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MAGNETIC POLYMETHYLMETHACRYLATE MICROBEADS CARRYING AMINE FUNCTIONAL GROUPS FOR REMOVAL OF Pb(II) FROM AQUEOUS SOLUTIONS

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MAGNETIC POLYMETHYLMETHACRYLATE MICROBEADS CARRYING AMINE FUNCTIONAL GROUPS FOR REMOVAL OF Pb(II) FROM AQUEOUS SOLUTIONS

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Key Words: Polymethylmethacrylate, Magnetic Microbeads, Hexamethyle Diamine Heavy Metal Removal, Lead(II)

ABSTRACT

Magnetic polymethylmethacrylate [mPMMA] microbeads (150-200 μm in diameter) carrying hexamethylene diamine (HMDA) were prepared for the removal of Pb(II) ions from aqueous solutions containing different amounts of Pb(II) ions (5-100 mg/L) and at different pH values (2.0-6.0). Adsorption rates were observed as high at the beginning of the adsorption process, and then equilibrium was reached in about 20 minutes. Adsorption of Pb(II) ions on the unmodified mPMMA microbeads was negligible (4.2 μmol/g). While HMDA-incorporation significantly increased the Pb(II) adsorption was (128 μmol/g). The adsorption of Pb(II) ions increased with an increasing pH, and reached a plateau value at around pH 5.0. The optimal pH range for Pb(II)

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removal was shown to be from 5.0 to 6.0. Desorption of Pb(II) ions was achieved using 0.1 M HNO_3. The maximum desorption value was as high as 98%. These microbeads are suitable for repeated use for more than five adsorption-desorption cycles without a considerable loss of adsorption capacity.

INTRODUCTION

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. [1]. Lead has a great affinity to certain radicals and functional groups such as -SH and -NH_2. Lead is a general metabolic poison and enzyme inhibitor, and can cause mental retardation and semi-permanent brain damage in young children. Lead has the ability to replace calcium in the bone to form sites for long-rem release. Of major clinical importance are the chronic effects on the blood cells and nervous system. In acute poisoning, gastrointestinal toxicity dominates, but encephalopathy may result in children, and kidney damage and other organ toxicity may also occur [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 methods described, adsorption technology 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 decrease the amount of heavy metal ions in wastewater streams, and subsequent possible reuse 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 a 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 as ideal carriers. The main disadvantage of inorganic supports is their limited functional groups for complexation with metal ions. Magnetic carriers can be either porous or non-

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porous [8-13]. Magnetic carriers are more commonly manufactured from polymers, since they have a variety of surface functional groups which can be tailored to use specific applications [8]. Poly(vinyl butyral) [9], polyethylene glycol [10], polyvinyl alcohol [11] polyacrylamide [12] and alginate [13] are typical polymeric carriers which are used in heavy metal removal.

The present paper describes the preparation and characterization of magnetic PMMA microbeads carrying hexamethylene diamine for the removal of heavy metal ions. Lead was selected because of its environmental significance. Magnetic PMMA microbeads was prepared by a modified solvent evaporation method. Ester groups in the mPMMA structure were converted to amino groups by reacting with hexamethylene diamine in the presence of p-toluenesulfonic acid as a functional groups where coordination complexes with metals can be formed. The present work deals with the preparation and characterization of mPMMA microbeads, and the potential for their use in Pb(II) adsorption/desorption studies.

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EXPERIMENTAL

Production of Polymethylmethacrylate Microbeads

Methylmethacrylate (MMA, Röhm, Germany) was purified by extraction with 10% (w/v) of NaOH solution and then 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 chloride (BPO, 97% active compound, BDH Chemicals Ltd., UK). All polymerizations were performed by using distilled-deionized water.

