

# Adsorption of Heavy-Metal Ions on Poly(ethylene imine)-Immobilized Poly(methyl methacrylate) Microspheres

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**ABSTRACT:** Poly(methyl methacrylate) (PMMA) microspheres carrying poly(ethylene imine) (PEI) were prepared for the removal of heavy-metal ions (copper, cadmium, and lead) from aqueous solutions with different amounts of these ions (50–600 mg/L) and different pH values (3.0–7.0). Ester groups in the PMMA structures were converted to imine groups in a reaction with PEI as a metal-chelating ligand in the presence of NaH. The adsorption of heavy-metal ions on the unmodified PMMA microspheres was very low [3.6  $\mu\text{mol/g}$  for Cu(II), 4.6  $\mu\text{mol/g}$  for Cd(II), and 4.2  $\mu\text{mol/g}$  for Pb(II)]. PEI immobilization significantly increased the heavy-metal adsorption [0.224 mmol/g for Cu(II), 0.276 mmol/g for Cd(II), and 0.126 mmol/g for Pb(II)]. The affinity order of adsorption (in moles) was Cd(II) > Cu(II) > Pb(II). The adsorption of heavy-metal ions increased with increasing pH and reached a plateau value around pH 5.5. Their adsorption behavior was approximately described with the Langmuir equation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 197–205, 2001

**Key words:** poly(methyl methacrylate); poly(ethylene imine); heavy-metal removal; adsorption

## INTRODUCTION

The effective removal of toxic metals still remains a major topic of present research. Increased awareness of the toxicity of metals has prompted the implementation of strict regulations for its disposal, causing traditional treatment processes such as chemical precipitation to undergo changes. Modern metal-removal technologies such as ion exchange, reverse osmosis, and membrane systems are now becoming components in integrated systems that produce effluents of better quality while allowing the recovery and reuse of metals.<sup>1</sup>

The immobilized chelation process for the removal of soluble metals has become an important

option in the integrated approach to aqueous waste treatment.<sup>2</sup> This process incorporates the principle of metal coordination into traditional ion-exchange technology, thus affecting major changes in the application of adsorbents. In the past, many types of metal-chelating adsorbents have been synthesized.<sup>3</sup> Processes have been developed with either polymerization or simple functionalization principles. The former involves the polymerization of monomers containing the desired ligands. Although techniques for enhancing metal selectivity are easily developed with this method, difficulties in achieving regularly shaped polymers with sufficient porosity still remain the major drawback. In the other approach, the modification of preshaped polymers via the principle of polystep functionalization is considered. Ease in performing functionalization reactions and confidence that the properties of the

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product will be closely related to the starting materials make this a favorite process for much research.

Poly(ethylene imine) (PEI) is a cationic polymer used for a wide variety of applications. These include electrochemical biosensors,<sup>4</sup> cell flocculating agents,<sup>5</sup> permeabilization of bacterial cell walls,<sup>6</sup> retention of nicotinamide adenine dinucleotide (NADH) in membrane reactors,<sup>7</sup> adsorption of biomass,<sup>8</sup> and microencapsulation of silicone oils.<sup>9</sup> PEI acts as a chelating agent for many metals and has also been used for the removal of cadmium. PEI was used for metal binding, and this was followed by an ultrafiltration operation to retain the PEI polymer.<sup>10</sup> The immobilization of PEI in a suitable matrix can provide an attractive alternative to membrane processes. Chanda and Rempel<sup>11</sup> applied PEI-containing granular sorbents for the selective removal of Cr(III) in a mixture of Cr(III), Cu(II), Ni(II), and Fe(III). This sorbent was found to be superior to the commercial resin Chelex-100. Navarro et al.<sup>12</sup> prepared cellulose-based sorbents containing crosslinked PEI. These sorbents were used for the selective removal of mercury from aqueous solutions.

The aim of this work was to evaluate the chelating properties toward some metal ions, such as Pb(II), Cd(II), and Cu(II), of PEI-immobilized poly(methyl methacrylate) (PMMA) microspheres. PMMA as an adsorbent offers several advantages in terms of economy (i.e., low cost), ease of polymerization/derivatization, and high stability.

## EXPERIMENTAL

### Preparation of the PMMA Microspheres

#### Materials

Methyl methacrylate (MMA; Röhm, Germany) was purified by extraction with a 10% (w/v) NaOH solution and distilled water to remove the inhibitor prior to polymerization. Tricalcium phosphate (TCP; Yarpet, Turkey) was selected as the disperse phase component (i.e., stabilizer) in the suspension polymerization. The polymerizations were initiated with benzoyl peroxide (BPO; 97% active compound; BDH Chemicals Ltd., United Kingdom). All polymerizations were performed with distilled–deionized water. PEI (relative molecular mass = 25 000) was supplied by Sigma Chemical Co. (St. Louis, MO).

