

Preparation and Characterization of Magnetic Polymethylmethacrylate Microbeads Carrying Ethylene Diamine for Removal of Cu(II), Cd(II), Pb(II), and Hg(II) from Aqueous Solutions

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ABSTRACT: Magnetic polymethylmethacrylate (mPMMA) microbeads carrying ethylene diamine (EDA) were prepared for the removal of heavy metal ions (i.e., copper, lead, cadmium, and mercury) from aqueous solutions containing different amount of these ions (5–700 mg/L) and at different pH values (2.0–8.0). Adsorption of heavy metal ions on the unmodified mPMMA microbeads was very low (3.6 $\mu\text{mol/g}$ for Cu(II), 4.2 $\mu\text{mol/g}$ for Pb(II), 4.6 $\mu\text{mol/g}$ for Cd(II), and 2.9 $\mu\text{mol/g}$ for Hg(II)). EDA-incorporation significantly increased the heavy metal adsorption (201 $\mu\text{mol/g}$ for Cu(II), 186 $\mu\text{mol/g}$ for Pb(II), 162 $\mu\text{mol/g}$ for Cd(II), and 150 $\mu\text{mol/g}$ for Hg(II)). Competitive adsorption capacities (in the case of adsorption from mixture) were determined to be 79.8 $\mu\text{mol/g}$ for Cu(II), 58.7 $\mu\text{mol/g}$ for Pb(II), 52.4 $\mu\text{mol/g}$ for Cd(II), and 45.3 $\mu\text{mol/g}$ for Hg(II). The observed affinity order in adsorption was found to be Cu(II) > Pb(II) > Cd(II) > Hg(II) for both under noncompetitive and competitive conditions. The adsorption of heavy metal ions increased with increasing pH and reached a plateau value at around pH 5.0. The optimal pH range for heavy-metal removal was shown to be from 5.0 to 8.0. Desorption of heavy-metal ions was achieved using 0.1 M HNO₃. The maximum elution value was as high as 98%. These microbeads are suitable for repeated use for more than five adsorption-desorption cycles without considerable loss of adsorption capacity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 81–89, 2000

Key words: polymethylmethacrylate; magnetic microbeads; ethylene diamine; heavy metal removal; copper(II); cadmium(II); mercury(II); lead(II)

INTRODUCTION

Heavy metals released into the environment affect ecological life owing to their tendency to accumulate in living organisms.¹ Heavy metals

such as lead, mercury, arsenic, copper, and cadmium are highly toxic metals when absorbed into the body. They can cause accumulative poisoning, cancer, brain damage, etc.² These heavy metals are released into the environment in a number of different ways. Coal combustion, sewage waste waters, automobile emissions, battery industry, mining activities, and the utilization of fossil fuels are just a few examples.³ Among the various

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methods described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents, and cost effectiveness.⁴ The necessity to reduce the amount of heavy metal ions in wastewater streams, and subsequent possible re-use of these metal ions, has led to an increasing interest in selective sorbents.⁵

The development of the magnetic carriers as a sorbent in chromatography promises to solve many of the problems associated with chromatographic separations in packed-bed and in conventional fluidized-bed systems.⁶ Magnetic carriers combine some of the best characteristics of fluidized beds (low-pressure drop and high-feed-stream solid tolerances) and of fixed beds (absence of particle mixing, high-mass transfer rates, and good fluid-solid contact).⁷ Recently, there has been increased interest in the use of magnetic carriers in the removal of heavy metals.³ Magnetic carriers can be produced using inorganic materials or a number of synthetic and natural polymers. High mechanical resistance, insolubility, and excellent shelf life make inorganic materials ideal carriers. The main disadvantage of inorganic supports is their limited functional groups for complexation with metal ions. Magnetic carriers can be porous or nonporous.^{8–13} Magnetic carriers are more commonly manufactured from polymers because they have a variety of surface functional groups that can be tailored to use specific applications.⁸ Poly(vinyl butyral),⁹ polyethylene glycol,¹⁰ polyvinyl alcohol,¹¹ polyacrylamide,¹² and alginate¹³ are typical polymeric carriers that are used in heavy-metal removal.