Polymethylmethacrylate (PMMA) microspheres were produced by a suspension polymerization method [14]. A typical procedure may be given as follows: The stabilizer, TCP (6.0 g) was dissolved within 480 ml water for the preparation of a continuous phase The monomer phase was prepared by dissolving the initiator BPO (6.0 g) in methylmethacrylate (240 ml). 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 within about 30 minutes by stirring the medium at 400 rpm. The monomer phase was charged to the reactor and polymerization was conducted at 80°C for 2 hours, and 90°C for 1 hour. Polymerization was carried out under nitrogen atmosphere. After the completion of polymerization, the reac-

tor 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.

Preparation of Magnetic Polymethylmethacrylate Microbeads

In order to prepare magnetic PMMA microbeads, the following modified solvent evaporation procedure was applied. The proper amount of PMMA was dissolved in chloroform (BDH, UK) and magnetite Fe_3O_4 (diameter was less than 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 hours at 20°C. The stirring rate was 700 rpm. After allowing the solvent to evaporate, magnetite particles (Fe_3O_4) completely encapsulated in polymeric structure. The polymerization recipe is given in Table 1. Tyler screen analysis series sieves were used to separate the microbeads has a diameter between 100-200 μm.

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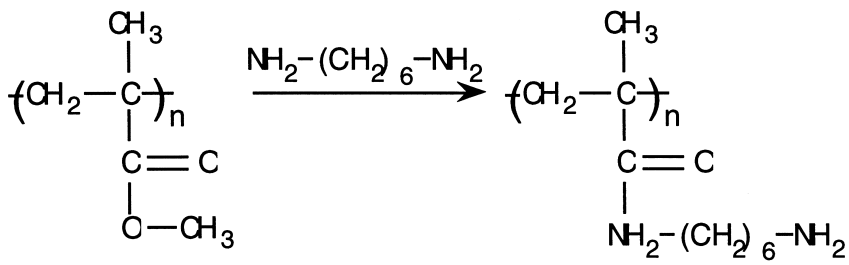
TABLE 1. Solvent Evaporation Polymerization Recipe for Magnetic PMMA Microbeads

Polymethylmethacrylate	20 g
Chloroform	100 ml
Polyvinylalcohol	4 g
Sodiumdodecyl sulfate	2 g
Pluronic PE 6800	5 ml (% 6, v/v)
Magnetite	0.5 g
Distilled Water	400 ml

Hexamethylene Diamine-Incorporated Magnetic Polymethylmethacrylate Microbeads

In order to prepare the HMDA-modified magnetic microbeads, the following procedure was applied. 20 g of dry magnetic microbeads was weighed and transferred into the benzene (Carlo Erba, Italy)-hexamethylene diamine (BDH, England) solution mixture (60 ml/10 ml) containing 300 mg of p-tolunesulphonic acid (Sigma Chem. Co., USA). This reaction medium was boiled in Dean-Stark apparatus at reflux for the removal of water. The coupling process was carried for 48 hours. At the end of this reaction period, the HMDA-incorporated microbeads were removed by filtration and washed with methanol several times, and then dried in vacuum for 24 hours. Chemical coupling reaction between the magnetic polymer and hexamethylene diamine is as follows:



mPMMA HMDA-Incorporated mPMMA

Microbead Characterization

Analysis of Magnetism

The degree of magnetism of the PMMA microbeads was measured in a magnetic field by using a vibrating-sample magnetometer (Princeton Applied Reseach Corporation, 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 SEM (Model: Raster Electronen Microscopy, Leitz-AMR-1000, Germany).

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FTIR Studies

FTIR spectra of the unmodified and hexamethylene diamine-incorporated mPMMA microbeads were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, 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 hexamethylene diamine incorporated to the mPMMA microbeads was determined from the elemental-analysis device (Leco, CHNS-932, USA).

Pb(II) Adsorption/Desorption Studies

Pb(II) 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 Pb(II) solutions with different concentrations (in the range of 5-100 mg/L) were treated with the unmodified and hexamethylene diamine 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 to 6.0. 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 minutes), the microbeads were separated from the adsorption medium, and analyses for Pb(II) ions in the aqueous phase was performed using a graphite furnace atomic absorption spectrophotometer (AAS, GBC 932 AA, Australia). Each sample was read three times, and a mean value and relative standard deviation was computed. Calibrations were performed in the analysis range 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 (μmol/g dry microbead) is defined as the ratio of the adsorption of heavy metal ions (μmol) to the dry weight of the microbeads (g).