#### Polymerization Method

PMMA microspheres were produced by a suspension polymerization method described else-

where.<sup>13</sup> A typical procedure was as follows. The stabilizer TCP (6.0 g) was dissolved in 480 mL of water for the preparation of the continuous phase. The monomer phase was prepared by the dissolution of the initiator BPO (6.0 g) in MMA (240 mL). The continuous phase was transferred within a glass-sealed polymerization reactor (1000 mL) placed in a water bath equipped with a temperature control system. The polymerization reactor was heated to 60°C in about 30 min by the stirring of the medium at 400 rpm. The monomer phase was charged to the reactor, and the polymerization was conducted at 80°C for 2 h and 90°C for 1 h. The polymerization was carried out under a nitrogen atmosphere. After the completion of the polymerization, the reactor content was cooled down to room temperature. An extensive washing procedure was applied after polymerization to remove any possible unreacted monomer and other polymerization ingredients.

#### PEI Immobilization

The following procedure was applied for the covalent attachment of PEI onto the PMMA microspheres. After the removal of water in the PEI solution with benzene, 10 g of PEI was dissolved in tetrahydrofuran. NaH (3.0 g) was added to this solution. Dry microspheres (10 g) were weighed and transferred into this solution mixture. The reaction medium was boiled in a Dean–Stark apparatus at reflux for 24 h. At the end of this reaction period, the PEI-immobilized microspheres were removed by filtration and washed with methanol several times and then dried *in vacuo* at room temperature for 24 h. Preliminary experiments showed that PEI attachment to the PMMA surface reached equilibrium within the selected time period under the studied conditions. To find the equilibrium PEI-immobilization capacity of the PMMA microspheres, the final PEI concentration (i.e., after completion of the adsorption period) was determined by potentiometric titration of a sample (5 mL) withdrawn from the adsorption medium with a 0.10M standard HCl solution. The equilibrium PEI-immobilization capacity ( $Q$ ; mg of PEI/g of microspheres) was calculated with the following expression:

$$Q = (C_i - C_f)V/m \quad (1)$$

where  $C_i$  and  $C_f$  (mg/mL) are the initial and final PEI concentrations in the adsorption medium, respectively, and  $V$  (mL) and  $m$  (g) are the volume of the reaction medium and the amount of PMMA

microspheres, respectively. PEI-immobilized PMMA microspheres were extensively washed with distilled water to remove any physically adsorbed PEI from the microspheres. To determine the leakage of covalently immobilized PEI, the washing solutions were collected and analyzed with the same procedure. Then, the amount of PEI released per gram of microspheres during the washing was determined. This value was subtracted from the equilibrium adsorption capacity ( $Q$ ) to calculate PEI covalently bound onto the microsphere surface. Approximately 10% (w/w) of the PEI present on the microsphere surface after the immobilization process was released by the washing. The reported PEI-immobilization capacity was based on the covalently attached amount of PEI per gram of PMMA microspheres.

The free amine content of the PEI-immobilized PMMA microspheres was determined by potentiometric titration. For this purpose, PEI-immobilized PMMA microspheres (1 g) were treated with a 0.10M standard HCl solution (100 mL) for 6 h with a 120-cpm shaking rate. After the consumption of HCl by free amine groups of PMMA microspheres, the final HCl concentration in the aqueous medium was determined by potentiometric titration with a 0.1M NaOH solution.

### Microsphere Characterization

#### Scanning Electron Microscopy (SEM)

To observe the surface topography of the PMMA microspheres, we took scanning electron micrographs of the gold-coated samples with a scanning electron microscope (Raster Elektronen Mikroskopie, Leitz-AMR-1000, Germany).

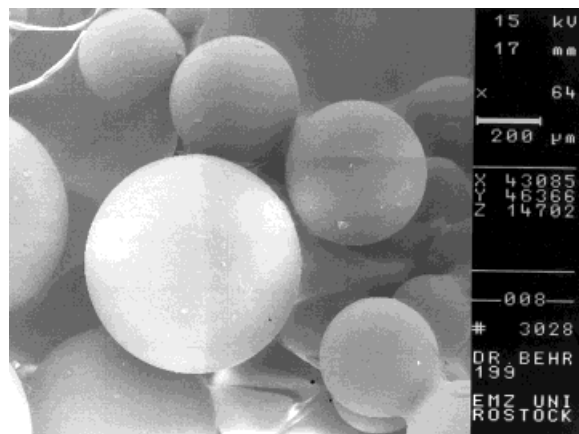
#### Elemental Analysis

The amount of PEI immobilized to the PMMA microspheres was also determined with an elemental analysis device (Leco CHNS-932, United States) for comparison with titration results.