In the present study, we have focused our attention on the development of magnetic polymethylmethacrylate (mPMMA) microbeads carrying ethylene diamine (EDA) for removal of heavy metal ions. The four metals selected in this study were copper, lead, cadmium, and mercury because of their environmental significance. mPMMA microbeads was prepared by modified solvent evaporation method. Ester groups in the mPMMA structure were converted to amino groups by reacting with EDA in the presence of p-toluenesulfonic acid as a functional groups where coordination complexes with heavy metals can be formed. The present work deals with preparation and characterization of mPMMA microbeads, and potential for their use in heavy metal adsorption/desorption studies.

Table I Polymerization Recipe

Polymethylmethacrylate	20.0 g
Chloroform	100 mL
Polyvinylalcohol	4.0 g
Sodiumdodecyl sulfate	2.0 g
Pluronic PE 6800	5.0 mL (%6, v/v)
Magnetite	0.50 g
Distilled Water	400 mL

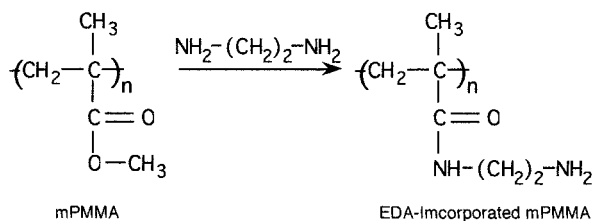
EXPERIMENTAL

Preparation of mPMMA Microbeads

Polymethylmethacrylate microbeads were prepared as in a previous paper.¹⁴ In order to prepare mPMMA microbeads the following modified solvent evaporation procedure was applied. The proper amount of PMMA was dissolved in chloroform (BDH, UK) and magnetite Fe₃O₄ (diameter: 5.0 μm, Sigma Chem. Co., USA) was added very quickly and mixed very well. Then this mixture was transferred immediately into the distilled water as the dispersion medium containing the proper amount of emulsifier (polyvinylalcohol, Merck, sodium dodecyl sulfate, Sigma, and Pluronic F6800, Basf). This polymer solution was transferred into the glass polymerization reactor (volume: 1 L) and stirred with a mechanical stirrer for 16 h at 20°C. The stirring rate was 700 rpm. After allowing the solvent to evaporate, magnetite particles (Fe₃O₄) completely encapsulated in polymeric structure. Polymerization recipe was given in Table I Tyler series sieves were used to separate the microbeads has the diameter between 100–200 μm.

EDA-Incorporated mPMMA Microbeads

In order to prepare the EDA-modified magnetic microbeads the following procedure was applied. A 20 g sample of dry magnetic microbeads was weighed and transferred into the benzene (Carlo Erba, Italy)-EDA (BDH, England) solution mixture (60 mL/10 mL) containing 300 mg of p-toluene-sulfonic acid (Sigma). This reaction medium was boiled in Dean-Stark apparatus at reflux for removal of water. EDA-coupling process was carried out under nitrogen atmosphere at room temperature for 48 h. At the end of this reaction period, the EDA-incorporated microbeads were removed by filtration and washed with methanol several times and then dried in vacuum at room temperature for 24 h. Chemical coupling reaction between the magnetic polymer and EDA is as follows:



Microbead Characterization

Analysis of Magnetism

The degree of magnetism the PMMA microbeads was measured in a magnetic field by using a vibrating-sample magnetometer (Princeton Applied Research Corporation, New Jersey, USA). The presence of magnetite in the polymeric structure was investigated with ESR spectrophotometer (EL 9, Varian).

Scanning Electron Microscopy

In order to observe the surface topography of the mPMMA microbeads, scanning electron micrographs of the gold-coated samples were taken with a scanning electron microscope (SEM) (Model: Raster Elektronen Microscopy, Leitz-AMR-1000, Frankfurt, Germany).

FTIR Studies

FTIR spectra of the unmodified and ethylene diamine-incorporated mPMMA microbeads were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Tokyo, Japan). The dry mPMMA microbeads (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed into a pellet form and the spectrum was then recorded.

Elemental Analysis

The amount of ethylene diamine incorporated to the mPMMA microbeads was determined from the elemental-analysis device (Leco, Chicago, CHNS-932, USA).

