

# Poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole) beads for heavy metal removal

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## Abstract

Poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole) [poly(EGDMA–VIM)] hydrogel (average diameter 150–200 μm) was prepared by copolymerizing ethylene glycol dimethacrylate (EGDMA) with *n*-vinyl imidazole (VIM). The copolymer hydrogel bead composition was characterized by elemental analysis and found to contain 5 EGDMA monomer units each VIM monomer unit. Poly(EGDMA–VIM) beads had a specific surface area of 59.8 m<sup>2</sup>/g. Poly(EGDMA–VIM) beads were characterized by swelling studies and scanning electron microscopy (SEM). These poly(EGDMA–VIM) beads with a swelling ratio of 78% were used for the heavy metal removal studies. Chelation capacity of the beads for the selected metal ions, i.e., Cd(II), Hg(II) and Pb(II) were investigated in aqueous media containing different amounts of these ions (10–750 mg/l) and at different pH values (3.0–7.0). Chelation rate was very fast. The maximum chelation capacities of the poly(EGDMA–VIM) beads were 69.4 mg/g for Cd(II), 114.8 mg/g for Pb(II) and 163.5 mg/g for Hg(II). The affinity order on molar basis was observed as follows: Hg(II) > Cd(II) > Pb(II). Chelation behavior of heavy metal ions could be modelled using both the Langmuir and Freundlich isotherms. pH significantly affected the chelation capacity of VIM incorporated beads. Chelation of heavy metal ions from synthetic wastewater was also studied. The chelation capacities are 45.6 mg/g for Cd(II), 74.2 mg/g for Hg(II) and 92.5 mg/g for Pb(II) at 0.5 mmol/l initial metal concentration. Regeneration of the chelating-beads was easily performed with 0.1 M HNO<sub>3</sub>. These features make poly(EGDMA–VIM) beads potential candidate adsorbent for heavy metal removal.

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**Keywords:** Heavy metal removal; Chelating beads; *N*-vinyl imidazole; Cadmium(II); Lead(II); Mercury(II)

## 1. Introduction

In the last decades, a remarkable increase of heavy metal contaminant volume has posed many serious environmental problems due to their toxicity to many life forms [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 can not 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 waste-waters, automobile emissions, battery industry, mining activities, tanneries, alloy industries and the utilization of fossile fuels are just a few examples [4]. Nu-

merous research efforts are being done to develop methods to remove heavy metal ions, particularly in waste streams of hydrometallurgy and related industries, and to subsequently reuse them. These techniques are filtration, chemical precipitation, neutralization, chelating ion-exchange and adsorption [3–7]. Among these techniques, 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. Toxic metal ion removal by using chelating polymers would be of great importance in environmental applications [8–18]. 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 as well as the reusability of the metal-chelating polymer. A large number of polymers incorporating a variety of metal-chelating ligands including polyethyleneimine, amidoxime, acrylamide; dithiocarbamate, thiazolidine and amino acids have been prepared and their adsorption and analytical properties were

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investigated [14–24]. An expensive and critical step in this preparation process is coupling of a chelating ligand to the adsorption matrix. The major issue is that of slow release of this covalently bonded chelators off the matrix. Release is a general problem encountered in any ligand chelation technique which caused a decrease in chelation capacity [15–20]. The time consuming and high cost of chelating procedure has inspired a search for suitable low-cost adsorbents.

For these reasons, we have focused our attention on the development of chelating beads for the assembly of a new class of novel heavy metal adsorbents. In this work we show that poly(EGDMA–VIM) beads can be used directly for heavy metal removal. This novel approach for the preparation of metal-chelating matrix has many advantages over conventional preparation techniques, those needed the activation of the matrix for metal-chelating ligand immobilization. In this procedure, comonomer VIM acted as the metal-chelating ligand, and there is no need to activate the matrix for the chelating-ligand immobilization. Chelating-ligand immobilization step was also eliminated. VIM was polymerized with EGDMA and there is no leakage of the ligand also.