## RESULTS AND DISCUSSION

### Properties of the PMMA Microbeads

The presence of PEI in the PMMA structure was confirmed by potentiometric titration and elemental analysis. The maximum amount of PEI immobilized onto the PMMA microsphere surface was 165.2 mg of PEI/g of polymer (4.0 mequiv of PEI/g of polymer).



**Figure 1** SEM micrograph of PMMA microspheres.

Figure 1 shows an SEM micrograph of PMMA microspheres. As clearly shown, the PMMA microspheres have a spherical form and a rough surface. These surface properties of the microspheres favor better adsorption of the heavy-metal ions because of an increase in surface area. Moreover, PMMA microspheres had a uniform and spherical form with smooth surface characteristics after PEI immobilization.

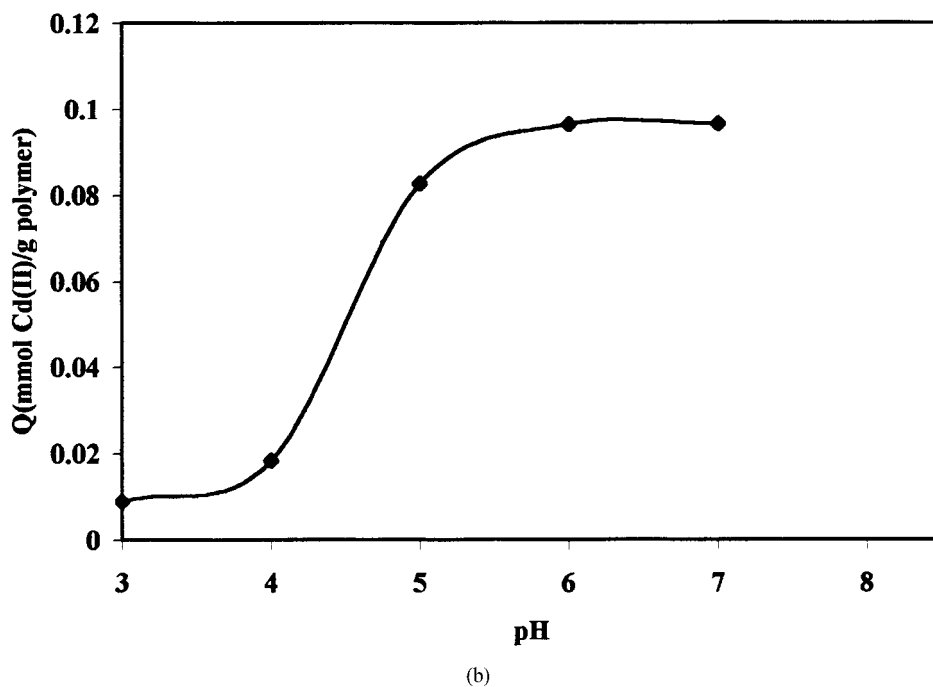
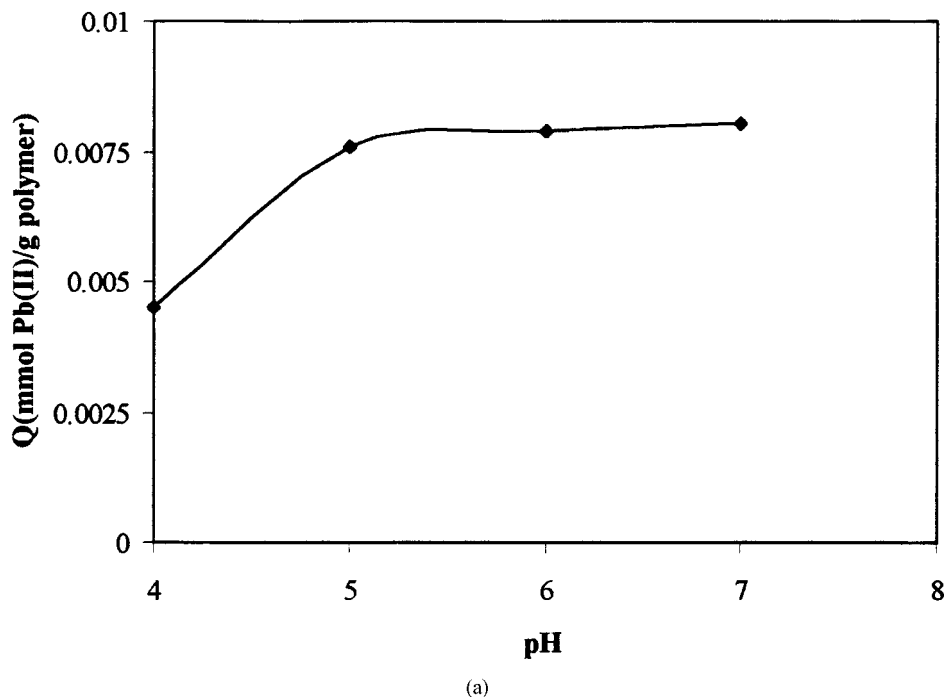
### Effect of pH on the Adsorption Capacity