Heavy Metal Adsorption/Desorption

Heavy metal adsorption from the single metal aqueous solutions was investigated in batch adsorption-equilibrium experiments. Effects of the initial concentration of metal ions and pH on the adsorption capacity were studied. 20 mL of aqueous metal ion solutions with different concentrations (in the range of 5–700 mg/L) were treated

with the unmodified and EDA-incorporated mPMMA microbeads at room temperature. Adsorption flasks were agitated magnetically at 600 rpm. The suspensions were brought to the desired pH for each metal by adding sodium hydroxide (NaOH) and hydrochloric acid (HCl). The pH was maintained in a range of ± 0.1 Units until equilibrium was attained. Investigations were made for pH values in the range of 2.0–6.0 for copper and 8.0 for lead, cadmium, and mercury. In all experiments, polymer concentration was kept constant at 250 mg/20 mL. Blank trials without polymeric microbeads addition were performed for each tested metal concentration. After the predetermined adsorption time (60 min), the microbeads were separated from the adsorption medium, and analyses for heavy metal ions in the aqueous phase was performed using a graphite furnace atomic absorption spectrophotometer (AAS, GBC 932 AA, Victoria, Australia). Hg(II) concentration was determined by AAS connected to a hydride generator (GBC HG3000). Each sample was read three times, and a mean value and relative standard deviation was computed. Calibrations were performed in the range of analysis, and a correlation coefficient for the calibration curve of 0.98 or greater was obtained. The instrument response was periodically checked with known metal solution standards. The molar adsorption capacity ($\mu\text{mol/g}$ dry microbead) is defined as the ratio of the adsorption of heavy metal ions (μmol) to the dry weight of the microbeads (g).

Competitive adsorption of heavy metal ions from their mixture was also investigated in batch-wise form. A solution (20 mL) containing 50 mg/L from each metal ions was treated with the EDA-incorporated mPMMA microbeads at a pH of 7.0 at room temperature, in the flasks agitated magnetically at 600 rpm. Adsorption process was carried out for 60 min. After adsorption, concentration of the metal ions in the supernatant was obtained by an atomic absorption spectrophotometer.

In order to determine the reusability of the EDA-incorporated mPMMA microbeads, consecutive adsorption-desorption cycles were repeated five times by using the same affinity microbeads. Desorption of heavy metal ions was performed by using 0.1 M HNO_3 solution. The mPMMA microbeads loaded heavy metal ions were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final metal ion concentration in the aqueous phase was de-

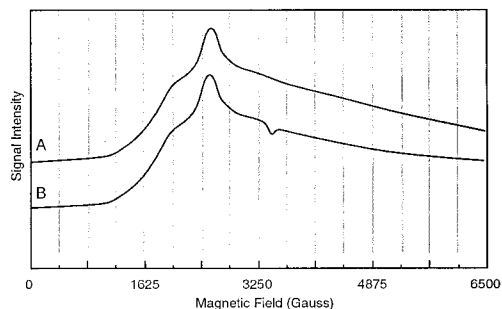


Figure 1 ESR spectra of mPMMA microbeads. (A) EDA-incorporated microbeads; (B) Unmodified microbeads.

terminated by using an atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of metal ions adsorbed on the microbeads and the final metal ions concentration in the desorption medium.

RESULTS AND DISCUSSION

Properties of PMMA Microbeads

The presence of magnetite particles in the PMMA structure was confirmed by the electron spin resonance (ESR). After the EDA attachment, the intensity of the magnetite peak did not change anymore. A peak of magnetite (i.e., Fe_3O_4 fine particles) was detected in the ESR spectrum as shown in Figure 1. The behavior of magnetic microbeads in a magnetic field using a vibrating magnetometer was given in Figure 2 in terms of electromagnetic unit (emu), which is related to the intensity of magnetization of the sample vs

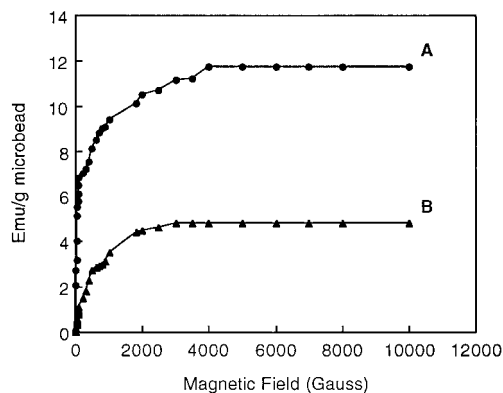


Figure 2 The magnetic behavior of PMMA microbeads. (A) Unmodified microbeads; (B) EDA-incorporated microbeads.