## 2. Experimental

### 2.1. Materials

Ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina and stored at 4 °C until use. *N*-Vinyl imidazole (VIM, Aldrich, Steinheim, Germany) was distilled under vacuum (74–76 °C, 10 mm Hg). 2,2'-Azobisisobutyronitrile (AIBN) was obtained from Fluka A.G. (Buchs, Switzerland). Poly(vinyl alcohol) (PVAL; Mw: 100.000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (USA). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the chelation experiments was purified using a Barnstead (Dubuque, IA, USA) 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. The resulting purified water has a specific conductivity of 18 mS.

### 2.2. Preparation of poly(EGDMA–VIM) beads

EGDMA and VIM were polymerized in suspension by using AIBN and poly(vinyl alcohol) as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as the diluent (as a pore former). A typical preparation procedure was exemplified below. Continuous medium was prepared by dissolving poly(vinyl alcohol) (200 mg) in the purified water (50 ml). For the preparation of dispersion phase, EGDMA (6 ml; 30 mmol) and toluene (4 ml) were stirred for 15 min at room temperature. Then,

VIM (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 stirring the mixture magnetically (400 rpm), in a sealed-cylindrical pyrex polymerization reactor. The reactor content was heated to 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. Final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 4 °C.

### 2.3. Characterization of poly(EGDMA–VIM) beads

#### 2.3.1. FTIR Studies

Infrared spectrum was recorded on Shimadzu FTIR 8000 Series, FTIR spectrophotometer (Japan), 15 scans were taken at 4 cm<sup>-1</sup> resolution. Polymer samples were prepared by dispersing in dry KBr pellets and recorded between 4000 and 500 cm<sup>-1</sup>.

#### 2.4. Elemental analysis

In order to evaluate the degree of VIM incorporation, the synthesized poly(EGDMA–VIM) beads were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932, USA).

#### 2.5. Surface area measurements

The specific surface area of the poly(EGDMA–VIM) beads was determined in BET apparatus. The average size and size distribution of the poly(EGDMA–VIM) beads were determined by screen analysis performed by using Tyler Standard Sieves.

#### 2.6. Swelling test

Water uptake ratio of the poly(EGDMA–VIM) beads was determined in distilled water. The experiment was conducted as follows—initially dry beads were carefully weighed before being placed in a 50 ml vial containing distilled water. The vial was put into an isothermal water bath with a fixed temperature (25 ± 0.5 °C) for 2 h. The bead sample was taken out from the water, wiped using a filter paper, and weighed. The weight ratio of dry and wet samples was recorded.

#### 2.7. Surface morphology

The surface morphology of the beads was examined using scanning electron microscopy (SEM). The samples were initially dried in air at 25 °C for 7 days before being analyzed. A fragment of the dried bead was mounted on a SEM sample mount and was sputter coated with gold for 2 min. The sample was then mounted in a scanning electron microscope (Model: Raster Electronen Microscopy, Leitz-AMR-1000, Germany). The surface of the sample was then scanned at

the desired magnification to study the morphology of the beads.

### 2.8. Single-component heavy metal chelation

Chelation of heavy metal ions from aqueous solutions was investigated in batch experiments. Effects of the initial heavy metal ion concentration and pH of the medium on the chelation rate and capacity were studied. 100 ml aliquots of aqueous solutions containing different amounts of heavy metal ions (in the range of 10–750 mg/l) were treated with the chelating beads. Chelation flasks were stirred magnetically at 600 rpm. The suspensions were brought to the desired pH by adding sodium hydroxide (NaOH) and hydrochloric acid (HCl). The pH was maintained in a range of  $\pm 0.1$  units until equilibrium was attained. Investigation amount was kept constant at 100 mg per 100 ml of solution. Blank trials without polymer beads addition were performed for each tested metal concentration. The concentration of the sample was analyzed by using a Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer (Japan). For mercury determinations, MVU-1A (Mercury Vapor Unit) was employed. 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 heavy 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 in order to determine the margin of error. Chelation experiments were carried out at 20 °C. The amount of metal ions adsorbed  $q$  (mg/g polymer) was obtained as follows:

