

Synthesis and Characterization of Poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole) Copolymer Beads for Heavy-Metal Removal

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ABSTRACT: We prepared poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole) [poly(EGDMA-VTAZ)] beads (average diameter = 150–200 μm) by copolymerizing ethylene glycol dimethacrylate (EGDMA) with 1-vinyl-1,2,4-triazole (VTAZ). The copolymer composition was characterized by elemental analysis and found to contain five EGDMA monomer units for each VTAZ monomer unit. The poly(EGDMA-VTAZ) beads had a specific surface area of 65.8 m^2/g . Poly(EGDMA-VTAZ) beads were characterized by Fourier transform infrared spectroscopy, elemental analysis, surface area measurements, swelling studies, and scanning electron microscopy. Poly(EGDMA-VTAZ) beads with a swelling ratio of 84% were used for the heavy-metal removal studies. The adsorption capacities of the beads for Cd(II), Hg(II), and Pb(II) were investigated in aqueous media containing different amounts of these

ions (5–750 mg/L) and at different pH values (3.0–7.0). The maximum adsorption capacities of the poly(EGDMA-VTAZ) beads were 85.7 mg/g (0.76 mmol/g) for Cd(II), 134.9 mg/g (0.65 mmol/g) for Pb(II), and 186.5 mg/g (0.93 mmol/g) for Hg(II). The affinity order toward triazole groups on a molar basis was observed as follows: Hg(II) > Cd(II) > Pb(II). pH significantly affected the adsorption capacity of the VTAZ-incorporated beads. The equilibrium data were well fitted to the Redlich–Peterson isotherm. Consideration of the kinetic data suggested that chemisorption processes could have been the rate-limiting step in the adsorption process. Regeneration of the chelating-beads was easily performed with 0.1M HNO_3 . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4276–4283, 2006

Key words: adsorption; chromatography; hydrogels

INTRODUCTION

Water pollution due to heavy metals is an issue of great environmental concern.¹ Heavy metals pose serious health hazards through entry into the food chain by anthropogenic pathways. The major effects of heavy-metal poisoning are manifested as neurological and renal disturbances.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 wastewaters, automobile emissions, battery manufacturing, mining activities, tanneries, alloy manufacturing, and the utilization of fossil fuel are just a few examples.⁴ Numerous research studies are being done to develop methods to remove heavy-metal ions, particularly in waste streams of hydrometal-

lurgy and related industries and to subsequently reuse them. These techniques are chemical precipitation, evaporation, ion exchange, solvent extraction, and membrane separation.^{5–8} In the past few decades, adsorption with polymeric materials, has emerged as a potential technique for heavy-metal removal. Polymeric adsorbents are generally preferred for the removal of heavy-metal ions due to their high efficiency, easy handling, availability of different adsorbents, reusability, and cost effectiveness. Toxic metal-ion removal with chelating polymers would be of great importance in environmental applications.^{9–17} Several criteria are important in the design of metal-chelating polymers with substantial stability for the selective removal of metal ions, including specific and fast complexation of the metal ions and the reusability of the metal-chelating polymer. Polymeric adsorbents incorporated with ethylenediamine, poly(ethylenimine), amidoxime, acrylamide, dithiocarbamate, poly-aniline, thiazolidine, and reactive amino acids have been used for the removal of heavy-metal ions.^{18–24}

For these reasons, we focused our attention on the development of chelating beads for the assembly of a new class of adsorbent. In this study, we showed that poly(ethylene glycol dimethacrylate-1-vinyl-

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1,2,4-triazole) [poly(EGDMA-VTAZ)] beads can be used directly for mercury, lead, and cadmium removal. Reactive functional groups containing polymers have many advantages over conventional metal-chelating supports. An expensive and critical step in this preparation process is the coupling of a chelating ligand to the adsorption matrix. The major issue is that of the slow release of this covalently bonded chelators from the matrix. Release, which causes a decrease in chelation capacity, is a general problem encountered in any ligand chelation technique.²⁵ The time-consuming and high cost of the chelating procedure has inspired the search for suitable low-cost reusable adsorbents. In this procedure, 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. 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); we purified it by passing it through active alumina and stored it 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 A. G. (Buchs, Switzerland). Poly (vinyl alcohol) (PVAL; average molecular weight = 100,000; 98% hydrolyzed) was supplied by Aldrich Chem Co. (Steinheim, Germany). All other reagents, unless specified, were analytical grade and were used without further purification. Laboratory glassware was kept overnight in a 5% nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in a dust-free environment. All water used in the chelation experiments was purified with a Barnstead (Dubuque, IA) ROpure LP reverse-osmosis unit with a high-flow cellulose acetate membrane (Barnstead D2731) and a Barnstead D3804 NANO-pure organic/colloid removal and ion-exchange, packed-bed system.

