

Removal of Heavy-Metal Ions by Magnetic Beads Containing Triazole Chelating Groups

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ABSTRACT: The aim of this study was to prepare magnetic beads that could be used for the removal of heavy-metal ions from synthetic solutions. Magnetic poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole) [*m*-poly(EGDMA-VTAZ)] beads were produced by suspension polymerization in the presence of a magnetite Fe₃O₄ nanopowder. The specific surface area of the *m*-poly(EGDMA-VTAZ) beads was 74.8 m²/g with a diameter range of 150–200 μm, and the swelling ratio was 84%. The average Fe₃O₄ content of the resulting *m*-poly(EGDMA-VTAZ) beads was 14.8%. The maximum binding capacities of the *m*-poly(EGDMA-VTAZ) beads from aqueous solution were 284.3 mg/g for Hg²⁺, 193.8 mg/g for Pb²⁺, 151.5 mg/g for Cu²⁺,

128.1 mg/g for Cd²⁺, and 99.4 mg/g for Zn²⁺. The affinity order on a mass basis was Hg²⁺ > Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺. The binding capacities from synthetic waste water were 178.1 mg/g for Hg²⁺, 132.4 mg/g for Pb²⁺, 83.5 mg/g for Cu²⁺, 54.1 mg/g for Cd²⁺, and 32.4 mg/g for Zn²⁺. The magnetic beads could be regenerated (up to ca. 97%) by a treatment with 0.1M HNO₃. These features make *m*-poly(EGDMA-VTAZ) beads potential supports for heavy-metal removal under a magnetic field. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2246–2253, 2009

Key words: adsorption; magnetic polymers; conjugated polymers; gels

INTRODUCTION

Contamination of water by heavy-metal ions is a serious hazard to the environment and health because of the toxic effects of these ions at very low concentrations.¹ Heavy metals are metabolic poisons and enzyme inhibitors.² They can cause mental retardation and semipermanent brain damage. Heavy metals are classified as persistent environmental toxic substances because they cannot be rendered harmless by chemical or biological remediation processes.³ Heavy metals are released into the environment in a number of different ways. Coal combustion, sewage wastewater, automobile emissions, battery manufacturing, mining activities, tanneries, alloy industries, and the utilization of fossil fuels are just a few examples.⁴

Much research is being conducted to develop methods to remove heavy-metal ions, particularly from waste streams of hydrometallurgy and related industries, and to subsequently reuse them. The conventional treatments used to remove heavy metals from

wastewater are precipitation, coagulation, solvent extraction, reduction, neutralization, electrochemical separation through membranes, ion exchange, and adsorption.^{3–8}

Adsorption is considered to be an effective and economical method for the removal of heavy-metal ions. Toxic-metal-ion removal with polymers would be of great importance in environmental applications.^{9–16} Several criteria are important in the design of metal-chelating polymers with substantial stability for the selective removal of metal ions: specific and fast complexation of the metal ions and the reusability of the metal-chelating polymer.¹⁷ A large number of polymers incorporating a variety of chelating ligands have been investigated.^{18–24} An expensive and critical step in the preparation process is the coupling of a chelating ligand to the support. The major issue is the slow release of the covalently bonded chelators off the matrix. Release is a general problem encountered in any ligand binding technique and causes a decrease in the binding capacity.^{15–20} The length of time and high cost of the chelating procedure have inspired a search for suitable low-cost supports.

Magnetic beads are currently enjoying a fairly ample range of applications in many fields, including biotechnology, nanotechnology, biochemistry, colloid sciences, and medicine.²¹ Their magnetic character implies that they respond to a magnet, and this makes sampling and collection easier and faster,

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but their magnetization disappears once the magnetic field is removed. A magnetically stabilized fluidized bed promises to solve many of the problems associated with chromatographic separations in packed beds and in conventional fluidized bed systems.²² Magnetic carriers combine some of the best characteristics of fluidized beds (a low pressure drop and high feed-stream solid tolerances) and fixed beds (an absence of particle mixing, high mass-transfer rates, and good fluid–solid contact). Magnetic beads are more commonly manufactured from polymers because they have a variety of surface functional groups that can be tailored for use in specific applications. Different synthetic and natural polymeric magnetic beads in the diameter range of 50–300 μm are used in different applications.^{23,24}

For these reasons, we focused our attention on the development of magnetic beads for the assembly of a new class of novel heavy-metal supports. In this work, we show that magnetic poly(ethylene glycol dimethacrylate–1-vinyl-1,2,4-triazole) [*m*-poly(EGDMA–VTAZ)] beads can be used directly for heavy-metal removal under a magnetic field. This novel approach for the preparation of supports has many advantages over conventional supports, which need the activation of a matrix for metal-chelating ligand immobilization. In this study, the comonomer 1-vinyl-1,2,4-triazole (VTAZ) acted as the metal-chelating ligand, and there was no need to activate the matrix for the chelating-ligand immobilization. The ligand immobilization step was also eliminated. VTAZ was polymerized with ethylene glycol dimethacrylate (EGDMA), and there was no leakage of the ligand.