$$q = \frac{[(C_0 - C)V]}{m} \quad (1)$$

Where,  $C_0$  and  $C$  are the initial and equilibrium concentrations (mg/l), respectively;  $V$  is the volume of the aqueous phase (L); and  $m$  is the mass of the beads used (g).

### 2.9. Multi-component heavy metal chelation

Chelation of heavy metal ions from synthetic wastewater was carried out in a batch system. A solution (20 ml) containing 0.5 mmol/l from each metal ions [i.e., Cd(II), Pb(II) and Hg(II)] was incubated with the poly(EGDMA–VIM) beads at a pH of 7.0 at room temperature, in the flasks stirred

magnetically at 600 rpm. Synthetic wastewater also contains Ni(II), Zn(II), Fe(II), Co(II), Sn(II) and Ag(I). Concentration of each metal ions in synthetic wastewater is 0.1 mmol/l. In order to adjust salinity, 700 ppm NaCl was added to the synthetic wastewater. After chelation, the concentration of the metal ions in the remaining solution was determined by AAS as described above.

### 2.10. Elution and reuse

Elution efficiency from the polymer beads was measured for all the metals. Elution of the metals from the polymer beads was carried out in 25 ml of 0.1 M  $\text{HNO}_3$  solution for 30 min. The chelating beads 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 by using a flame atomic absorption spectrometer according to the guidelines of the manufacturers. The elution ratio was calculated from the amount of metal ions adsorbed on the beads and the final metal ions concentration in the desorption medium, by using the following expression.

$$\begin{aligned} \text{Desorption Ratio} \\ &= \frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on the microbeads}} \\ &\quad \times 100 \end{aligned} \quad (2)$$

In order to determine the reusability of the chelating beads, consecutive chelation–elution cycles were repeated ten times by using the same chelating beads.

## 3. Results and discussion

### 3.1. Properties of polymer beads

The suspension polymerization procedure provided crosslinked poly(EGDMA–VIM) beads in the spherical form in the size range of 150–200  $\mu\text{m}$ . The surface morphology and internal structure of polymer beads are investigated by the electron micrographs in Fig. 1. As clearly seen here, the beads have a spherical form and very rough surface due to the pores which formed during the polymerization procedure. The roughness of the surface should be considered as a factor providing an increase in the surface area. In addition, these pores reduce mass transfer resistance and facilitate the diffusion of metal ions because of high internal surface area. This also provides higher metal chelation capacity. Specific surface area of the poly(EGDMA–VIM) beads was found to be 59.8  $\text{m}^2/\text{g}$ . The poly(EGDMA–VIM) beads are crosslinked hydrogels. They do not dissolve in aqueous media, but do swell, depending on the degree of cross-linking and on the hydrophilicity of the matrix. The equilibrium swelling ratio of the chelating beads used in this study is 78%. The water molecules penetrate into the