Preparation of the poly(EGDMA-VTAZ) beads

EGDMA and VTAZ were polymerized in suspension with AIBN and PVAL as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as the diluent (a pore former). A typical preparation procedure is as follows. A continuous medium was prepared by the dissolution of PVAL (200 mg) in purified water (50 mL). For the preparation of dispersion phase, EGDMA (6 mL; 32 mmol) and toluene (4 mL) were stirred for 15 min at room temperature. Then, VTAZ (3 mL; 35 mmol) and AIBN (100 mg) were dissolved in the homogene-

ous organic phase. We dispersed the organic phase in the aqueous medium by stirring the mixture magnetically (400 rpm) in a sealed cylindrical Pyrex 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 80°C. The final beads were washed extensively with ethanol and water to remove any unreacted monomer and diluent and were then stored in distilled water at 4°C.

Characterization of the poly(EGDMA-VTAZ) beads

Fourier transform infrared (FTIR) measurements

FTIR measurements were performed on a Shimadzu FTIR 8000 series spectrometer (Kyoto, Japan) in normal transmission mode with a KBr detector over the range 400–4000 cm^{-1} at a resolution of 2 cm^{-1} averaged over 64 scans. All spectra were baseline corrected and normalized to a thickness of 1 μm . The beads were degassed overnight in a vacuum oven maintained at 60°C before the FTIR measurements.

Elemental analysis

To evaluate the degree of VTAZ incorporation, the poly(EGDMA-VTAZ) beads were subjected to elemental analysis with a Leco elemental analyzer (model CHNS-932, St. Joseph, MI).

Surface area and pore size measurements

The polymeric beads were dried in a vacuum oven at 50°C for 24 h. Pore diameters greater than 20 Å were determined by mercury porosimeter up to 2000 kg/cm^2 with a Carlo Erba model 200 (Milano, Italy). The specific surface area of the polymeric beads was determined in a Brunauer Emmet Teller (BET) isotherm of nitrogen with an ASAP2000 instrument (Micromeritics). The average size and size distribution of the beads were determined by screen analysis performed with Tyler standard sieves (Retsch GmbH; Haan, Germany).

Swelling test

The water uptake ratio of the poly(EGDMA-VTAZ) beads was determined in distilled water. The experiment was performed as follows. Initially, dry beads were carefully weighed before they were placed in a 50-mL vial containing distilled water. The vial was put into an isothermal water bath with a fixed temperature ($25 \pm 0.5^\circ\text{C}$) for 2 h. The bead sample was taken from the water, wiped with filter paper, and weighed. The weight ratios of dry and wet samples was recorded.

Scanning electron microscopy studies

The surface morphology and internal structure of the poly(EGDMA-VTAZ) beads were observed via

a scanning electron microscope (Jeol, JEM 1200EX, Tokyo). The poly(EGDMA-VTAZ) beads were dried at room temperature and coated with a thin layer of gold (ca. 100 Å) *in vacuo* and photographed in the electron microscope with 1000× magnification. We determined the particle size by measuring at least 100 beads on photographs taken on a scanning electron microscope.

Single-component heavy-metal adsorption

The adsorption of heavy-metal ions from aqueous solutions was investigated in batch experiments. The effects of the metal-ion concentration and the pH of the medium on the chelation rate and capacity were studied. Aliquots (100 mL) of aqueous solutions containing different amounts of heavy-metal ions (in the range 5–750 mg/L) were treated with the chelating beads. Flasks were stirred magnetically at 600 rpm. The suspensions were brought to the desired pH by the addition of sodium hydroxide (NaOH) and hydrochloric acid (HCl). The pH was maintained in the range of ± 0.1 units until equilibrium was attained. The bead amount was kept constant at 100 mg/100 mL of solution. For kinetic determinations, the solution was centrifuged for certain time intervals, and the supernatant was removed and analyzed for remaining metal ions. Blank trials without polymer bead addition were performed for each tested metal concentration. The concentration of the sample was analyzed with a Shimadzu model AA-6800 flame atomic absorption spectrophotometer. For mercury determinations, a MVU-1A mercury vapor unit was employed (Shimadzu, Kyoto, Japan). Deuterium background correction was applied throughout the experiments, and the spectral slit width was 0.5 nm. The working current/wavelength values and the optimized experimental conditions for mercury measurements were as follows: working current/wavelength = 6 mA/253.6 nm; concentration of $\text{SnCl}_2 = 1\%$ (w/v); concentration of $\text{KMnO}_4 = 0.5\%$ (w/v); concentration of $\text{H}_2\text{SO}_4 = 5\%$ (w/v). The working current/wavelength values for cadmium and lead determinations were 8 mA/228.8 nm and 10 mA/283.3 nm, respectively. The instrument response was periodically checked with known 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 presented, 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. Chelation experiments were carried out at 20°C. The amount of metal ions adsorbed was calculated from mass balance.