EXPERIMENTAL

Materials

EGDMA was obtained from Merck (Darmstadt, Germany), purified by passage through active alumina, and stored at 4°C until use. VTAZ (Aldrich, Steinheim, Germany) was distilled *in vacuo* (74–76°C, 10 mmHg). 2,2'-Azobisisobutyronitrile (AIBN) was obtained from Fluka AG (Buchs, Switzerland). Poly(vinyl alcohol) (PVAL; weight-average molecular weight = 100,000, 98% hydrolyzed) was supplied by Aldrich. Magnetite nanopowder (Fe_3O_4 ; diameter = 20–50 nm) was obtained from Sigma (USA). All other chemicals were reagent-grade and were purchased from Merck AG. All water used in the binding experiments was purified with 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. Buffer and sample solutions were prefil-

tered through a 0.2- μm membrane (Sartorius, Göttingen, Germany). All glassware was extensively washed with dilute nitric acid before use.

Preparation of the *m*-poly(EGDMA–VTAZ) beads

EGDMA and VTAZ were polymerized in a suspension with AIBN and PVAL as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as a pore former. A typical preparation procedure was as follows. A continuous medium was prepared by the dissolution of PVAL (200 mg) in purified water (50 mL). For the preparation of the dispersion phase, EGDMA (6 mL, 30 mmol), magnetite Fe_3O_4 nanopowder (1.0 g), and toluene (4 mL) were stirred for 15 min at room temperature. Then, VTAZ (3 mL; 30 mmol) and AIBN (100 mg) were dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by mechanical stirring of the mixture (400 rpm) in a sealed Pyrex (USA) cylindrical polymerization reactor. The reactor content was heated to the polymerization temperature (i.e., 70°C) within 4 h, and the polymerization was conducted for 2 h with a 600 rpm stirring rate at 90°C. The final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then dried at 50°C in a vacuum oven. The magnetic beads then were sieved to different sizes. An inspection with a microscope showed that almost all the magnetic beads were perfectly spherical.

Characterization experiments

The porosity was measured with an N_2 gas sorption technique performed on a Flowsorb II (Micromeritics Instrument Corp., Norcross, GA). The specific surface area of the beads in a dry state was determined with a multipoint Brunauer–Emmett–Teller (BET) apparatus (Nova 2200E, Quantachrome, USA). The beads (0.5 g) were placed in the BET sample holder and degassed by passage through N_2 gas at 150°C for 1 h. The adsorption of the N_2 gas onto the beads was performed at –210°C, whereas the desorption was performed at room temperature. Experimental values obtained from the desorption step were used to calculate the specific surface areas of the beads. Pore volumes and average pore diameters for the beads were determined with the Barrett–Joyner–Halenda (BJH) model. The average size and size distribution of the beads were determined by screen analysis performed with standard sieves (model AS200, Retsch GmbH & Co., Haan, Germany).

The water uptake ratios for the beads were determined with distilled water. The water uptake experiments were conducted as follows: dry beads were carefully weighed out (± 0.0001 g) before being

soaked into 50-mL vials containing distilled water. The vials were then placed into an isothermal water bath at 25°C for 2 h, after which the wet bead samples were taken out of the vials, wiped with filter paper, and weighed out. The water content of the beads was calculated with the following expression:

$$\text{Water uptake ratio(\%)} = [(W_s - W_o)/W_o] \times 100 \quad (1)$$

where W_o and W_s are the weights of the beads before and after water uptake, respectively.

The surface structures of the beads were visualized and examined with scanning electron microscopy (SEM). After the bead samples were dried at 25°C for 7 days, tiny fragments of the bead samples were mounted on SEM sample holders on which they were sputter-coated for 2 min. The samples were then consecutively mounted in a scanning electron microscope (JEM 1200EX, JEOL, Tokyo, Japan) to visualize the surface structure of each bead sample at desired magnification levels.