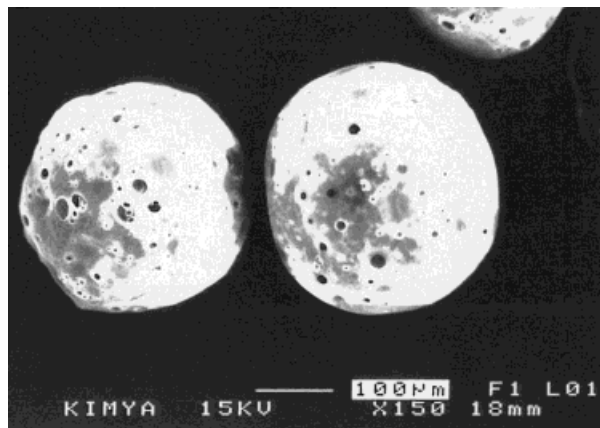


Figure 3 SEM photograph of mPMMA microbeads.

applied magnetic field. In this ESR spectra, 3000 Gauss magnetic field was found sufficient to excite all of the dipole moments of 1.0 g polymer sample that consists of magnetite. After EDA incorporation, the intensity of the magnetization of the sample is affected with the applied magnetic field. This value will be an important design parameter for a magnetically fluidized bed or for magnetic filtration system using these microbeads. The value of this magnetic field is a function of the flow velocity, particle size, and magnetic susceptibility of solids to be removed. In the literature, this value changes from 8 kG to 20 kG for various applications, thus our magnetic microbeads will need less magnetic intensity in a magnetically fluidized bed or for a magnetic filter.

Figure 3 shows the SEM micrograph of the mPMMA microbeads. As clearly seen, the magnetic microbeads have a spherical form and rough surface due to the abrasion of magnetite crystals (diameter $< 5 \mu\text{m}$) during the encapsulation and polymerization procedure. These surface properties of the magnetic microbeads would favor better adsorption of the heavy metal ions due to increase in surface area. It should be also mentioned that nonmagnetic microbeads were in uniform and spherical form with smooth surface characteristics.

Ester groups in the mPMMA structure were converted to amino groups by reacting with ethylene diamine as a metal-complexing group in the presence of p-toluenesulfonic acid for heavy metal adsorption. The main problem in surface modification is to prevent deformation and/or destruction of microbeads. If there is any deformation, encapsulated magnetites (i.e., iron particles) can easily release from the polymeric structure. This

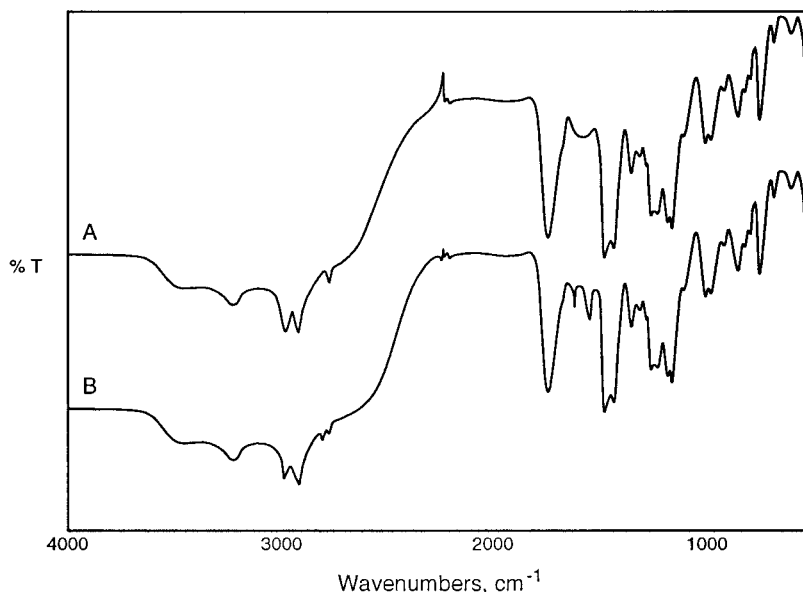


Figure 4 FTIR Spectra of (A) unmodified mPMMA; (B) EDA-incorporated mPMMA.