Multicomponent heavy-metal adsorption

The adsorption of heavy-metal ions from synthetic wastewater was carried out in a batch system. A solu-

tion (20 mL) containing 0.5 mmol/L of each metal ion [i.e., Cd(II), Pb(II), and Hg(II)] was incubated with the poly(EGDMA-VTAZ) beads at pH 7.0 and at room temperature in the flasks stirred magnetically at 600 rpm. The synthetic wastewater also contained Ni(II), Zn(II), Fe(II), Co(II), Sn(II), and Ag(I). The concentration of each metal ion in the synthetic wastewater was 0.1 mmol/L. To adjust salinity, 700-ppm NaCl was added to the synthetic wastewater. The synthetic wastewater solution was prepared according to the European Union Directive 91/271/EEC. After adsorption, the concentration of the metal ions in the remaining solution was determined by atomic absorption spectroscopy as described previously.

Elution and reuse

Elution efficiency was measured for all of the metals. Elution studies were carried out in 25 mL of a 0.1M HNO_3 solution for 30 min. The chelating beads with adsorbed metal ions were placed in the elution medium and stirred with a magnetic stirrer at 600 rpm at room temperature. The final metal-ion concentration in the aqueous phase was determined via with flame atomic absorption spectrometry. The elution ratio was calculated from the amount of metal ions adsorbed on the beads and the final metal-ion concentration in the desorption medium.

To determine the reusability of the chelating beads, consecutive chelation–elution cycles were repeated 10 times with the same chelating beads.

RESULTS AND DISCUSSION

Properties of the copolymer beads

The crosslinked poly(EGDMA-VTAZ) beads were hydrophilic polymer networks capable of imbibing large amounts of water yet remaining insoluble and preserving their three-dimensional shape. The equilibrium swelling ratio of the poly(EGDMA-VTAZ) beads was 84%. The suspension polymerization procedure provided spherical poly(EGDMA-VTAZ) beads in the size range 150–200 μm . According to mercury porosimetry data, the average pore size of the beads was 740 nm. This indicated that the beads contained mainly macropores. This macropore diameter range was possibly available for the diffusion of heavy-metal ions. The surface morphology and bulk structure of the polymer beads were investigated with the scanning electron photograph in Figure 1. The polymeric beads had a rough surface. The roughness of the surface probably caused an increase in the surface area. This also provided a higher metal adsorption capacity. The specific surface area of the poly(EGDMA-VTAZ) beads was found to be 65.8 m^2/g .

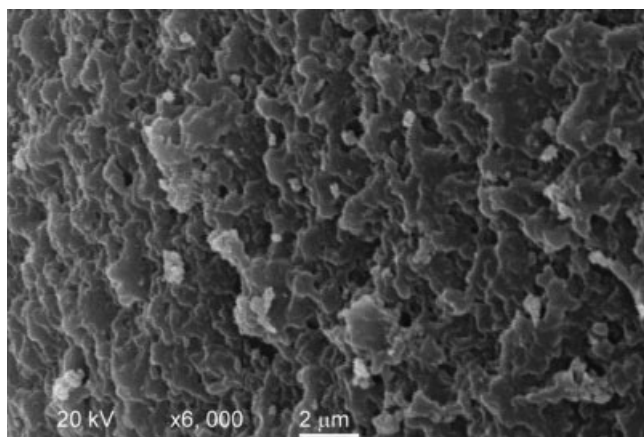


Figure 1 Scanning electron microscopy photograph of the poly(EGDMA-VTAZ) beads.