In order to determine the reusability of the hexmethylene diamine-incorporated mPMMA microbeads, consecutive adsorption-desorption cycles were

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repeated five times by using the same affinity microbeads. Desorption of Pb(II) was performed by using 0.1 M HNO_3 solution. The mPMMA microbeads loaded Pb(II) were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final Pb(II) concentration in the aqueous phase was determined by using an atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of Pb(II) adsorbed on the microbeads and the final Pb(II) concentration in the desorption medium.

RESULTS AND DISCUSSION

Properties of Polymethylmethacrylate Microbeads

The presence of magnetite particles in the polymethylmethacrylate structure was confirmed by the ESR. After the hexamethylene diamine attachment, the intensity of the magnetite peak did not change further. 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 emu which is related to the intensity of magnetization of the sample vs applied magnetic field. In this spectra, the 3000 Gauss magnetic field was found sufficient to excite all the dipole

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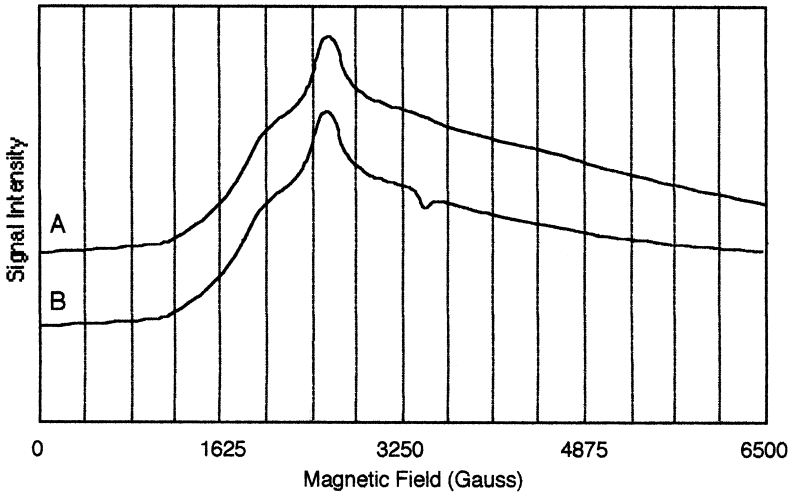

Figure 1. ESR spectra of mPMMA microbeads; (A) Hexamethylene diamine-incorporated microbeads; (B) Unmodified microbeads.

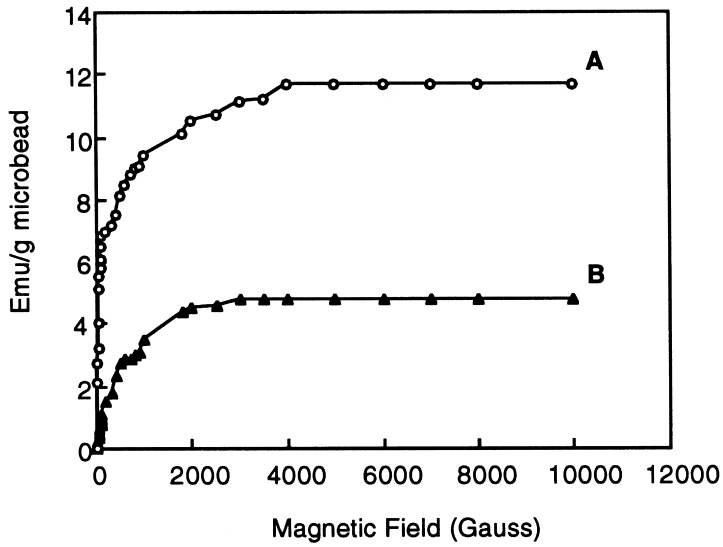

Figure 2. The magnetic behavior of PMMA microbeads; (A) Unmodified microbeads; (B) HMDA-incorporated microbeads.

