

# Alanine Containing Porous Beads for Mercury Removal from Artificial Solutions

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**ABSTRACT:** *N*-methacryloyl-(L)-alanine (MALA) was synthesized by using methacryloyl chloride and alanine as a metal-complexing ligand or comonomer. Spherical beads with an average diameter of 150–200  $\mu\text{m}$  were obtained by suspension polymerization of MALA and 2-hydroxyethyl methacrylate (HEMA) conducted in an aqueous dispersion medium. Poly(HEMA–MALA) beads were characterized by SEM, swelling studies, surface area measurement, and elemental analysis. Poly(HEMA–MALA) beads have a specific surface area of 68.5  $\text{m}^2/\text{g}$ . Poly(HEMA–MALA) beads with a swelling ratio of 63%, and containing 247  $\mu\text{mol}$  MALA/g were used in the removal of  $\text{Hg}^{2+}$  from aqueous solutions. Adsorption equilibrium was achieved in about 60 min. The adsorption of  $\text{Hg}^{2+}$  ions onto PHEMA beads was negligible (0.3 mg/g). The MALA incorporation into the polymer structure significantly increased the mercury adsorption capacity (168 mg/g). Adsorption capacity of MALA contain-

ing beads increased significantly with pH. The adsorption of  $\text{Hg}^{2+}$  ions increased with increasing pH and reached a plateau value at around pH 5.0. Competitive heavy metal adsorption from aqueous solutions containing  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  was also investigated. The adsorption capacities are 44.5 mg/g for  $\text{Hg}^{2+}$ , 6.4 mg/g for  $\text{Cd}^{2+}$ , 2.9 mg/g for  $\text{Pb}^{2+}$ , and 2.0 mg/g for  $\text{Cu}^{2+}$  ions. These results may be considered as an indication of higher specificity of the poly(HEMA–MALA) beads for the  $\text{Hg}^{2+}$  comparing to other ions. Consecutive adsorption and elution operations showed the feasibility of repeated use for poly(HEMA–MALA) chelating beads. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1222–1228, 2006

**Key words:** alanine; metal-chelating beads; amino acid-ligands; mercury removal

## INTRODUCTION

Environmental pollution by mercury arising mainly from metal smelting and caustic-chlorine production in mercury cells, metal processing, plating, and metal finishing industries. Mercury causes significant economic and public health problems by its presence in aquatic ecosystems.<sup>1</sup> Mercury is converted into more toxic form, i.e., methylmercury chloride by aquatic living-organisms, and accumulated in the tissue of fishes and birds. The illness, which came to be known as Minamata disease, was caused by mercury poisoning as a result of eating contaminated fish.<sup>2</sup> Although it is emphasized that metals play important roles in biological processes and some of them are classified as essential, the toxic symptoms will manifest when a metal ion level exceeds a certain threshold level. The symptoms of the toxic effects of heavy metals may vary widely at the physiological level, but the basic toxicity mechanisms at the molecular level may be limited. The toxicities of heavy metals may be caused by the following mechanisms: blocking the essential

functional groups of biomolecules such as enzymes; displacing essential metal ions from biomolecules; modifying the active conformation of biomolecules, especially enzymes and disrupting the integrity of biomembranes; and modifying some other biologically active agents. These toxicity mechanisms are all based on the strong binding abilities of these metallic ions and as in the case of selectivity in uptake mechanism, substitution of a metallic ion by another is relatively simple.  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ , for example, can replace the native  $\text{Zn}^{2+}$  from many proteins and enzymes to a degree that depends on their affinities. Mercury has very high tendency for binding to proteins and it mainly affects the renal and nervous systems.<sup>3</sup> In humans, the initial symptoms include numbness of the lips and limbs. As the sickness progresses, permanent damage is done to the central nervous system, and the victim experiences visual constriction, loss of motor coordination, and, in the final stages prior to death, loss of memory, speech, hearing, and taste.