The magnetization curves of the bead samples were measured with a vibrating sample magnetometer (model 150A, Princeton Applied Research, USA).

The presence of magnetite nanopowders in the bead samples was investigated with an electron spin resonance (ESR) spectrophotometer (EL 9, Varian, USA).

Removal of heavy-metal ions from aqueous solutions

The removal of heavy-metal ions from aqueous solutions was studied for the *m*-poly(EGDMA-VTAZ) beads. The heavy-metal solutions (Hg^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+}) were prepared in ultrapure water by gradual dilution of the stock solution (1000 ppm) to the desired concentrations. Nitrate salt was used as the source of heavy-metal ions. The beads suspended in pure water were degassed under reduced pressure (with a water suction pump) and magnetically stabilized into a column (10 cm \times 0.9 cm internal diameter) equipped with a water jacket for temperature control. The magnetic field was generated by two direct-current-powered modified Helmholtz coils (1.5 cm in diameter and 2.5 cm thick) spaced 4 cm apart. At a current of 1.6 A (50 W), each coil produced a magnetic field of 4.0×10^{-3} T. The heavy-metal solution was introduced into the column from underneath the grid with a peristaltic pump and circulated in the system via the storage tank. The volumetric flow rate of the circulating heavy-metal solution was measured by a flowmeter incorporated into the flow circuit, from which the superficial velocity was calculated. The dynamic binding capacity was calculated from metal-ion breakthrough curves. The pressure differences across

the grid under all the investigated flow conditions were negligible (<5 Pa). The concentration of the heavy-metal ions in the aqueous phase after the desired treatment periods was measured with a graphite furnace atomic absorption spectrophotometer (Analyst 800, PerkinElmer, USA). The instrument response was periodically checked with known metal 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 metal-ion binding per unit mass of the beads was evaluated with a mass balance.

Removal of heavy-metal ions from synthetic wastewater

The binding of heavy-metal ions from synthetic wastewater was carried out in the continuous system described previously. A solution (100 mL) containing 0.5 mmol/L of each metal ion [i.e., Hg^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , and Cu^{2+}] was pumped through the column at pH 7.0 and room temperature. The synthetic wastewater also contained Ni^{2+} , Fe^{2+} , Co^{2+} , Sn^{2+} , and Ag^+ . The concentration of each metal ion in the synthetic wastewater was 0.1 mmol/L. To adjust the salinity, 700 ppm NaCl was added to the synthetic wastewater. The synthetic wastewater solution was prepared according to European Union Directive 91/271/EEC. After the binding, the concentration of the metal ions in the remaining solution was determined by AAS as described previously.

Regeneration and repeated use

Metal ions bound to *m*-poly(EGDMA-VTAZ) in a column were eluted by the circulation of a desorbing agent, a solution of 0.1M HNO_3 , through the magnetically stabilized fluidized bed. The elution agent (50 mL) was recirculated through the magnetically stabilized fluidized bed for 1 h at room temperature. The final metal-ion concentration in the elution medium was determined with the graphite furnace atomic absorption spectrometer. The elution ratio was calculated from the amount of metal ions adsorbed on the *m*-poly(EGDMA-VTAZ) beads and the final metal-ion concentration in the elution medium. To evaluate the reusability of the magnetically stabilized fluidized bed, the metal-ion binding-elution cycle was repeated five times for the same magnetically stabilized fluidized bed.

TABLE I
Physical Properties of the *m*-Poly(EGDMA) and *m*-Poly(EGDMA-VTAZ) Beads

Polymer	Surface area (m ² /g) ^a	Total pore volume (mL/g) ^b	Average pore diameter (Å) ^c
<i>m</i> -Poly(EGDMA)	65.8	0.095	740
<i>m</i> -Poly(EGDMA-VTAZ)	74.8	0.122	800

^a Determined with the multipoint BET method.

^b BJH cumulative desorption pore volume between 20 and 245 Å.

^c BJH desorption average pore diameter between 20 and 245 Å.