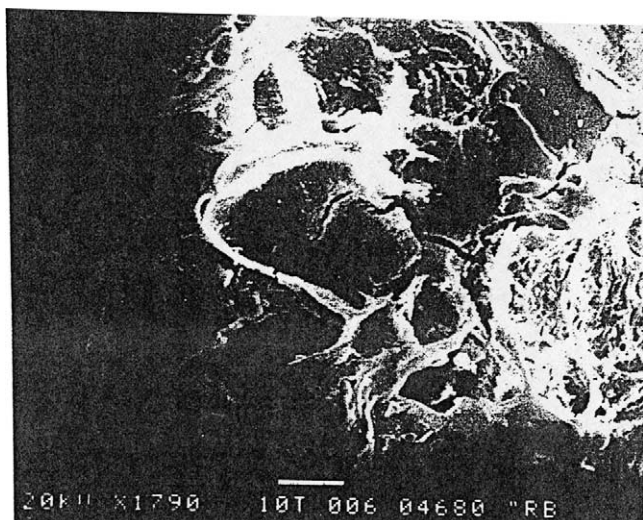
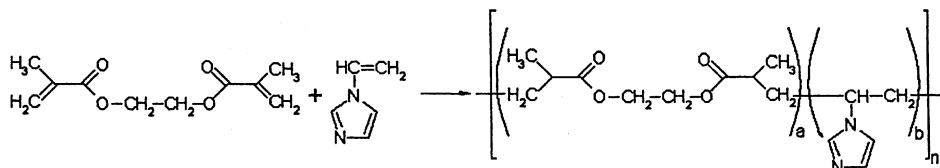


Fig. 1. SEM micrographs of poly(EGDMA-VIM) beads.

entanglement polymer chains more easily, resulting in an increase of polymer water uptake in aqueous solutions. It should be also noted that these beads are quite rigid, and strong enough due to highly cross-linked structure therefore they are suitable for column applications.

The poly(EGDMA-VIM) beads were prepared by copolymerizing EGDMA with VIM at a 1:1 molar ratio in the presence of the initiator AIBN according to the following reaction:



Ethylene glycol dimethacrylate (EGDMA) Vinyl imidazole (VIM)

Table 1  
Elemental analysis of poly(EGDMA-VIM) beads

	C (%)	H (%)	N (%)
Experimental values	50.18	9.86	9.98
Theoretical values	56.96	6.33	8.86

merization reaction was exactly completed, as some VIM monomers did not form part of the polymer and would have been removed during extensive washing.

### 3.2. Single-component heavy metal chelation

#### 3.2.1. Chelation isotherms

Fig. 2 shows the Cd(II), Pb(II) and Hg(II) chelation curves of the chelating beads. The amount of metal ions adsorbed per unit mass of the polymer (i.e., chelation capacity) increased first with the initial concentration of metal ions then reached a plateau value which represents saturation of the active chelation sites (which are available for metal ions) on the beads. Chelation of metal ions reached a saturation level at a lower bulk concentration, i.e., at about 100 mg/l. Due to 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 are 69.4 mg/g for Cd(II), 114.8 mg/g for Pb(II) and 163.5 mg/g for Hg(II). It appears that the chelating beads had the strongest affinity for Hg(II) ions. The order of these three kinds of metal ion

Poly (EGDMA-co-VIM)

FTIR and Elemental analysis were undertaken to determine the composition and structure (i.e., *a* and *b*) of the copolymer beads. The FTIR spectrum of poly(EGDMA-VIM) with characteristic peaks appear at  $3120\text{ cm}^{-1}$  (characteristic imidazole ring, C=C-H/N=C-H),  $1500\text{ cm}^{-1}$  (C-C/N-C stretching),  $1220\text{ cm}^{-1}$  (ring vibration) and  $1098\text{ cm}^{-1}$  (in-plane ring C-H bending). The carbonyl peak appears at  $1720\text{ cm}^{-1}$  and the peak at  $1150\text{ cm}^{-1}$  is associated with the C-O vibration of EGDMA. These data confirmed that the poly(EGDMA-VIM) copolymer beads was formed with functional groups VIM. Elemental analysis of poly(EGDMA-VIM) beads was performed to determine the values of *a* and *b*. The elemental analysis indicated a C/H/N ratio of 5:1:1 (Table 1). The molar ratio of EGDMA and VIM in the poly(EGDMA-VIM) beads, as calculated from the nitrogen stoichiometry based on the data shown in Table 1, was 5.02:1 or approximately, 5:1. This result suggested that most of the polymer is made of repeat units of EGDMA in a ratio of 5:1 with the VIM units, i.e.,  $a = 5b$ . This result also showed that the poly-