FTIR and elemental analysis were undertaken to determine the composition and structure of the copolymer beads. The FTIR spectrum of poly(EGDMA-VTAZ) with characteristic peaks appeared at 3120 cm^{-1} (characteristic triazole ring, $\text{C}=\text{C}-\text{H}/\text{N}=\text{C}-\text{H}$), 1458 cm^{-1} ($\text{C}-\text{C}/\text{N}-\text{C}$ stretching), 1272 cm^{-1} (ring vibration), and 1098 cm^{-1} (in-plane ring $\text{C}-\text{H}$ bending; Fig. 2). The carbonyl peak appeared at 1736 cm^{-1} , and the peak at 1149 cm^{-1} was associated with the $\text{C}-\text{O}$ vibration of EGDMA. These data confirmed that the poly(EGDMA-VTAZ) beads con-

tained VTAZ functional groups. Elemental analysis of poly(EGDMA-VTAZ) beads was performed to determine the values of a and b . Elemental analysis indicated a $\text{C}/\text{H}/\text{N}$ ratio of 5:1:1 (Table I). The molar ratio of EGDMA and VTAZ in the poly(EGDMA-VTAZ) beads, as calculated from the nitrogen stoichiometry based on the data shown in Table I, was 5.06:1 or approximately 5:1. This result suggests that most of the polymer was made of repeat units of EGDMA in a ratio of 5:1 with the VTAZ units, that is, $a = 5b$. This result also shows that the copolymerization reaction was complete, as VTAZ monomers that did not form a part of the polymer would have been removed during extensive washing.

The poly(EGDMA-VTAZ) beads were prepared by the copolymerization of EGDMA with VTAZ at a 1:1 molar ratio in the presence of the initiator AIBN. On the basis of the previous information, the general composition of the poly(EGDMA-VTAZ) copolymer is proposed to be

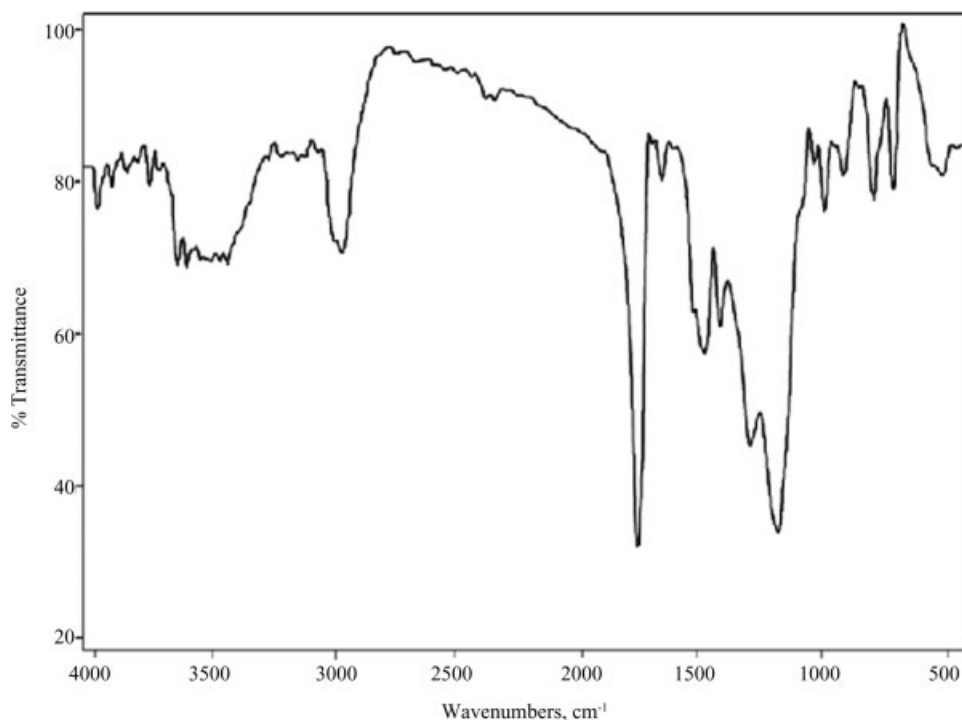
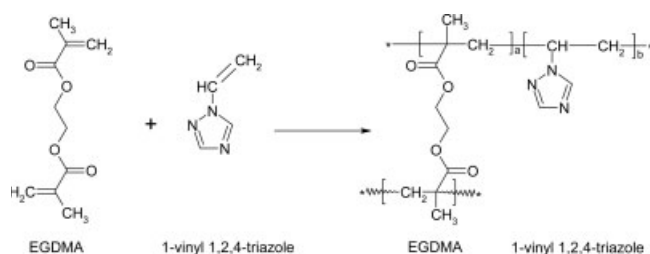


Figure 2 FTIR spectrum of the poly(EGDMA-VTAZ) beads.