RESULTS AND DISCUSSION

Characterization studies

m-Poly(EGDMA-VTAZ) beads were prepared in the diameter range of 150–200 μm. The specific surface areas, total pore volumes, and average pore diameters of the *m*-poly(EGDMA) and *m*-poly(EGDMA-VTAZ) beads are presented in Table I. The specific surface area of the *m*-poly(EGDMA-VTAZ) beads was found to be 74.8 m²/g polymer by multipoint BET measurements. According to the BJH method, the pore diameter of the *m*-poly(EGDMA-VTAZ) beads changed between 20 and 1000 Å, and the average pore diameter was 800 Å. This indicated that the *m*-poly(EGDMA-VTAZ) beads contained mainly mesopores. This pore diameter is possibly in the range of diffusion of heavy-metal ions. The ionic radius of the heavy-metal ions studied here is in the range of 72–120 pm. On the basis of these data, it was concluded that the *m*-poly(EGDMA-VTAZ)

beads had effective pore volumes and dimensions for heavy-metal ions. The equilibrium swelling ratio for *m*-poly(EGDMA-VTAZ) was 84%. This pore diameter is possibly in the range of diffusion of metal ions.

The surface morphology and bulk structures of the *m*-poly(EGDMA-VTAZ) beads were visualized with SEM; SEM images are presented in Figure 1. All the beads had a spherical form and rough surface. In the SEM image of the bulk structure, a large quantity of well-distributed pores could be observed, and they were netlike. It is well known that, to facilitate the diffusion of metal ions, the beads should have large pores. The *m*-poly(EGDMA-VTAZ) beads prepared in this study had these characteristics, and these mesopores would increase the specific surface area and binding capacity of the beads as well as the mass-transfer rate of binding metal ions.

Magnetic characteristics of magnetic materials are generally related to their types, whereas those of magnetic materials are usually related to the content of the magnetic component inside. Therefore, the Fe₃O₄ content is very important to the magnetic responsiveness of magnetic materials. In general, a higher Fe₃O₄ content leads to stronger magnetic responsiveness.²⁵ For this reason, the average Fe₃O₄ content of the *m*-poly(EGDMA-VTAZ) beads was determined by density analysis. The hydrated density of the *m*-poly(EGDMA-VTAZ) beads measured at 25°C was 1.28 g/mL. By the same procedure, the density of Fe₃O₄ particles was found to be 1.97 g/mL at 25°C. The density of nonmagnetic poly(EGDMA-VTAZ) beads measured at 25°C was 1.16 g/mL. The magnetic particle volume fraction (ϕ) in the *m*-poly(EGDMA-VTAZ) beads could be

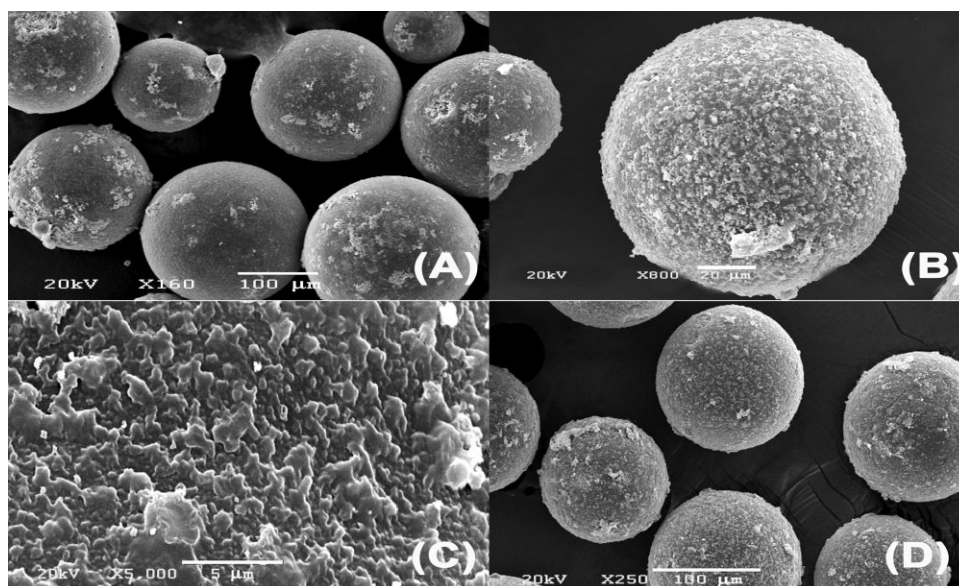


Figure 1 SEM photographs of the *m*-poly(EGDMA-VTAZ) beads: (A–C) before and (D) after ball milling.