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moments of a 1.0 gram sample which consists of magnetite. After hexamethylene diamine 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, particles 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 μm) during the encapsulation and polymerization procedure. These surface properties of the magnetic microbeads would better favor adsorption of the heavy metal ions due to an increase in the surface area. It should be also mentioned that non-magnetic microbeads were in uniform and spherical form with smooth surface characteristics.

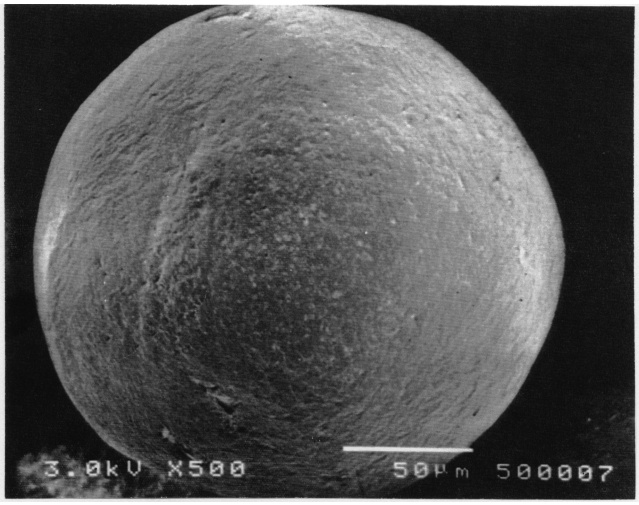

Figure 3. SEM photograph of mPMMA microbeads.

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Ester groups in the mPMMA structure were converted to amino groups by reacting with hexamethylene diamine as a metal-complexing group in the presence of p-toluenesulfonic acid for heavy metal adsorption. Elemental analysis of the HMDA-incorporated mPMMA microbeads were performed, and the incorporation amount of the amino functional groups was found to be 85 μmol/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 due to reducing steric hindrances, HMDA-incorporated mPMMA microbeads were prepared for heavy metal removal. The HMDA release from the HMDA-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 HMDA molecules from the derived microbeads was satisfactory.

Figure 4 shows the FTIR spectra of unmodified and HMDA-incorporated microbeads are given in Figure 3. The FTIR spectra of HMDA-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} represent symmetric stretching of seconder amide (amide II) and amide I, respectively, are due to HMDA bonded to microbeads.