Because of the protonation and deprotonation of the acidic and basic groups of the metal complexation ligand, its adsorption behavior for metal ions is influenced by the pH value, which affects the surface structure of sorbents, the formation of metal hydroxides, and the interaction between sorbents and metal ions. Therefore, the pH dependence of adsorption for metal ions was investigated in detail. Figure 2 shows the pH profile data for metal-ion adsorption. This figure shows that the complexation behavior of metal ions is more sensitive to pH changes, especially at lower pH regions. The inhibition of metal chelation with a decrease in pH has been observed by several authors and in different sorbents.<sup>14</sup> Therefore, it has been proposed that protons and metal ions compete for the same binding sites. It was observed that the adsorption capacities increased with increasing pH, reaching plateau values around pH 5.5 for Cu(II) and Pb(II) and pH 6.0 for Cd(II).

### Adsorption Studies

#### Adsorption Rate

Figure 3 shows equilibrium adsorption times of the metal ions interested on the PEI-immobilized



**Figure 2** Effect of pH on the adsorption of metal ions on the PEI-immobilized PMMA microspheres: (A) Pb(II) ions, (B) Cd(II) ions, and (C) Cu(II) ions. The initial concentrations were 35 mg/L for Pb(II) ions, 30 mg/L for Cd(II) ions, and 10 mg/L for Cu(II) ions; the temperature was 20°C.

PMMA microspheres from aqueous solutions at a constant pH of 5.5. Note that these batch experiments were performed with single solutions of the metal ions with initial concentrations between 20 and 60 mg/L. As can be seen from the figure, the

adsorption capacity of metal ions increases with time during the first 20 min for Pb(II) and Cd(II) and during the first 5 min for Cu(II) and then levels off toward the equilibrium adsorption capacity. The adsorption rate of Cu(II) ions is higher

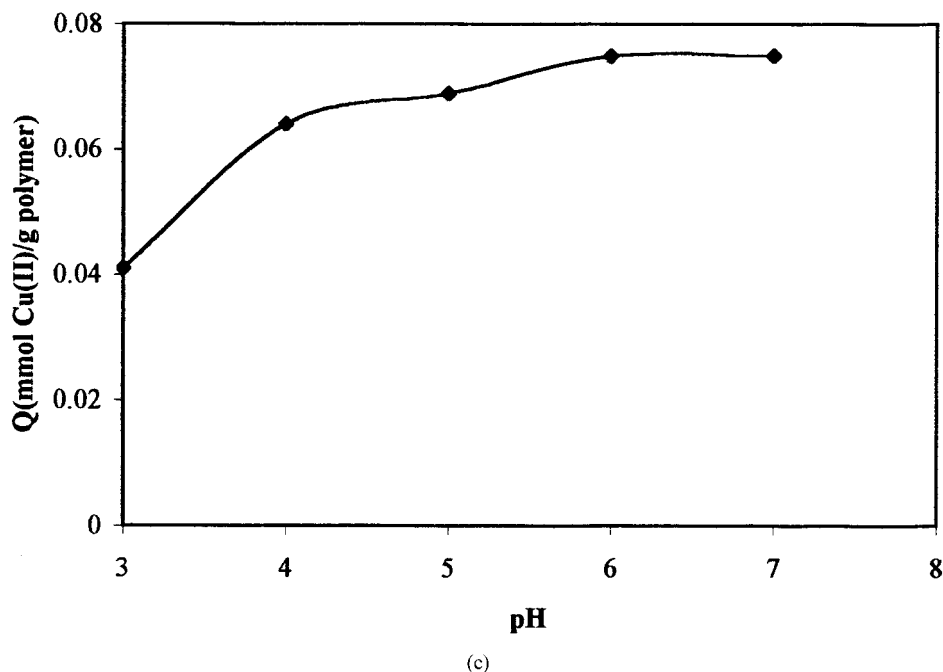


Figure 2 (Continued from the previous page)