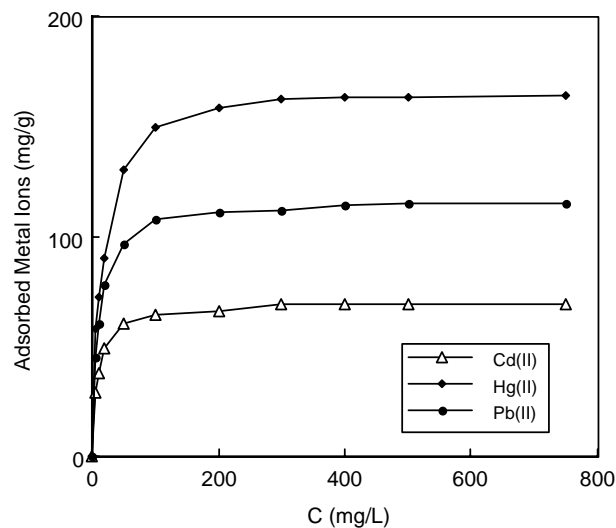


Fig. 2. Chelation capacity of chelating beads: pH, 5.0; *T*, 20 °C; Each data is average of five parallel studies.

Table 2  
Adsorption parameters of heavy metal ions on beads

Metal ions	Langmuir			Freundlich		
	$q_{\max}$	$b$	$R^2$	$K_F$	$n$	$R^2$
Cd(II)	71.4	0.106	0.99	24.4	5.25	0.93
Pb(II)	117.6	0.098	0.99	38.0	5.19	0.96
Hg(II)	172.4	0.070	0.99	43.0	4.17	0.90

chelation on mass basis for the single component metals is  $\text{Hg(II)} > \text{Pb(II)} > \text{Cd(II)}$ .

This affinity trend is presented on the mass basis (mg) metal chelation per gram beads and these units are important in quantifying respective metal capacities in real terms. However, a more effective approach, for this work is to compare metal chelation on a molar basis; this gives a measure of the total number of metal ions adsorbed, as opposed to total mass, and is an indication of the total number of binding sites available on the adsorbent matrix, to each metal. Additionally the molar basis of calculation is the only accurate way of investigating competition in multi-component metal mixtures. Molar basis units are measured as mmol per gram of dry-adsorbent. The binding capacities of the chelating beads on molar basis are 0.61 mmol/g for Cd(II), 0.55 mmol/g for Pb(II) and 0.81 mmol/g for Hg(II). The order of capacity of the chelating beads on molar basis for the single component metals is  $\text{Hg(II)} > \text{Cd(II)} > \text{Pb(II)}$ . The difference in the behavior of these metal ions may be related to the strength of their coordination complexes with imidazole.

A chelation isotherm is used to characterize the interaction of the each metal ion with the adsorbents. This provides a relationship between the concentration of metal ion in the solution and the amount of metal ion adsorbed on to solid phase when the two phases are at equilibrium [25]. The results were well fitted to either the Langmuir [ $q = q_{\max} b C_{\text{eq}} / (1 + b C_{\text{eq}})$ ] or Freundlich ( $q = K_F \times C_e^{1/n}$ ) isotherms. Some model parameters were determined by nonlinear regression with commercially available software and are shown in Table 2. It must be noted that the standard deviation of the values determined by regression analysis is comparatively low. It must be also pointed out that the measured chelation capacities for poly(EGDMA–VIM) beads are observed lower according to the calculated chelation capacities. This difference is due to the steric/geometric hindrances (i.e., accessibility) between the metal ions and the metal-chelating groups (i.e., *n*-vinylimidazole) on the surface of poly(EGDMA–VIM) beads.

### 3.3. Effect of pH on metal binding

Metal ion chelation on chelating adsorbents is pH dependent. In the absence of metal chelating groups, the precipitation of the metal ions are affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by hydroxide or carbonate concentration.