decreases the magnetic properties of the polymeric sorbent. In order to prevent structural destructions/deformations, coupling reactions were carried out under mild experimental conditions at long reaction period (e.g., up to 1 week). Acid catalysis was used for the incorporation of amine groups on/in to the ester containing structures^{15–17} under mild conditions. That's why we used *p*-toluene sulfonic acid for the elimination of methoxy group. Elemental analysis of the EDA-incorporated mPMMA microbeads were performed, and the incorporation amounts of the amine group was found to be 142 $\mu\text{mol/g}$ from the nitrogen stoichiometry. On the basis of its complexation properties (i.e., complexation rate, selectivity and capacity) with heavy metal ions, amine ligands are common. Largely for this reason, and also owing to reduce steric hindrances, EDA-incorporated mPMMA microbeads were prepared for heavy metal removal. EDA release from the EDA-incorporated microbeads was also monitored continuously. There was no amine leakage in any of the adsorption and desorption media, which assured that the washing procedure used for removal of physically adsorbed EDA molecules from the derived microbead was satisfactory.

FTIR spectra of unmodified and EDA-incorporated microbeads are given in Figure 4. The FTIR spectra of EDA-modified mPMMA microbeads has some absorption bands different than those of unmodified mPMMA. The most important absorption bands at 1665 cm^{-1} and 1550 cm^{-1} rep-

resent amide I (mainly due to C=O stretching) and amide II (mainly due to N—H bending), respectively, are due to EDA bonded to microbeads.

Adsorption of Heavy Metal Ions

Effects of EDA-Derivatization

Table II shows the effects of EDA-incorporation on the heavy metal adsorption. First, it should be noted that there was a very low nonspecific adsorption of heavy metal ions on the unmodified mPMMA microbeads. The heavy metal adsorption values on the unmodified microbeads (without EDA-derivatization) are determined to be 3.6 $\mu\text{mol/g}$ for Cu(II), 4.2 $\mu\text{mol/g}$ for Pb(II), 4.6 $\mu\text{mol/g}$

Table II Effect of EDA-Incorporation on Adsorption of Heavy Metal Ions

Ions	Adsorption Capacity ($\mu\text{mol/g}$)		Molar Ratio (mol of metal/mol of EDA)
	mPMMA	EDA-Modified mPMMA	
Cu(II)	3.6	201	1.42
Pb(II)	4.2	186	1.30
Cd(II)	4.6	162	1.14
Hg(II)	2.9	150	1.06

EDA incorporation, 142 $\mu\text{mol/g}$; adsorption conditions, initial concentration of metal ions, 60 mg/L for Cu(II); 400 mg/L for other metal ions; pH, 5.0; T, 25°C.

for Cd(II), and 2.9 $\mu\text{mol/g}$ for Hg(II). These metal ions can be adsorbed nonspecifically by physical adsorption, associated with the weak forces of physical attraction such as van der Waals forces, or by chemical adsorption, associated with the exchange of electrons and the formation of a chemical bond between the metal ions and the mPMMA surfaces (especially with the carbonyl groups of the mPMMA chain). In addition, these microbeads are porous, which therefore heavy metal ions may diffuse and absorb (or entrap) within the pores of the microbeads that may cause these nonspecific adsorption, although higher adsorption values were obtained when the EDA-incorporated microbeads were used (201 $\mu\text{mol/g}$ for Cu(II), 186 $\mu\text{mol/g}$ for Pb(II), 162 $\mu\text{mol/g}$ for Cd(II), and 150 $\mu\text{mol/g}$ for Hg(II)). This may be due to presence of chelating amino groups on the microbead surface. The specificity of the metal-chelating ligand (i.e., amine groups) may also contribute to this high adsorption capacity. Unit mass of the mPMMA microbeads carries 142 μmol EDA, which was found by elemental analysis. EDA molecule includes two nitrogen atoms that have unpaired electrons for interaction with metal ions. It seems that a stoichiometry of around two metal ions per EDA molecule is consistent with the given data (Table II).