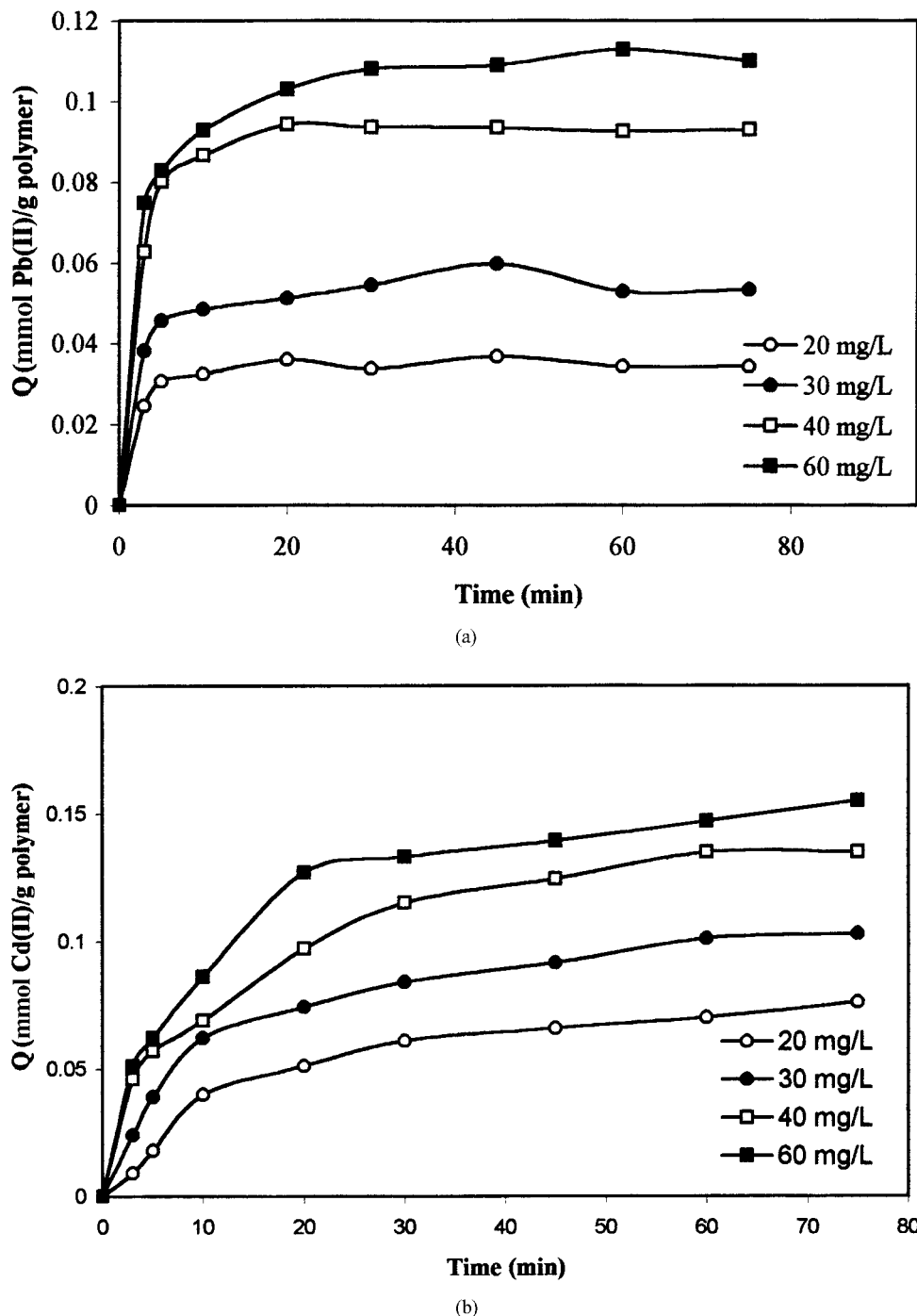
than that of the other metal ions. This is due to the high complex formation rate between Cu(II) ions and PEI on the surface of PMMA microspheres.