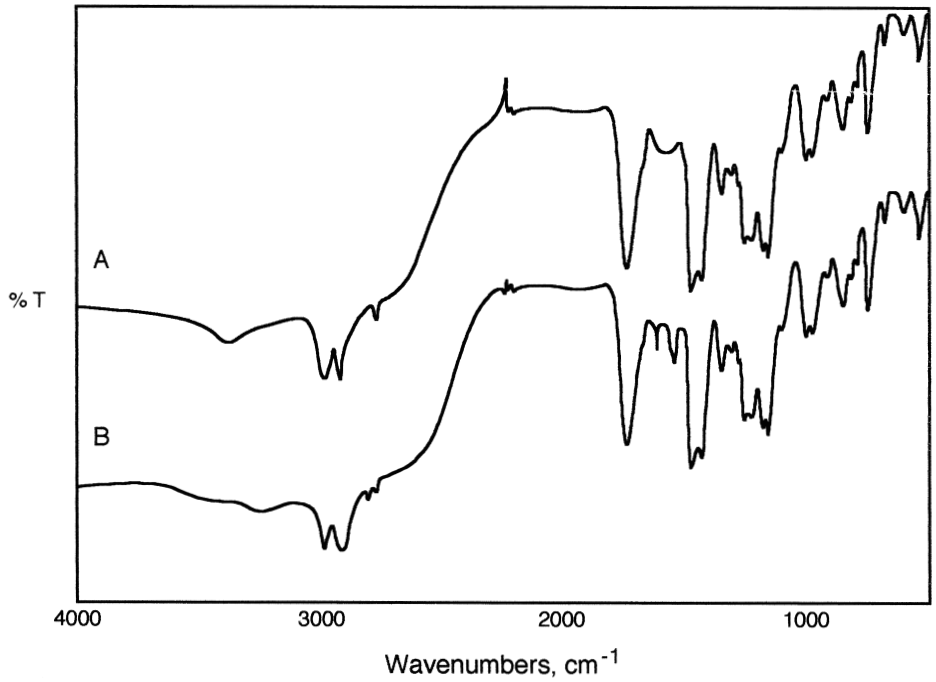

Figure 4. FTIR Spectra of (A) unmodified mPMMA; (B) HMDA-incorporated mPMMA.

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Adsorption of Pb(II) Ions

Adsorption Rate

Figure 5 shows adsorption rates of Pb(II) on the HMDA-incorporated mPMMM microbeads from aqueous solutions containing different amounts of Pb(II) (in the range of 10-100 ppm) at constant pH of 6.0. As seen here, the Pb(II) adsorption capacity increases with time during the first 10 minutes, and then levels off toward the equilibrium adsorption capacity. In addition, the adsorption of Pb(II) was quite fast especially when the Pb(II) concentration was high. This is due to the high complexation rate between the Pb(II) and the amino functional groups on the surface of mPMMA microbeads. Mass transfer limitations were also overcome by a high driving force, which was the concentration difference of Pb(II) between the liquid and the solid phases, in the case of high Pb(II) concentration. It should be also mentioned that the adsorption is not a diffusion-controlled process since the adsorption seems to be faster for Pb(II) for all concentrations which was studied.

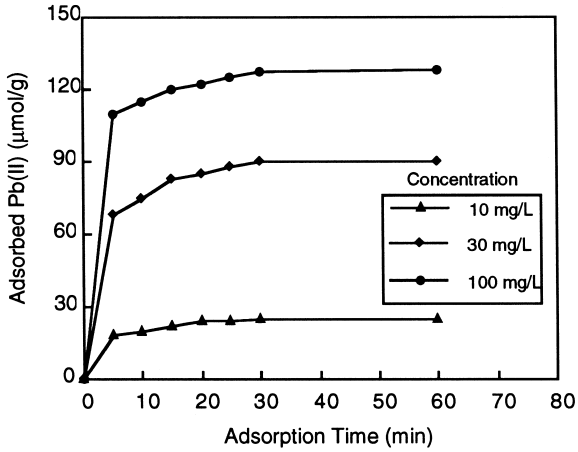

Figure 5. Adsorption rates of Pb(II) on the HMDA-incorporated mPMMA microbeads.

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Data on the adsorption kinetics of heavy metal ions by various sorbents have shown a wide range of adsorption rates. Konishi *et al.* Studied the recovery of cadmium by biopolymer gel particles of alginic acid and they reported high adsorption rates, in which equilibrium was achieved in about 60-90 minutes [15]. Reed and Matsumoto reported 6 hours as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent [16]. Sarkar *et al.* studied the effect of shaking time on the adsorption of heavy metals on silica and reported that the equilibrium time is 2 hours [17]. Shreedhara-Murthy and Ryan investigated mercury, copper, cadmium, lead, and uranium adsorption on cellulose-dithiocarbamate resins and reported that the adsorption rates were very slow [18]. Egawa has studied uranium adsorption on polyacrylonitrile fibers containing amidoxime groups and reported a 7 hour equilibrium adsorption time [19]. There are several parameters which determine the adsorption rate such as stirring rate (or flow) in the aqueous phase, structural properties of sorbent (e.g., surface area and topography, porosity, swelling degree), amount of sorbent, ion properties (e.g., hydrated ionic radius, coordination complex number), initial concentration of heavy metal ions, chelate-formation rate between the ligand and the metal ions, and of course, the existence of other metal ions which may compete with the metal ions of interest for the same active binding sites. Therefore, it is too difficult to compare the adsorption rates reported. However, the adsorption rates obtained with the HMDA-incorporated mPMMA microbeads produced by us seem to be rather good.