Effects of Initial Concentration of Metal Ions

Adsorption capacities of the heavy metal ions of the EDA-incorporated mPMMA microbeads are given as a function of the initial concentration of metal ions within the aqueous phase in Figure 5. Note that these adsorption curves were obtained in the experiments where adsorptions from the single metal aqueous solutions were studied. It was found that the amount of adsorption was significantly increased with increasing of the initial concentration of heavy metal ions. The maximum adsorption capacities of the EDA-incorporated microbeads in the studied range are 201 $\mu\text{mol/g}$ for Cu(II), 186 $\mu\text{mol/g}$ for Pb(II), 162 $\mu\text{mol/g}$ for Cd(II), and 150 $\mu\text{mol/g}$ for Hg(II), respectively. The observed affinity order is Cu(II) > Pb(II) > Cd(II) > Hg(II). Note that at pH 6.0, copper precipitates as cupric hydroxide $[\text{Cu}(\text{OH})_2]$ if Cu(II) concentrations will be greater than 60 mg/L; therefore, we did not study above 60 mg/L for Cu(II) ions.

Different polymeric sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Shreedhara-Murthy and Ryan¹⁸

found 34.8–128 $\mu\text{mol Cd(II)/g}$ and 75.5–425 $\mu\text{mol Cu(II)/g}$ removal by cellulose-dithiocarbamate resins. Roozmond et al.¹⁹ showed 357 $\mu\text{mol Cd(II)/g}$ and 502 $\mu\text{mol Cu(II)/g}$ with pyrazole-containing poly(styrene-divinylbenzene) sorbents. Konishi et al.²⁰ reported 42.8–857 $\mu\text{mol Cd(II)/g}$ with alginic acid gels. Liu et al.²¹ achieved 460 $\mu\text{mol Pb(II)/g}$ and 259 $\mu\text{mol Cu(II)/g}$ adsorption capacities with N-hydroxymethyl thioamide resin. Hudson and Matejka²² investigated the length of pendants groups on adsorption of Cu(II) ions onto poly(styrene-divinyl benzene) copolymer beads and concluded that the type of pendent groups is important in the adsorption of heavy metal ions. They reported adsorption capacities between 239 $\mu\text{mol/g}$. Sağ and Kutsal²³ have used *Zoogloea ramigera* microorganisms for heavy metal adsorption. The maximum amounts of adsorption capacities achieved were 551 $\mu\text{mol Cu(II)}$ and 420 $\mu\text{mol Pb(II)/g}$ dry weight of microorganisms. Shambhu et al.²⁴ immobilized polyamines (i.e., EDA, diethylene triamine, and triethylene tetramine) onto polystyrene and reached an adsorption value of 519 $\mu\text{mol Cu(II)/g}$ polymer. Janus et al.²⁵ used poly(vinyl amine) sorbent for copper adsorption and reported an adsorption capacity of 7.9 $\mu\text{mol Cu(II)/g}$. Denizli et al.²⁶ used Alkali Blue 6B-attached P(EGDMA-HEMA) sorbents, in which the maximum adsorption capacities were 36.2 $\mu\text{mol Cu(II)/g}$, 49.1 $\mu\text{mol Cd(II)/g}$, and 618 $\mu\text{mol Pb(II)/g}$. Marzal et al.²⁷ immobilized EDA and hexamethylene diamine by glow-discharge method and obtained 83.5 $\mu\text{mol Cu(II)/g}$ for EDA and 107 $\mu\text{mol Cu(II)/g}$ for HMDA-plasma treatment. Denizli et al.²⁸ re-

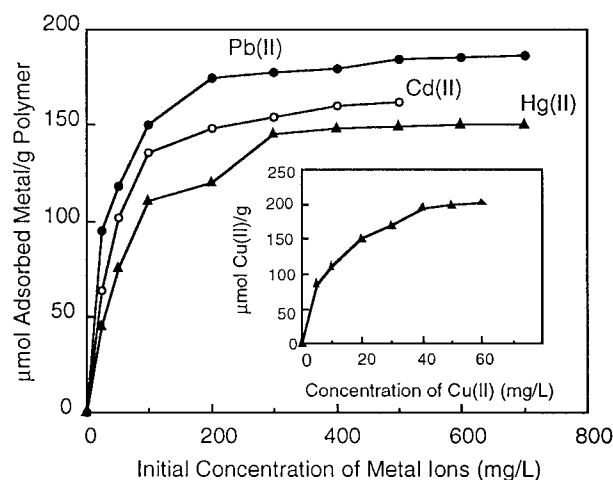


Figure 5 Heavy metal ions adsorption capacity of the EDA-incorporated microbeads. $T = 20^\circ\text{C}$ and $\text{pH} = 5.0$.