Data on the adsorption kinetics of heavy-metal ions by various polymer sorbents have shown a wide range of adsorption rates. Dev and Rao<sup>15</sup> studied the sorption of different metal ions, including Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Zn(II), and Mn(II), by a poly(styrene-divinylbenzene)-based macroreticular resin functionalized with bis(*N,N'*-salicylidene) 1,3-propanediamine ligands, and they reported that the kinetics of the resin-metal interaction was sufficiently rapid for most of the metal ions. Sorption reaches equilibrium within 60 min. Roozmond et al.<sup>16</sup> studied the Cu(II) and Cd(II) uptake of 3,5-dimethyl-1-hydroxymethyl pyrazole-attached *p*-aminomethyl-substituted poly(styrene-*co*-divinylbenzene) chelating polymer. They showed that adsorption was rather slow; after only 2 days, the resin appeared to reach equilibrium. Ebraheem and Hamdi<sup>17</sup> studied the effect 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.<sup>17</sup> Latha et al.<sup>18</sup> studied ethylenediamine-functionalized polyacrylamide resin for the extraction of several metal ions such as Fe(III), Fe(II), Cu(II),

and Ni(II) and reported that the complexation reaction proceeded very slowly (equilibrium time = 5 h). Konishi et al.<sup>19</sup> studied the sorption of Zn(II), Cd(II), and La(III) with biopolymer gel beads of alginic acid and reported high adsorption rates, in which equilibrium was achieved in about 2 h. Note that there are a lot of experimental and structural parameters that determine the adsorption rate, such as the stirring rate in the aqueous phase, the structural properties of the sorbent (e.g., porosity, surface area, topography, and swelling degree), the amount of sorbent, the ion properties (e.g., hydrated ionic radius and coordination complex number), the initial concentration of heavy-metal ions, the chelate-formation rate between the complexing ligand and the metal ions, and, of course, the existence of other metal ions that may compete with the metal ions of interest for the same active complexation sites. Therefore, it is too difficult to compare the adsorption rates reported. However, the adsorption rates obtained with the PEI-immobilized PMMA microspheres produced by us seem to be rather good.

#### Effect of the Initial Concentration of Metal Ions

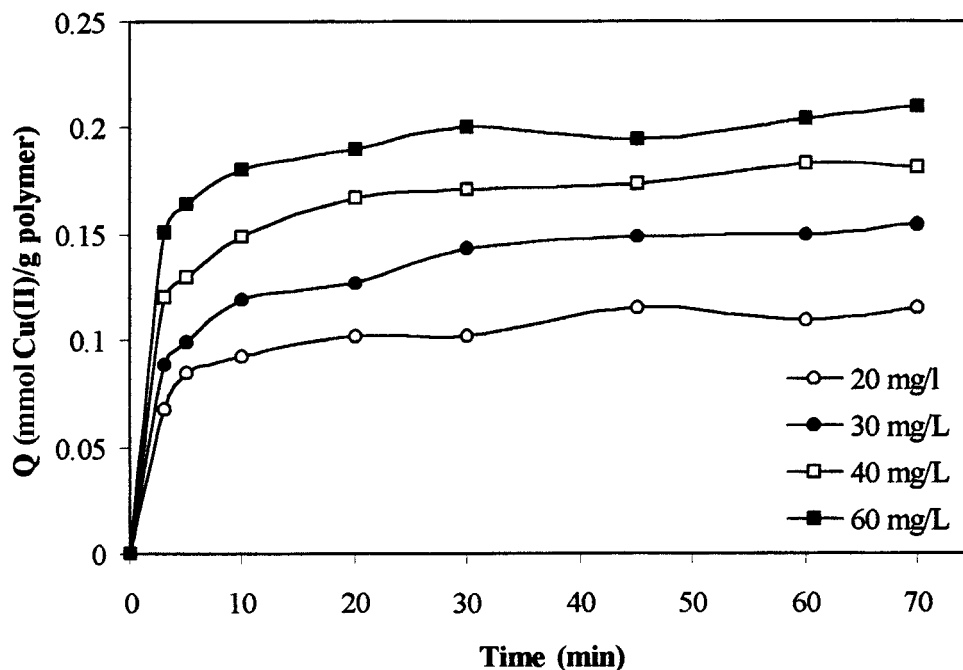
The adsorption capacities of the metal ions of PEI-immobilized PMMA microspheres are given as a function of the initial concentration of the