Adsorption Capacity

Effect of Initial Concentration of Pb(II)

The adsorption capacities of the Pb(II) ions of the HMDA-incorporated mPMMA microbeads are given as a function of the initial concentration of metal ions within the aqueous phase in Figure 6. It should be noted that the non-specific adsorption of Pb(II) onto the plain microbeads was low, about 4.2 μmol/g. There is no ion-exchange or metal chelating groups onto the plain mPMMA microbeads. This adsorption may be due to the residuals of the surfactant molecules (i.e., polyvinyl alcohol) on the mPMMA microbeads entrapped during the solvent evaporation polymerization. Pb(II) ions can be also adsorbed non-specifically 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 heavy metal ions therefore may diffuse and absorb (or entrap) within the pores of the microbeads which may cause these non-specific-adsorption.

While higher adsorption values were obtained when the HMDA-incorporated microbeads. Pb(II) adsorption capacity of the HMDA-incorporated mPMMA microbeads increased first with the increasing of initial concentration of Pb(II) then reached a plateau value at about an initial Pb(II) concentration of 50 mg/L. The maximum Pb(II) adsorption capacity is 128 μmol/g. This may be

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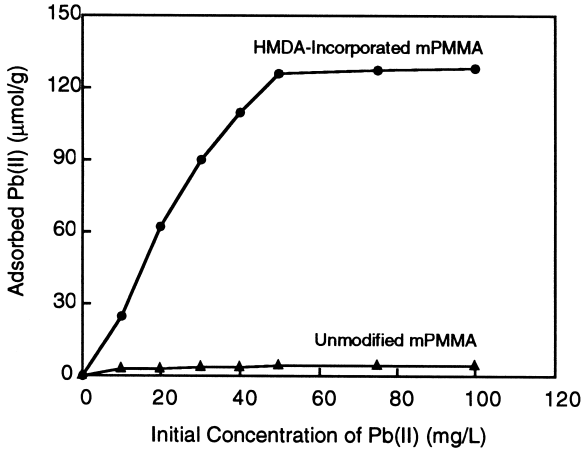

Figure 6. Pb(II) adsorption capacity of the HMDA-incorporated microbeads. T: 20ºC and pH: 6.0.

due to the 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 85 μmol HMDA which was found by elemental analysis. From the mass-stoichiometry, it seems that one attached HMDA molecule interacts from one to two Pb(II) ions. Note that the nitrogen atoms of HMDA are available for interaction with heavy metal ions.

Different polymeric sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Liu *et al.* achieved 460 μmol Pb(II)/g adsorption capacity with N-hydroxymethyl thioamide resin [20]. Saglam *et al.* have used *Phanerochaete chrysosporium* microorganisms for biosorption of inorganic mercury and alkylmercury species [21]. The maximum amounts of adsorption capacity achieved was around 300 μmol/g dry weight of microorganisms. Denizli *et al*. used Alkali Blue 6B-attached P(EGDMA-HEMA) sorbents, in which the maximum adsorption capacity was 618 μmol Pb(II)/g [22]. Denizli et al reported 120 μmol Pb(II)/g removal capacity for cibacron blue F3GA carrying polyethyleneglycolmethacrylate gel beads [23]**.** From the data that we found in this study, we may conclude that the HMDA-incorporated magnetic polymethylmethacrylate micro-beads is promising for the removal of Pb(II) ions from aqueous media.

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Effects of pH

The complexation of heavy metal ions by a chelating-ligand is usually a strong function of pH [24]. The hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species. As discussed in detail by several researchers [25], hydrolysis of Pb(II) ions becomes significant at approximately pH 7.0-8.0. Therefore, in the present study we changed the pH range between 2.0-6.0. Figure 7 shows the pH profile data for Pb(II) adsorption. This figure shows that complexation behavior of Pb(II) 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 [26, 27]. Thus 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 at around pH 5.0. High adsorption at higher pH values implies that Pb(II) ions interact with amino (unprotonated) groups by chelating. Plateau value is 128 μmol/g.