ported 83.5 $\mu\text{mol Cu(II)/g}$ and 674 $\mu\text{mol Pb(II)/g}$ for diamine glow discharge treated polyhydroxyethylmethacrylate microbeads. We obtained maximum heavy metal adsorption capacities as 201 $\mu\text{mol/g}$ for Cu(II), 186 $\mu\text{mol/g}$ for Pb(II), 162 $\mu\text{mol/g}$ for Cd(II), and 150 $\mu\text{mol/g}$ for Hg(II). By considering these data, we concluded that the EDA-incorporated mPMMA microbeads is a promising polymeric carrier for the removal of heavy metal ions from aqueous media.

Effects of pH

The complexation of heavy metal ions by a chelating-ligand is usually a strong function of pH.^{25,28} The hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species. As discussed in details by several researchers,²⁹ hydrolysis of metal ions becomes significant at approximately pH 7.5–8.5 for studied heavy metal ions. Therefore, in the present study we changed the pH range between 2.0–8.0 except for Cu(II) ions. Because at pH 6.0, copper precipitates as cupric hydroxide [Cu(OH)₂] if Cu(II) concentration will be greater than 60 mg/L (calculated from the solubility product). Figure 6 shows the pH profile data for heavy metal adsorption. This figure shows that complexation behavior of heavy metal ions is more sensitive to pH changes, especially at lower pH region. The inhibition of metal chelation with a decrease in pH was observed by several authors and in different sorbents.^{23,29} Thus it has been proposed that protons and metal ions com-

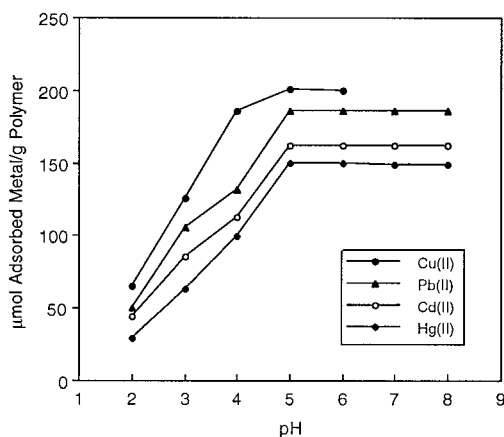


Figure 6 Effect of pH on adsorption of heavy metal ions on the EDA-incorporated microbeads. Initial concentration of metal ions: 60 mg/L for Cu(II) and 400 mg/L for other metal ions; T = 20°C.

Table III Competitive Adsorption of Heavy Metal Ions on the EDA-Incorporated mPMMA Microbeads

Ions	Adsorption Capacity ($\mu\text{mol/g}$)	
	Non-Competitive	Competitive
Cu(II)	198.6	79.8
Pb(II)	118.2	58.7
Cd(II)	101.5	52.4
Hg(II)	75.3	45.3

EDA incorporation, 142 $\mu\text{mol/g}$; Concentration of each metal ions, 50 mg/L; pH, 5.0, T, 20°C.

pete for the same binding sites. It was observed that the adsorption capacities increased with increasing pH, reaching plateau values at around pH 5.0. High adsorption at higher pH values implies that metal ions interact with amino (unprotonated) groups by chelating as also stated in the related literature.^{26,28,29} Plateau values are 201 $\mu\text{mol/g}$ for Cu(II), 186 $\mu\text{mol/g}$ for Pb(II), 162 $\mu\text{mol/g}$ for Cd(II), and 150 $\mu\text{mol/g}$ for Hg(II). The difference in adsorption values can be explained by the different affinity of the heavy metal ions for the donor atoms (i.e., nitrogen) in the metal-chelating-ligand EDA.