**Figure 3** Adsorption rates of heavy-metal ions on the PEI-immobilized PMMA microspheres: (A) Pb(II) ions, (B) Cd(II) ions, and (C) Cu(II) ions. The pHs were 5.0 for Pb(II) and Cd(II) ions and 4.0 for Cu(II) ions; the temperature was 20°C.

ions within the aqueous phase in Figure 4. The metal-ion adsorption capacity of the PEI-immobilized microspheres increased first with the increasing initial concentration of the ions and then reached a saturation level. The nonspecific ad-

sorption capacities of the unmodified PMMA microspheres are very low [ $3.6 \mu\text{mol/g}$  for Cu(II),  $4.6 \mu\text{mol/g}$  for Cd(II), and  $4.2 \mu\text{mol/g}$  for Pb(II)]. The maximum adsorption capacities of the PEI-immobilized PMMA microspheres are 0.126, 0.224, and



(c)

Figure 3 (Continued from the previous page)

0.276 mmol/g for Pb(II), Cd(II), and Cu(II), respectively. The increase in the adsorption capacity of the PEI-immobilized PMMA microspheres is due to the presence of metal-chelating ligand PEI on the surface of the sorbent.

Different polymeric sorbents with a wide range of adsorption capacities for heavy-metal ions have been reported. Shreedhara-Murthy and Ryan<sup>20</sup> found that 3.9–14.4 mg of Cd(II)/g and 4.8–27 mg of Cu(II)/g were removed by cellulose–dithiocar-

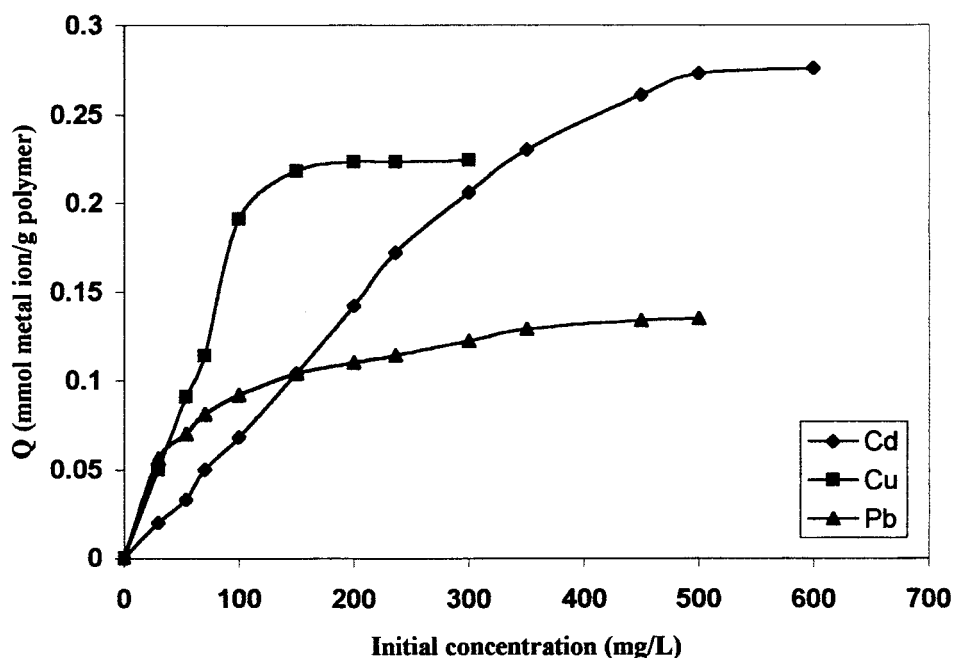


Figure 4 Adsorption capacities of PEI-immobilized PMMA microspheres for Pb(II), Cd(II), and Cu(II). The pH was 5.5, and the temperature was 20°C.