TABLE I
Elemental Analysis of the Poly(EGDMA-VTAZ) Beads

	C (%)	H (%)	N (%)
Found	49.85	10.06	9.85
Calcd	53.78	8.45	9.23

Single-component heavy-metal adsorption

Adsorption isotherms

Figure 3 shows the Cd(II), Pb(II), and Hg(II) adsorption curves of the chelating beads. The amount of metal ions adsorbed per unit mass of the polymer increased first with the concentration of metal ions then reached a plateau value, which represented the saturation of the active chelation sites. This was obvious because a more efficient utilization of the adsorption capacity of the adsorbent was expected due to greater driving force by a higher concentration gradient pressure. Adsorption of metal ions reached a saturation level at about 300 mg/L. Because of the precipitation possibility of the heavy-metal ions, we did not increase the initial concentration over 750 mg/L. The binding capacities of the chelating beads were 85.7 mg/g for Cd(II), 134.9 mg/g for Pb(II), and 186.5 mg/g for Hg(II). It appeared that the chelating beads had the strongest affinity for Hg(II) ions. The order of metal-ion chelation was Hg(II) > Pb(II) > Cd(II) on a mass basis.

The expression for binding capacities on a mass basis is important in the quantification of respective metal capacities in real terms. However, a more effective approach is to express metal adsorption on a molar basis because this gives a measure of the total number of metal ions adsorbed, which is an indication of the total number of binding sites available on

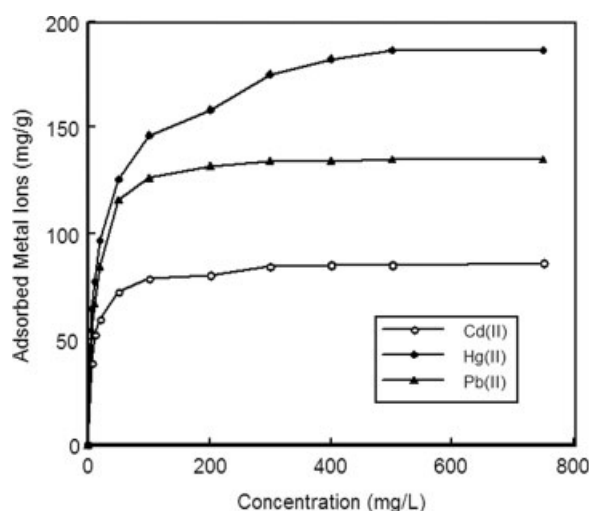


Figure 3 Adsorption capacity of the chelating beads: pH = 5.0; temperature = 20°C. Each datum is the average of five parallel studies.

the adsorbent matrix, to each metal. Additionally, the molar basis of calculation is the only accurate way to investigate competition in multicomponent metal mixtures. The binding capacities of the chelating beads on a molar basis were 85.7 mg/g for Cd(II), 134.9 mg/g for Pb(II), and 186.5 mg/g for Hg(II), respectively. The order of capacity of the chelating beads on a molar basis for the single-component metals was Hg(II) > Cd(II) > Pb(II).

Effect of pH on metal binding

Metal-ion adsorption on chelating adsorbents is pH dependent.²⁶ In the absence of metal-chelating groups, the precipitation of the metal ions is affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by hydroxide or carbonate concentration. The precipitation of metal ions becomes significant at approximately pH 7.0 for all metal ions and also depends on the concentration of metal ions in the medium. Therefore, to establish the effect of pH on the adsorption of metal ions onto the chelating beads, we repeated the batch equilibrium studies at different pH values in the range 3.0–7.0. In this group of experiments, the initial concentration of metal ions was 300 mg/L for all metal ions. No precipitation was observed, which implied that the only removal mechanism was adsorption via thiazole groups. Figure 4 shows the pH effect. It appeared that the newly synthesized chelating beads had the strongest affinity for Hg(II), which was true for all pH values. The affinity order of metal ions at an initial concentration of 300 mg/L was Hg(II) > Pb(II) > Cd(II).