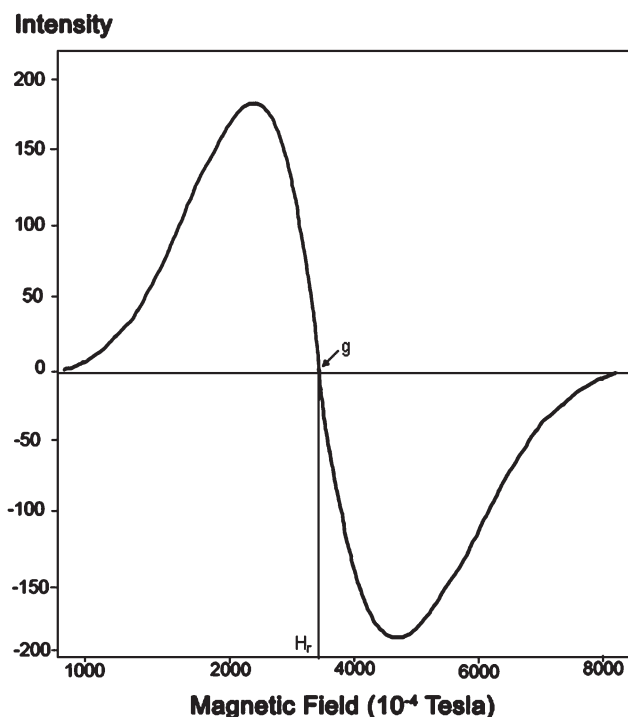


Figure 2 ESR spectrum of the *m*-poly(EGDMA-VTAZ) beads.

calculated with the following equation derived from the mass balance:

$$\phi = (\rho_C - \rho_M) / (\rho_C - \rho_A) \quad (2)$$

where ρ_A , ρ_C , and ρ_M are the densities of the nonmagnetic poly(EGDMA-VTAZ) beads, Fe_3O_4 nanopowder, and *m*-poly(EGDMA-VTAZ) beads, respectively. Thus, with the density data mentioned previously, the gel volume fraction of the *m*-poly(EGDMA-VTAZ) beads was estimated to be 85.2%. Therefore, the average Fe_3O_4 content of the resulting *m*-poly(EGDMA-VTAZ) beads was 14.8%.

The presence of magnetite nanopowder in the polymer structure was also confirmed by ESR. The intensity of the magnetite peak against the magnetic field (T) is shown in Figure 2. A peak of magnetite was detected in the ESR spectrum. It should be noted that the nonmagnetic beads could not be magnetized under this condition. This reflects the responsiveness of magnetic materials to changes in the external magnetic field first, and it characterizes the ability of magnetic materials to retain magnetic field strength when an external magnetic field is removed. To show the magnetic stability, the *m*-poly(EGDMA-VTAZ) beads were kept in distilled water and ambient air for 3 months, and the same ESR spectrum was obtained.

With the goal of testing the mechanical stability of the *m*-poly(EGDMA-VTAZ) beads, a bead sample

was treated in a ball mill for 12 h. SEM photographs showed that 0% of the sample was broken.

The *g* factor given in Figure 2 can be considered a quantity characteristic of the molecules in which the unpaired electrons are located, and it is calculated with eq. (3). The measurement of the *g* factor for an unknown signal can be a valuable aid in the identification of a signal. In the literature, the *g* factor for Fe^{3+} is reported to be between 1.4 and 3.1 for low-spin complexes and between 2.0 and 9.7 for high-spin complexes.²⁶ The *g* factor was found to be 3.22 for the *m*-poly(EGDMA-VTAZ) structure:

$$g = hv / \beta H_r \quad (3)$$

where *h* is Planck's constant (6.626×10^{-34} J.s), *v* is the frequency (9.707×10^9 Hz), β is a universal constant (9.274×10^{-18} J/T), and H_r is the resonance of the magnetic field (T).

Magnetic properties of the polymeric structure were also determined with the electron mass unit (EMU), which shows the behavior of magnetic beads in a magnetic field with a vibrating magnetometer (Fig. 3), and with the H_r value, which is defined as the external magnetic field at resonance. In the EMU spectrum and from the H_r value, a magnetic field of 3450×10^{-4} T was found to be sufficient to excite all the dipole moments present in 1.0 g of a sample. This value will be an important design parameter for a magnetically stabilized fluidized bed or magnetic filtration using the beads. The value of this magnetic field is a function of the flow velocity, bead size, and magnetic susceptibility of the solids to be removed. In the literature, this value has been reported to change from 8 to 20 kG for various applications, so the magnetic beads presented in this study will need less magnetic intensity in a magnetically stabilized fluidized bed.²⁷