bamate resins.<sup>20</sup> Shambhu et al.<sup>21</sup> immobilized polyamines on polystyrene and reached an adsorption value of 33 mg of Cu(II)/g of polymer. Janus et al.<sup>22</sup> used poly(vinyl amine) as a sorbent for copper adsorption and reported an adsorption capacity of 0.5 mg of Cu(II)/g. Denizli et al.<sup>23</sup> showed 4.2 mg of Cd(II)/g with Procion Red MX-3B-immobilized poly(hydroxyethylmethacrylate-ethyleneglycoldimethacrylate) microspheres. Ibrahim et al.<sup>24</sup> used thionein-immobilized polyhydroxyethylmethacrylate microspheres and removed 45.2 mg of Cd(II)/g from an aqueous solution.<sup>24</sup> Denizli et al.<sup>25</sup> developed magnetic poly(vinyl butyral)-based microspheres carrying Cibacron Blue F3GA and reported 38.6 mg of Cd(II)/g. Dev and Rao<sup>15</sup> reported 29.2 mg of Cu(II)/g, 51.7 mg of Cd(II), and 80.8 mg of Pb(II)/g as the adsorption capacities for poly(styrene-vinylbenzene) macroreticular resin functionalized with bis-(*N,N'*-salicylidene) 1,3-propane-diamine. Delacour et al.<sup>26</sup> reported 38–127 mg of Pb(II)/g with PEI-coated silica gels. Chanda and Rempel<sup>27</sup> found 62.4 mg of Cr(III)/g of removal capacity with PEI granular sorbents.<sup>27</sup> Navarro et al.<sup>12</sup> showed high adsorption capacity with 288 mg of Hg(II)/g with a porous cellulose carrier modified with PEI.<sup>12</sup> Hudson and Matejka<sup>28</sup> used selective ion exchangers with pendent ethylene imine groups for the selective extraction of copper. Bahrami et al.<sup>29</sup> reached 80.64 mg of Cd(II)/g of polymer with PEI sol-gel sorbent. The maximum adsorption capacities, on the basis of weight, were 14.22–31.02 mg/g. Comparing these data, we believe that the adsorption capacities achieved with the PEI-immobilized PMMA microspheres are satisfactory.

An adsorption isotherm was used to characterize the interaction of each heavy-metal ion with the adsorbent. This provided a relationship between the concentration of heavy-metal ion in the solution and the amount of heavy-metal ion adsorbed onto the solid phase when the two phases were at equilibrium. The Langmuir adsorption model assumes that molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule. These sites are also assumed to be energetically equivalent and distant to each other so that there are no interactions between molecules adsorbed to adjacent sites.

The parameters  $Q_{\max}$  (maximum absorption capacity) and  $K_d$  (Langmuir constant) were determined by nonlinear regression with commercially available software and are shown in Table I. The standard deviation of the values determined by regression analysis is comparatively low. When

**Table I Adsorption Parameters of Heavy Metal Ions on PEI-Immobilized Microspheres**

Metal Ions	$Q_{\max}$ Measured (mg/g Polymer)	$Q_{\max}$ Calculated (mg/g Polymer)	$K_d$ (mg/mL)
Cu(II)	14.22	18.51	70.8
Cd(II)	31.02	34.92	95.0
Pb(II)	26.10	28.32	28.0

PEI-immobilized PMMA microspheres were used in the adsorption tests, the order of  $Q_m$  values for both cases was Cd(II) > Pb(II) > Cu(II).

## CONCLUSIONS

At least 20 metals are known to be toxic and fully half of these, including cadmium, arsenic, mercury, chromium, copper, lead, nickel, selenium, silver, and zinc, are released into the environment in quantities that pose a risk to human health. The removal of heavy-metal ions from aquatic systems is carried out with classical methods of adsorption techniques. PEI-immobilized PMMA microspheres, which were prepared by suspension polymerization and subsequent modifications, were applied to the removal of heavy-metal ions from aqueous solutions. The PEI-immobilized PMMA microspheres showed great promise in the removal of heavy-metal ions from aqueous media. The maximum amount of PEI immobilized onto the PMMA microspheres was 165.2 mg of PEI/g of polymer (4.0 mequiv of PEI/g of polymer). The PMMA microspheres had a spherical form and rough surface. These surface properties of the microspheres favored better adsorption of the heavy-metal ions because of an increased surface area. The adsorption capacity increased with increasing pH, reaching plateau values around pH 5.0. The adsorption rate of Cu(II) ions was higher than the rates of the other metal ions because of the high complex formation rate between the Cu(II) ions and PEI on the surface of the PMMA microspheres. The adsorption values of heavy-metal ions on unmodified PMMA microspheres was very low [3.6  $\mu\text{mol/g}$  for Cu(II), 4.6  $\mu\text{mol/g}$  for Cd(II), and 4.2  $\mu\text{mol/g}$  for Pb(II)]. The maximum adsorption capacities of the PEI-immobilized PMMA microspheres were 0.126, 0.224, and 0.276 mmol/g for Pb(II), Cd(II), and Cu(II), respectively. The increase in the adsorption capacity of the PEI-immobilized PMMA mi-



crosspheres was due to the presence of the metal-chelating ligand PEI on the surface of the sorbent.

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