Poly(EGDMA-VTAZ) chelating beads exhibited a low affinity for heavy-metal ions in acidic conditions

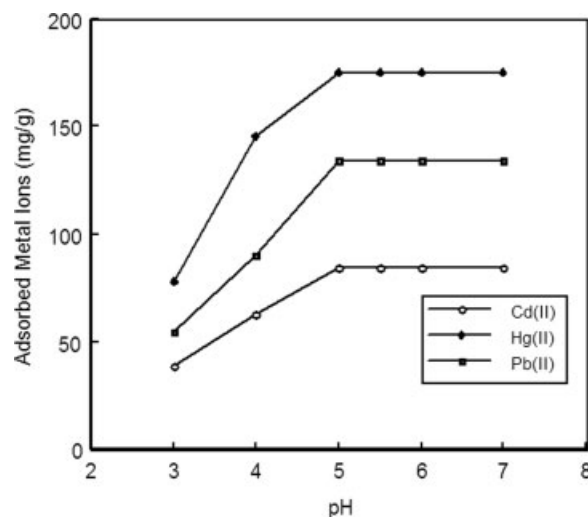


Figure 4 Effect of pH on adsorption of metal ions: concentration of metal ions = 300 mg/L; temperature = 20°C. Each datum is the average of five parallel studies.

(pH < 4.0), a somewhat higher affinity between pH 5.0 and 7.0. The difference in the adsorption behaviors of the heavy-metal ions could be explained by the different affinities of heavy-metal ions for the donor atoms (i.e., nitrogen) in the VTAZ. The difference in coordination behavior was most probably the cause of the relatively high chelation of metal ions at high pH values under noncompetitive chelation conditions.

Adsorption isotherm

Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the kinetics and the equilibria of adsorption. The modeling of the equilibrium data was done with the Langmuir, Freundlich, and Redlich–Peterson isotherms.^{27,28} The Langmuir and Freundlich equations are represented in eqs. (1) and (2), respectively:

$$1/q_e = (1/q_{\max}) + [1/(q_{\max}b)](1/C_e) \quad (1)$$

$$\ln q_e = 1/n(\ln C_e) + \ln K_F \quad (2)$$

where q_{\max} is the maximum adsorption capacity (mg/g), q_e is the experimental amount of heavy-metal ions adsorbed at equilibrium (mg/g), b is the Langmuir isotherm constant, K_F is the Freundlich constant, and n is the Freundlich exponent. $1/n$ is a measure of the surface heterogeneity ranging between 0 and 1, which becomes more heterogeneous as its value gets closer to zero. The ratio q_e gives the theoretical monolayer saturation capacity of poly(EGDMA-VTAZ) beads.

The Redlich–Peterson equation describes adsorption on heterogeneous surfaces, as it contains the heterogeneity factor (β). This equation has three parameters: A , B , and β . The parameter β ranges between 0 and 1. This reduces to the Langmuir equation as β approaches 1. A , B , and β were determined by curve fitting:

$$C_e/g_e = (B/A) + (1/A)C_e^\beta \quad (3)$$

Some model parameters were determined by nonlinear regression with commercially available software and are shown in Table II. A comparison of all of the

theoretical approaches used in this study showed that the Langmuir and Redlich–Peterson equations fit the experimental data best.

The standard deviation of the values determined by regression analysis was comparatively low. Also, the experimental adsorption capacities for the poly(EGDMA-VTAZ) beads were lower than to the theoretical adsorption capacities (i.e., obtained from adsorption models). This difference was due to the steric/geometric hindrances (i.e., accessibility) between the metal ions and the metal-chelating groups (i.e., VTAZ) on the surface of poly(EGDMA-VTAZ) beads.

The essential characteristic of the Langmuir equation can be expressed in terms of the dimension factor (R_L), which was defined by Ho and McKay²⁹ as

$$R_L = 1/(1 + b_L C_0) \quad (4)$$

where C_0 is the highest initial metal concentration (mg/L) and b is the Langmuir constant. The value of R_L indicates the nature of adsorption as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values were 0.0256 for Pb(II), 0.0309 for Cd(II), and 0.0721 for Hg(II). The obtained R_L values showed that the adsorption behavior of heavy-metal ions onto poly(EGDMA-VTAZ) beads was favorable ($R_L < 1$).

Adsorption dynamics

For adsorption kinetics, pseudo-first-order and pseudo-second-order models were used:²⁹

$$\log(q_e - q_t) = \log q_{1\text{cal}} - (k_1 t)/2.303 \quad (5)$$

where q_t is the amount of heavy-metal ions adsorbed at time t (mg/g), k_1 is the equilibrium rate constant of first-order adsorption (1/min), and $q_{1\text{cal}}$ is the adsorption capacity calculated by the pseudo-first-order model (mg/g).