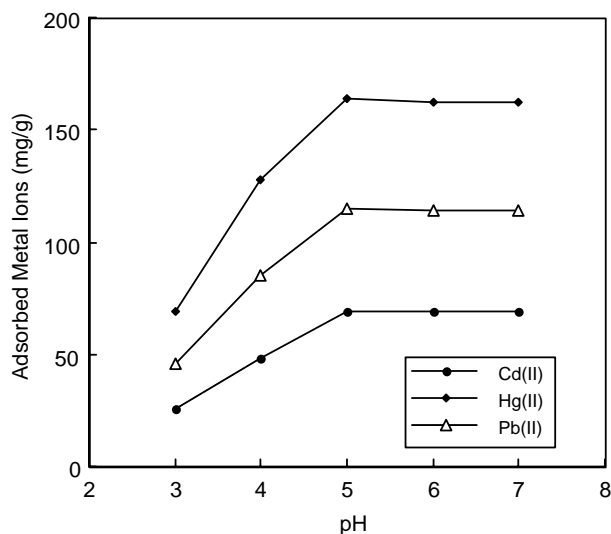


Fig. 3. Effect of pH on chelation of metal ions: Initial concentration of metal ions, 300 mg/l;  $T$ , 20 °C. Each data is average of five parallel studies.

Precipitation of metal ions becomes significant at approximately pH 7.0 for all metal ions. The theoretical and experimental precipitation curves indicate that precipitation begins above these pHs, which also depends on the concentration of metal ions in the medium. Therefore, in our study, in order to establish the effect of pH on the chelation of metal ions onto the chelating beads, we repeated the batch equilibrium studies at different pH in the range of 3.0–7.0. In this group of experiments, the initial concentration of metal ions was 300 mg/l for all metal ions. Fig. 3 shows the pH effect. The chelation capacities of the chelating beads are 112 mg/g for Pb(II), 69 mg/g for Cd(II) and 162 mg/g for Hg(II), respectively. It appears that the newly synthesized chelating beads had the strongest affinity for Hg(II). The affinity order of metal ions at initial concentration of 300 mg/l is  $\text{Hg(II)} > \text{Pb(II)} > \text{Cd(II)}$ .

Poly(EGDMA–VIM) chelating beads exhibited a low affinity for heavy metal ions in acidic conditions ( $\text{pH} < 4.0$ ), a somewhat higher affinity between pH 5.0 and 7.0. The difference in chelation behaviour of heavy metal ions can be explained by the different affinity of heavy metal ions for the donor atoms (i.e., nitrogen) in the VIM. A difference in coordination behaviour is most probably also case for the copolymerized VIM resulting in a relatively high chelation of metal ions at high pH under non-competitive chelation conditions.

### 3.4. Multi-component heavy metal chelation

Chelation capacities of the poly(EGDMA–VIM) beads from synthetic waste-water 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

Table 3  
Heavy metal ions chelation capacity of chelating beads after repeated chelation–elution cycle