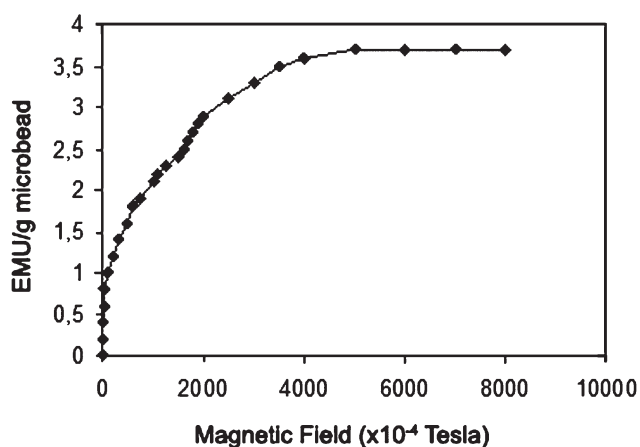


Figure 3 Magnetic behavior of the *m*-poly(EGDMA-VTAZ) beads.

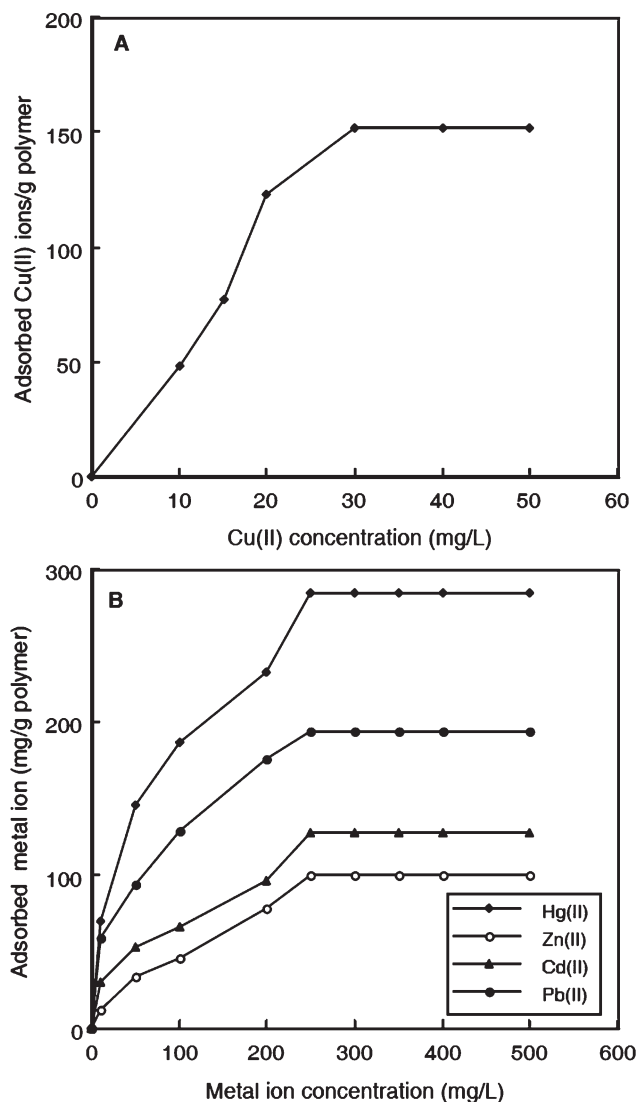


Figure 4 Binding isotherms of the *m*-poly(EGDMA-VTAZ) beads (flow rate = 0.5 mL/min, pH = 5.0, temperature = 25°C).

Heavy-metal removal from aqueous solutions

Binding isotherms

Figure 4 shows the dependence of the equilibrium concentration on the amount of metal ions bound onto the *m*-poly(EGDMA-VTAZ) beads. The amount of metal ions bound per unit mass of the polymer increased first with the concentration of metal ions and then reached a plateau value that represented saturation of the active binding sites on the magnetic beads. This was obvious because more efficient utilization of the binding capacities of the beads was expected on account of a greater driving force with a higher concentration gradient. The binding of metal ions reached a saturation level at a bulk concentration, that is, at about 250 mg/L. Because of the precipitation possibility of the Cu^{2+} ions, initial concentration values were much lower than the others;

therefore, a separate graph for the Cu^{2+} ions is given [Fig. 4(A)]. The binding capacities of the magnetic beads were 284.3 mg/g for Hg^{2+} , 193.8 mg/g for Pb^{2+} , 151.5 mg/g for Cu^{2+} , 128.1 mg/g for Cd^{2+} , and 99.4 mg/g for Zn^{2+} . It appears that the magnetic beads had the strongest affinity for Hg^{2+} ions. The binding order of these five kinds of metal ions on a mass basis for the single-component metals was $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$.