The rate constant for the second-order adsorption could be obtained from the following equation:

$$(t/q_t) = (1/k_2 q_{2\text{cal}}^2) + (1/q_{2\text{cal}})t \quad (6)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$) and $q_{2\text{cal}}$ is the adsorption capacity calculated by the pseudo-second-order kinetic model (mg/g).

TABLE II
Adsorption Parameters Obtained from Langmuir, Freundlich, and Redlich–Peterson Isotherms

Meta ion	Langmuir model			Freundlich model			Redlich–Peterson model			
	q_{\max}	b	R^2	K_F	$1/n$	R^2	A	B	β	R^2
Cd(II)	86.1	0.156	0.999	42.2	0.121	0.943	77.9	1.29	0.94	0.999
Pb(II)	135.1	0.190	0.995	56.2	0.152	0.908	59.9	0.43	0.96	0.995
Hg(II)	188.7	0.064	0.997	63.6	0.175	0.985	40.5	0.34	0.98	0.999

TABLE III
First-Order and Second-Order Kinetic Constants

	Experimental q_e (mg/g)	First-order kinetics			Second-order kinetics		
		k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg/g)	R^2
Cd(II)	85.7	0.060	95.3	0.951	0.0004	101.1	0.986
Pb(II)	134.9	0.069	180.9	0.867	0.0003	158.7	0.995
Hg(II)	186.5	0.092	190.5	0.969	0.0006	175.4	0.993

According to the values in Table III, the optimum results were for both the second- and first-order models, with the second-order mechanism (R^2) values being the highest. These results suggest that the pseudo-second-order mechanisms were predominant and that chemisorption might have been the rate-limiting step that controlled the adsorption process. The rate-controlling mechanism may have varied during the course of the adsorption process as three possible mechanisms may have been occurring.³⁰ There was an external surface mass transfer or film diffusion process that controlled the early stages of the adsorption process. This may have been followed by a reaction or constant-rate stage and, finally, by a diffusion stage where the adsorption process slowed down considerably.³¹

The pore diffusion coefficient (D) for the removal of heavy-metal ions was calculated with the following equation, with the assumption of spherical shape geometry for the adsorbent beads:²⁷

$$t_{1/2} = 0.03r_o^2/D \quad (7)$$

where $t_{1/2}$ is time for half adsorption, r_o is the diameter of the beads, and D is the pore diffusion coefficient (cm²/s). The values of D of heavy-metal ions were found 4.88×10^{-9} cm²/s for Cd(II), 6.01×10^{-9} cm²/s for Pb(II), and 7.82×10^{-9} cm²/s for Hg(II). Thus, the values of pore diffusion rate constants were on the order of 10^{-9} cm²/s for all of the heavy-metal ions studied here, which indicated that the pore diffusion was not significant.

Multicomponent heavy-metal adsorption

The adsorption capacities of the poly(EGDMA-VTAZ) beads from synthetic wastewater for Cd(II), Pb(II), and Hg(II) were also studied. The interactive effects of a metal mixture on a polymer matrix are extremely complex and depend on polymer type, number of metals competing for binding sites, metal combination, levels of metal concentration, residence time, and experimental conditions. Three types of responses may occur: (1) the effect of the mixture can be greater than each of the individual effects of the constituents in the mixture (synergism), (2) the effect of the mixture

can be less than each of the individual effects of the constituents in the mixture (antagonism), and (3) the effect of the mixture may be no more or less than each of the individual effects of the constituents in the mixture (noninteraction).³² The adsorption capacities of the 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 was the competition for the chelation sites on the polymer beads and/or a screening effect by the other metal ions. The adsorption capacities were 58.6 mg/g (0.52 mmol/g) for Cd(II), 81.4 mg/g (0.39 mmol/g) for Pb(II), and 97.2 mg/g (0.48 mmol/g) for Hg(II). The chelating beads exhibited the following metal-ion affinity sequence on molar basis: Cd(II) > Hg(II) > Pb(II). In this case, the chelating beads also adsorbed other metal ions [i.e., Ni(II), Zn(II), Fe(II), Co(II), Sn(II), and Ag(I)]. The presence of other metal ions in the synthetic wastewater decreased the chelation capacities of the chelating beads for Cd(II), Pb(II), and Hg(II) ions.