Cycle no	Cd(II)		Hg(II)		Pb(II)	
	Chelation (mg/g)	Elution (%)	Chelation (mg/g)	Elution (%)	Chelation (mg/g)	Elution (%)
1	69.4 (±2.3)	97.5 (±2.0)	163.5 (±2.4)	96.5 (±1.8)	114.8 (±3.0)	96.0 (±2.1)
2	69.0 (±5.2)	98.2 (±2.1)	163.0 (±2.6)	96.3 (±1.9)	114.2 (±2.5)	96.2 (±2.6)
3	68.7 (±4.9)	98.8 (±2.2)	162.8 (±2.8)	97.5 (±1.7)	113.5 (±2.7)	96.5 (±2.4)
4	68.5 (±5.4)	98.1 (±2.4)	162.6 (±2.7)	97.7 (±1.8)	112.5 (±2.5)	97.0 (±2.3)
5	68.0 (±4.8)	98.4 (±2.2)	161.9 (±2.4)	97.0 (±1.6)	112.0 (±2.6)	96.3 (±2.9)
5	68.3 (±4.7)	99.3 (±2.5)	161.2 (±3.0)	99.3 (±1.1)	112.4 (±3.6)	98.8 (±2.8)
6	68.1 (±4.5)	99.0 (±2.0)	161.6 (±3.1)	98.6 (±1.5)	112.2 (±3.2)	98.5 (±2.1)
7	67.9 (±4.9)	98.3 (±2.4)	161.3 (±2.8)	97.5 (±1.8)	111.8 (±3.2)	97.3 (±2.0)
8	67.5 (±5.1)	98.5 (±2.2)	160.2 (±2.5)	95.5 (±1.6)	112.0 (±3.2)	99.0 (±2.4)
9	67.8 (±4.0)	97.5 (±2.5)	160.4 (±3.2)	96.8 (±1.9)	111.5 (±3.2)	99.0 (±2.6)
10	67.3 (±4.6)	97.9 (±2.3)	160.6 (±3.3)	97.9 (±1.4)	111.3 (±3.2)	98.3 (±2.3)

Initial concentration of metal ions, 750 mg/l; pH, 5.0; T, 25 °C.

time and experimental conditions. Three types of responses may be occurred: (i) The effect of the mixture is greater than that of each of the individual effects of the constituents in the mixture (synergism); (ii) the effect of the mixture is less than that of each of the individual effects of the constituents in the mixture (antagonism); (iii) the effect of the mixture is no more or less than that of each of the individual effects of the constituents in the mixture (non-interaction) [26]. It is worth noting that the chelation capacities of the poly(EGDMA–VIM) beads from synthetic wastewater for all metal ions were much lower than the single solutions. The most logical reason for the antagonistic action is claimed to be the competition for the chelation sites on the polymer beads and/or a screening effect by the other metal ions. The chelation capacities were 45.6 mg/g (0.41 mmol/g) for Cd(II), 74.2 mg/g (0.36 mmol/g) for Pb(II) and 92.5 mg/g (0.46 mmol/g) for Hg(II). The chelating beads exhibited the following metal ion affinity sequence on molar basis: Hg(II) > Cd(II) > Pb(II). In this case, chelating beads adsorbed other metal ions also [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 chelating beads for Cd(II), Pb(II) and Hg(II) ions.

### 3.5. Elution and repeated use

The repeated use of the polymer beads is likely to be a key factor in improving process economics. Elution of the adsorbed metal ions from the poly(EGDMA–VIM) beads was also studied in a batch experimental set-up. The poly(EGDMA–VIM) beads loading the maximum amounts of the respective metal ions were placed within the elution medium containing 0.1 M HNO<sub>3</sub> and the amount of metal ions desorbed in 1 h was measured. The elution efficiency was then calculated. Elution efficiencies were very high (up to 99.3%) with the elution agent and conditions used for all metal ions. It must be pointed out that in metal chelating systems, chelation (i.e., binding of heavy metal ions with *n*-vinylimidazole) is completely reversible.

In order to obtain the reusability of the poly(EGDMA–VIM) beads, chelation–elution cycle was repeated 10 times by using the same adsorbent. As shown in Table 3, the adsorbents were reused for subsequent chelation–elution cycles with comparable chelation efficiencies over 10 cycles.

## 4. Conclusion

Adsorption technology enables the use of polymeric chelating-beads for rapid, cost-effective and selective heavy metal removal. In this study chelating-beads were prepared and, was 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 adsorbents. This novel approach for the preparation of metal-chelating matrix has many advantages over conventional preparation techniques, those needed the activation of the matrix for metal-chelating ligand immobilization. In this procedure, comonomer VIM acted as the metal-chelating ligand, and there is no need to activate the matrix for the chelating–ligand immobilization. Metal-chelating ligand immobilization step was also eliminated. VIM was polymerized with EGDMA and there is no leakage of the ligand also. This one step preparation method will come over the drawback of other multi-step preparation methods. Our results suggest that poly(EGDMA–VIM) beads can be good heavy metal adsorbents and have great potential applications in environmental protection.