The binding trend is presented on the mass basis (mg) metal binding per gram beads, and these units are important for quantifying respective metal capacities in real terms.²⁸ However, a more effective approach for this work is to compare metal binding on a molar basis; this gives a measure of the total number of metal ions adsorbed, in contrast to the total mass, and is an indication of the total number of binding sites available on the support for each metal. Additionally, calculation on a molar basis is the only accurate way of investigating competition in multicomponent metal mixtures. Molar basis units are measured as millimoles per gram of dry magnetic beads. The binding capacities of the magnetic beads on a molar basis were 1.41 mmol/g for Hg^{2+} , 0.93 mmol/g for Pb^{2+} , 2.38 mmol/g for Cu^{2+} , 1.14 mmol/g for Cd^{2+} , and 1.52 mmol/g for Zn^{2+} . The order of capacity of the magnetic beads on a molar basis for the single-component metals was $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$. The difference in the behavior of these metal ions may be related to the strength of their coordination complexes with triazole.

Effect of the flow rate

The flow rate of a heavy-metal solution through a magnetic column is a very important parameter for controlling the time of binding and analysis.^{29,30} The binding capacity of the *m*-poly(EGDMA-VTAZ) beads for metal ions at different flow rates is shown in Figure 5. The studies showed that the flow rate influenced the binding of the heavy-metal ions. Moreover, the magnetic beads showed homogenous fluidization over the whole range of flow rates without any agglomeration. The results showed that heavy-metal ions were bound quantitatively by the magnetic beads at a flow rate of 0.5–4.0 mL/min. The metal-ion binding capacity decreased drastically with an increase in the flow rate in the range of 0.5–4.0 mL/min. When the flow rate decreased, the contact time in the column was longer. Thus, the metal ions had more time to diffuse to the pores of the *m*-poly(EGDMA-VTAZ) beads and to bind to the triazole binding sites; hence, a greater binding capacity was obtained. At a flow rate greater than 4.0 mL/min, there was a decrease in the percentage binding

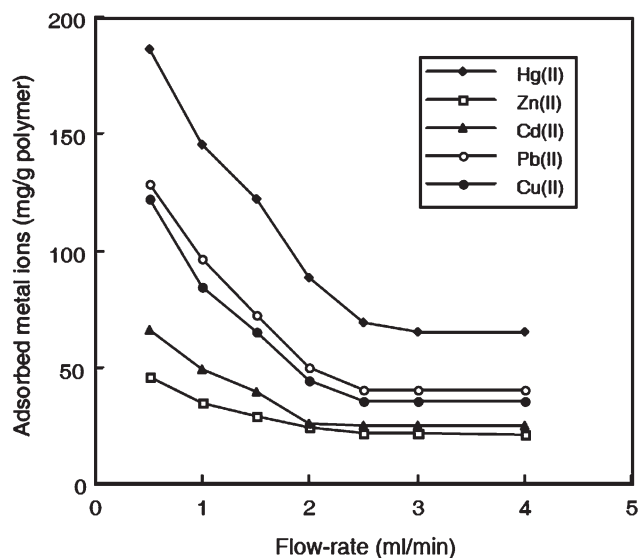


Figure 5 Effect of the flow rate on the metal-ion binding (metal-ion concentration = 20 mg/L for Cu^{2+} and 100 mg/L for other metal ions, temperature = 25°C).

as the heavy-metal ions could not equilibrate properly with the magnetic beads.

Removal of heavy-metal ions from synthetic wastewater

The binding capacities of the *m*-poly(EGDMA-VTAZ) beads from synthetic wastewater for Hg^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , and Cu^{2+} were also studied. The interactive effects of a metal mixture on a polymer matrix are extremely complex and depend on the polymer type, number of metals competing for binding sites, metal combination, levels of metal concen-

