMS beads. This nonspecific adsorption of Ni^{2+} ions may be due to diffusion of Ni^{2+} ions into the pores of the swollen matrix of the beads. The specific adsorption of Ni^{2+} ions, which was pH dependent, was much higher (up to 30.9 mg Ni^{2+} /g) than nonspecific adsorption. Ni^{2+} adsorption around pH 2.0–4.0 was very low, maybe due to protonation of the functional groups on the PEI structure. High adsorption at basic pH values implies that Ni^{2+} ions interact with PEI.

Desorption and Repeated Use

Desorption of the adsorbed Ni^{2+} ions from the PEI-attached PCMS beads was also studied in a batch experimental setup. Various factors are probably involved in determining rates of Ni^{2+} desorption, such as the extent of hydration of the ions and polymer microstructure. However, an important factor appears to be binding strength. In this study, the desorption time was found to be 2 h. The desorption ratio was then calculated by using the expression given in eq. (2). Desorption ratios are very high (up to 99%). To obtain the reusability of the PEI-attached PCMS beads, adsorption–desorption cycles were repeated 10 times by using the same beads. These PEI-attached affinity beads can be used repeatedly without significantly losing their adsorption capacities.

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