## References

- [1] P. Galiatsatou, M. Metaxas, V.K. Rigopoulou, J. Hazard. Mater. B91 (2002) 187.
- [2] L. Friberg, G.F. Nordberg, B. Vouk (Eds.), Handbook on the Toxicology of Metals, Elsevier, North-Holland, Biomedical Press, Amsterdam, 1979.
- [3] M. Devi, M. Fingermann, Bull. Environ. Contam. Toxicol. 55 (1995) 746.

- [4] K. Brajter, E. Dabek-Zlotorzynska, *Talanta* 37 (1990) 613.
- [5] B.E. Reed, W. Lin, M.R. Matsumoto, J.N. Jensen, *Water Environ. Res.* 69 (1997) 444.
- [6] R.A. Beuvais, S.D. Alexandratos, *React. Funct. Polym.* 36 (1998) 113.
- [7] B.L. Rivas, S.A. Pooley, H.A. Maturana, S. Villegas, *Macromol. Chem. Phys.* 202 (2001) 443.
- [8] C. Kantipuly, S. Katragadda, A. Chow, H.D. Goser, *Talanta* 37 (1990) 491.
- [9] T. Saito, *Sep. Sci. Technol.* 26 (1991) 1495.
- [10] B. George, V.N. Rajasekharan Pillai, B. Mathew, *J. Appl. Polym. Sci.* 74 (1999) 3432.
- [11] S.T. Beatty, R.J. Fischer, D.L. Hagers, E. Rosenberg, *Ind. Eng. Chem. Res.* 38 (1999) 4402.
- [12] M. Chanda, G.L. Rempel, *React. Funct. Polym.* 35 (1997) 197.
- [13] D.M. Manohar, K.A. Krishnan, T.S. Anirudhan, *Water Res.* 36 (2002) 1609.
- [14] W. Li, H. Zhao, P.R. Teasdale, R. John, S. Zhang, *React. Funct. Polym.* 52 (2002) 31.
- [15] A. Denizli, K. Kesenci, Y. Arica, E. Pişkin, *React. Funct. Polym.* 44 (2000) 235.
- [16] C.C. Wang, C.Y. Chang, C.Y. Chen, *Macromol. Chem. Phys.* 202 (2001) 882.
- [17] R.R. Navarro, K. Sumi, N. Fujii, M. Matsumura, *Water Res.* 30 (1996) 2488.
- [18] A. Sağlam, S. Bektaş, S. Patır, Ö. Genç, A. Denizli, *React. Funct. Polym.* 47 (2001) 185.
- [19] W. Li, H. Zhao, P.R. Teasdale, R. John, *Polymer* 43 (2002) 4803.
- [20] K. Kesenci, R. Say, A. Denizli, *Eur. Polym. J.* 38 (2002) 1443.
- [21] P.E. Duru, S. Bektaş, Ö. Genç, S. Patır, A. Denizli, *J. Appl. Polym. Sci.* 81 (2001) 197.
- [22] A. Denizli, R. Say, S. Patır, Y. Arica, *React. Funct. Polym.* 46 (2000) 157.
- [23] A. Denizli, R. Say, S. Patır, Y. Arica, *Sep. Sci. Technol.* 36 (2001) 2213.
- [24] R. Say, B. Garipcan, S. Emir, S. Patır, A. Denizli, *Macromol. Mater. Eng.* 287 (2002) 539.
- [25] Y. Sag, B. Akçael, T. Kutsal, *Process Biochem.* 37 (2001) 35.
- [26] Y. Sag, *Sep. Purif. Methods* 30 (2001) 1.