Competitive Adsorption

Adsorption capacities of the EDA-incorporated mPMMA microbeads for heavy metal ions under competitive conditions (adsorption from solutions containing all heavy metal ions) for Cu(II), Pb(II), Hg(II), and Cd(II) are given in Table III. It should be noted that the competitive adsorption capacities of the EDA-incorporated microbeads for all metal ions were lower than noncompetitive conditions. The noncompetitive adsorption capacities are 198.6 $\mu\text{mol/g}$ for Cu(II), 118.2 $\mu\text{mol/g}$ for Pb(II), 101.5 $\mu\text{mol/g}$ for Cd(II), and 75.3 $\mu\text{mol/g}$ for Hg(II) at 50 mg/L initial concentration. The competitive adsorption capacities are 79.8 $\mu\text{mol/g}$ for Cu(II), 58.7 $\mu\text{mol/g}$ for Pb(II), 52.4 $\mu\text{mol/g}$ for Cd(II), and 45.3 $\mu\text{mol/g}$ for Hg(II). The presence of other metal ions decreases the adsorption capacities as expected. The observed complexation order in adsorption was found to be same under competitive and noncompetitive conditions: Cu(II) > Pb(II) > Cd(II) > Hg(II). In both cases the EDA-incorporated mPMMA microbeads shows more affinity to Cu(II) ions.

Table IV Adsorption-Desorption Cycles for Heavy Metal Ions

Cycle No.	Cu(II)		Pb(II)		Cd(II)		Hg(II)	
	Adsorption (mmol/g)	Desorption (%)	Adsorption (mmol/g)	Desorption (%)	Adsorption (mmol/g)	Desorption (%)	Adsorption (mmol/g)	Desorption (%)
1	201.2	98.3	186.2	97.5	162.1	98.1	150.3	99.0
2	199.7	99.3	185.8	98.1	161.5	98.3	149.5	99.1
3	199.5	99.6	184.3	99.0	161.0	97.7	149.1	98.6
4	198.6	98.1	184.4	98.3	161.6	98.5	148.5	97.6
5	197.4	97.7	183.7	98.1	160.9	97.6	148.1	97.8

Regeneration of Microbeads

Elution experiments were carried out in 0.1 M HNO₃ solution. The EDA-incorporated microbeads loaded with the maximum amounts of the respective heavy metal ions were placed within the desorption medium and the amount of metal ions desorbed in 30 min was measured. Table III shows the adsorption-desorption data of heavy metal ions after several cycles of consecutive adsorption and desorption procedure. When HNO₃ was used as a desorption agent, the coordination spheres of chelated metal ions is disrupted and subsequently metal ions release from the solid surface into the desorption medium. Table IV clearly shows that these microbeads can be used repeatedly without losing significantly their adsorption capacities for all metal ions studied here.

CONCLUSION

Magnetic carrier technology enables the use of magnetic processing for rapid and selective heavy metal removal. EDA-carrying mPMMA microbeads (142 μmol EDA/g polymer) have shown great promise in removal of heavy metal ions (i.e., Cu(II), Pb(II), Cd(II), and Hg(II)) from aqueous media under noncompetitive and competitive conditions. Some results were summarized as follows: Adsorption of heavy metal ions on the unmodified mPMMA microbeads was very low (3.6 μmol/g for Cu(II), 4.2 μmol/g for Pb(II), 4.6 μmol/g for Cd(II), and 2.9 μmol/g for Hg(II)). The maximum adsorption capacities of these chemically modified microbeads from their single-metal ions solutions were 201 μmol/g for Cu(II), 186 μmol/g for Pb(II), 162 μmol/g for Cd(II), and 150 μmol/g for Hg(II). When the heavy metal ions competed (in the

case of the adsorption from their mixture) the amounts of adsorption were 79.8 μmol/g for Cu(II), 58.7 μmol/g for Pb(II), 52.4 μmol/g for Cd(II), and 45.3 μmol/g for Hg(II) at 50 mg/L concentration. The adsorption capacities increased with increasing pH, reaching plateau values at around pH 5.0. The EDA-incorporated mPMMA microbeads exhibits the following metal ion affinity sequence under non-competitive and competitive conditions: Cu(II) > Pb(II) > Cd(II) > Hg(II). Repeated adsorption and desorption cycles showed the feasibility of these amine-incorporated microbeads for heavy metal adsorption.

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