tration, residence time, and experimental conditions. Three types of responses may occur: (1) the effect of the mixture is greater than that of each of the individual effects of the constituents in the mixture (synergism), (2) the effect of the mixture is less than that of each of the individual effects of the constituents in the mixture (antagonism), and (3) the effect of the mixture is no more or less than that of each of the individual effects of the constituents in the mixture (noninteraction).³¹ It is worth noting that the binding capacities of the *m*-poly(EGDMA-VTAZ) beads from synthetic wastewater for all metal ions were much lower than those of the single solutions. The most logical reason for the antagonistic action has been claimed to be the competition for the binding sites on the polymer beads and/or a screening effect by the other metal ions. The binding capacities were 178.1 mg/g for Hg^{2+} , 132.4 mg/g for Pb^{2+} , 83.5 mg/g for Cu^{2+} , 54.1 mg/g for Cd^{2+} , and 32.4 mg/g for Zn^{2+} . The magnetic beads exhibited the following metal-ion affinity sequence on a mass basis: $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. In this case, magnetic beads adsorbed other metal ions also [i.e., Ni^{2+} , Fe^{2+} , Co^{2+} , Sn^{2+} , and Ag^{+}]. The presence of other metal ions in the synthetic wastewater decreased the binding capacities of the magnetic beads for Hg^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} ions.

Elution and repeated use

Regeneration is one of the most important strengths of supports, with this capability of supports being considered to have a great influence on their extended applications in improving the process

TABLE II
Heavy-Metal-Ion Adsorption Capacity of the *m*-Poly(EGDMA-VTAZ) Beads After Repeated Adsorption-Desorption Cycles

Cycle	Hg^{2+}		Pb		Cu^{2+}	
	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)
1	284.3 ± 4.2	98.4	193.8 ± 4.5	98.6	151.5 ± 3.3	97.5
2	284.0 ± 4.1	98.2	193.1 ± 4.7	98.2	150.8 ± 3.6	97.2
3	283.2 ± 5.3	97.9	192.6 ± 4.3	98.1	149.2 ± 3.8	97.9
4	282.8 ± 5.2	97.7	192.0 ± 4.9	98.4	148.8 ± 3.5	98.1
5	280.6 ± 4.0	98.3	191.8 ± 4.6	98.5	148.2 ± 3.6	98.2
Cycle	Cd^{2+}		Zn^{2+}			
	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)		
1	128.1 ± 4.4	98.0	99.4 ± 3.6	97.7		
2	127.6 ± 4.6	98.2	98.8 ± 3.2	97.4		
3	126.4 ± 4.3	97.7	98.0 ± 3.9	97.5		
4	125.8 ± 4.5	98.6	97.2 ± 3.8	98.0		
5	125.0 ± 4.6	98.5	96.4 ± 3.0	98.5		

The initial concentrations of metal ions were 50 mg/L for Cu^{2+} and 250 mg/L for the other ions. The flow rate was 0.5 mL/min, the pH was 6.0, and the temperature was 20°C.

economics.³² For this reason, the regeneration property of *m*-poly(EGDMA-VTAZ) beads is worthy of study. The elution of the metal ions from the magnetic beads was performed in a magnetic column. Various factors are probably involved in determining the rates of metal-ion elution, such as the extent of hydration of the metal ions and polymer microstructure. However, an important factor appears to be the binding strength. In this study, elution ratios were high (up to 95%). To determine the reusability of the magnetic beads, binding–elution cycles were repeated five times with the same group of magnetic beads. The binding capacity of the recycled magnetic beads could still be maintained at the 97% level in the fifth cycle (Table II). The magnetic beads can be regenerated and reused, so this provides a potential application.

CONCLUSIONS

Heavy-metal ions are known to be toxic; in particular, cadmium, arsenic, mercury, chromium, copper, lead, nickel, selenium, silver, and zinc are released into the environment in quantities that pose a risk to living systems. Adsorption technology enables the use of magnetic polymeric beads for rapid, cost-effective, reusable, and selective heavy-metal removal. In this study, *m*-poly(EGDMA-VTAZ) beads were prepared and applied to the removal of copper, lead, mercury, zinc, and cadmium ions from aqueous solutions. *m*-Poly(EGDMA-VTAZ) beads have shown great promise in the removal of heavy-metal ions from aqueous media. Some results were as follows: The binding capacities of the *m*-poly(EGDMA-VTAZ) beads were 284.3 mg/g for Hg²⁺, 193.8 mg/g for Pb²⁺, 151.5 mg/g for Cu²⁺, 128.1 mg/g for Cd²⁺, and 99.4 mg/g for Zn²⁺. The affinity order of metal ions on a mass basis was Hg²⁺ > Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺. The binding capacity decreased with an increasing flow rate. Repeated binding and elution cycles showed the feasibility of these newly synthesized *m*-poly(EGDMA-VTAZ) beads for heavy-metal adsorption.

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