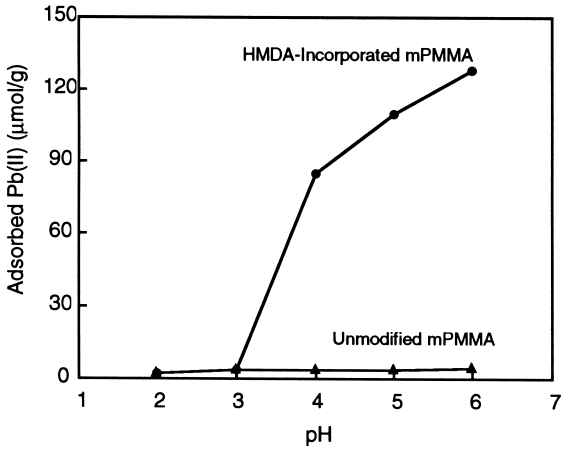

Figure 7. Effect of pH on adsorption of Pb(II) ions on the HMDA-incorporated microbeads. Initial concentration of Pb(II): 60 mg/L; T: 20°C.

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Regeneration of Microbeads

Elution experiments were carried out in 0.1 M HNO_3 solution. The HMDA-incorporated microbeads loaded with the maximum amounts of Pb(II) were placed within the desorption medium and the amount of Pb(II) desorbed in 30 minutes was measured. Figure 8 shows the adsorption-desorption data of Pb(II) after several cycles of consecutive adsorption and desorption procedure. When HNO_3 was used as a desorption agent, the coordination spheres of chelated

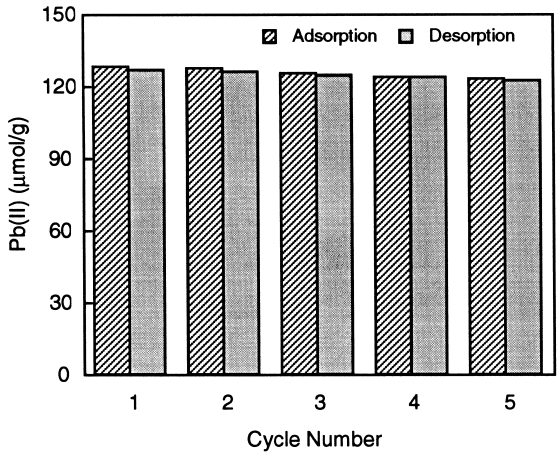

Figure 8. Adsorption-desorption cycles for heavy metal ions.

Pb(II) ions is disrupted and subsequently Pb(II) release from the solid surface into the desorption medium. This figure clearly shows that these microbeads can be used repeatedly without significantly losing their adsorption capacities for Pb(II) ions.

CONCLUSION

Magnetic carrier technology enables the use of magnetic processing for rapid and selective heavy metal removal. Magnetic polymethylmethacrylayte microbeads carrying hexamethyl-ene diamine (85 μmol/g) were used for adsorption/desorption of Pb(II) ions from aqueous solution under different experimental conditions. High adsorption rates are observed at the beginning of adsorption process, and then plateau values (i.e., adsorption equilibrium) are gradually reached in about 20 minutes. Adsorption of Pb(II) ions on the unmodified mPMMA microbeads was very low [4.2 μmol/g]. Maximum Pb(II) adsorption capacity of HMDA incorporated microbeads was 128 μmol/g. Adsorption amounts of Pb(II) ions increased with increasing pH and reached almost a plateau value around pH 5.0. Desorption was performed by using 0.1 M HNO_3 and very high desorption ratios were achieved up to 98%. From the results presented in this paper it can be concluded that the HMDA-incorporated magnetic PMMA microbeads may effectively (means with high adsorption rates and capacities) be used

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