Elution and repeated use

The elution of the heavy metals from the poly(EGDMA-VTAZ) beads was examined to better understand the adsorption mechanisms and elucidate the feasibility of recovery of both the polymeric beads and metal ions. Elution of the adsorbed metal ions was studied in a batch experimental setup. The poly(EGDMA-VTAZ) beads loaded with the maximum amounts of the respective metal ions were placed within the elution medium containing 0.1M HNO₃, and the amount of metal ions desorbed in 1 h was measured. The elution efficiency was then calculated. The elution efficiencies were very high (up to 99.3%) with the elution agent and conditions used for all of the metal ions. In metal-chelating systems, adsorption (i.e., binding of heavy-metal ions with VTAZ) is completely reversible.

The repeated use of the commercial adsorbents is likely to be a key factor in the improvement of process economics.³³ To determine the reusability of the poly(EGDMA-VTAZ) beads, the adsorption-elution cycle was repeated 10 times with the same adsorbent. As shown in Table IV, the adsorption capacity of the recycled beads was still maintained at the 95% level

TABLE IV
Heavy-Metal-Ion Adsorption Capacity of the Chelating Beads After Repeated Adsorption-Elution Cycles

Cycle	Cd(II)		Pb(II)		Hg(II)	
	Chelation (mg/g)	Elution (%)	Chelation (mg/g)	Elution (%)	Chelation (mg/g)	Elution (%)
1	85.7 ± 4.2	98.0 ± 1.5	134.9 ± 2.1	97.4 ± 1.9	186.5 ± 2.0	97.5 ± 2.4
2	85.2 ± 4.6	98.7 ± 1.7	134.8 ± 2.3	97.7 ± 1.9	186.4 ± 2.1	97.2 ± 2.5
3	85.0 ± 4.5	98.9 ± 1.8	134.4 ± 2.0	98.5 ± 1.8	186.0 ± 2.2	98.5 ± 2.2
4	84.7 ± 3.9	98.6 ± 1.6	134.0 ± 2.1	98.2 ± 1.8	185.7 ± 2.0	98.9 ± 2.2
5	84.5 ± 3.9	98.8 ± 1.5	133.8 ± 2.0	98.1 ± 1.5	185.1 ± 2.1	98.8 ± 2.4
5	84.2 ± 4.0	99.0 ± 1.5	133.5 ± 1.9	98.8 ± 1.5	185.0 ± 2.6	98.9 ± 2.5
6	84.0 ± 4.8	98.5 ± 1.4	133.2 ± 1.8	98.9 ± 1.8	184.6 ± 2.2	98.4 ± 2.3
7	83.7 ± 4.5	98.8 ± 1.6	133.1 ± 1.7	98.1 ± 1.9	184.3 ± 2.2	98.3 ± 2.3
8	83.5 ± 5.0	98.4 ± 1.8	132.8 ± 1.9	97.3 ± 1.9	184.0 ± 2.1	99.0 ± 2.2
9	83.2 ± 5.0	98.5 ± 1.5	132.6 ± 2.2	97.8 ± 1.8	183.6 ± 2.1	98.5 ± 2.0
10	83.0 ± 4.3	98.9 ± 1.7	132.0 ± 2.3	98.0 ± 1.8	183.3 ± 2.0	98.7 ± 2.1

Initial concentration of metal ions = 750 mg/L; pH = 5.0; temperature = 25°C.

in the 10th cycle. Consequently, we concluded that the poly(EGDMA-VTAZ) beads could be used economically in an actual large-scale process.

CONCLUSIONS

Adsorption technology enables one to use polymeric chelating beads for rapid, cost-effective, and selective heavy-metal removal. In this study, chelating beads were prepared and were applied to the removal of lead, mercury, and cadmium ions from aqueous solutions. In this study, we focused our attention on the development of metal-chelating beads for the assembly of a new class of adsorbents. This novel approach for the preparation of a metal-chelating matrix has many advantages over conventional adsorbent preparation techniques, those needed the activation of the matrix for metal-chelating ligand immobilization. In this procedure, the comonomer VTAZ acted as the metal-chelating ligand, and there was no need to activate the matrix for the chelating-ligand immobilization. VTAZ was polymerized with EGDMA, and no leakage of the ligand was observed. This one-step preparation method overcame the drawback of other multistep preparation methods. Our results suggest that poly(EGDMA-VTAZ) beads can be good heavy-metal adsorbents for environmental applications.

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