It has been suggested that adsorbents could be used to decontaminate these wastewaters and to concentrate metals. Polymer-based chelating adsorbents would be of great importance in heavy metal removal from aqueous systems due to their selectivity and

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efficiency, easy handling and cost effectiveness.<sup>4-6</sup> The conventional chelating ligands suffer mainly from two shortcomings, namely, slow metal-ion adsorption and lack of selectivity toward a particular metal ion. Several criteria are important in the design of chelating polymers with substantial stability for the selective removal of heavy metal ions: specific and fast complexation of the metal ions as well as reusability of the chelating ligands.<sup>7</sup> Different polymers incorporating a variety of chelating-ligands including polyethyleneimine, iminodiacetate, amidoxime, sulfonic/carboxylic groups, phosphoric acid, dithiocarbamate, and reactive textile dyes have been prepared and their analytical properties investigated.<sup>8-10</sup> Recently, incorporation of amino acids and/or polyamino acids into a polymer matrix has been reported in a series of publications for diverse environmental and biomedical applications.<sup>11-15</sup> The idea of using different amino acids by these researchers stems from the fact that amino acids are very reactive substances with different chemicals, including metal ions and proteins. The higher flexibility and durability of these metal-chelating ligands as well as significantly lower material and manufacturing costs are also very important.

The aim of this study was to prepare a novel alanine containing metal-complexing beads for mercury removal. In the first part, metal-complexing ligand *N*-methacryloyl-(L)-alanine (MALA) was synthesized using methacryloyl chloride and L-alanine hydrochloride. Poly(2-hydroxyethyl methacrylate-*N*-methacryloyl-(L)-alanine) [poly(HEMA-MALA)] beads were obtained by suspension polymerization of MALA and HEMA. The poly(HEMA-MALA) beads were characterized by surface area measurement (SEM), elemental analysis, and swelling tests. Then, Hg<sup>2+</sup> adsorption on the poly(HEMA-MALA) beads from aqueous solutions containing different amounts of Hg<sup>2+</sup>, at different pH's, was also performed. Elution of Hg<sup>2+</sup> and reusability of these metal-chelating beads were also evaluated.

## EXPERIMENTAL

### Materials

L-Alanine hydrochloride and methacryloyl chloride were supplied by Sigma (St Louis, MO). 2-Hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4°C until use. Benzoyl peroxide (BPO) was obtained from Fluka (Switzerland). Poly(vinyl alcohol) (PVAL; MW: 100,000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (Milwaukee, WI). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All

water used in the adsorption experiments was purified using a Barnstead (Dubuque, IA) ROpure LP<sup>®</sup> reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure<sup>®</sup> organic/colloid removal and ion exchange packed-bed system.

### Synthesis of MALA

Details of the preparation and characterization of the *N*-methacryloyl-(L)-alanine (MALA) was reported elsewhere.<sup>16</sup> Briefly, the following experimental procedure was applied for the synthesis of MALA monomer: 5.0 g of L-alanine hydrochloride and 0.2 g of hydroquinone were dissolved in 100 mL of dichloromethane solution. This solution was cooled down to 0°C. Then, 13.0 g triethylamine was added to the solution and 4.0 mL of methacryloyl chloride was poured slowly into this solution under nitrogen atmosphere. This solution was stirred magnetically at room temperature for 2 h. At the end of this chemical reaction period, unreacted methacryloyl chloride was extracted with 10% NaOH. The aqueous phase was evaporated in a rotary evaporator and residue (i.e., MALA) was dissolved in ethyl alcohol.

### Preparation of poly(HEMA-MALA) beads

Suspension polymerization method was used for the preparation of poly(HEMA-MALA) beads. A typical preparation procedure is described below. Continuous medium was prepared by dissolving PVAL (200 mg) in the water (50 mL). For the preparation of dispersed phase, HEMA (6.0 mL), MALA (1.5 mg), EGDMA (8.0 mL), and toluene (12.0 mL) were mixed and benzoyl peroxide (100 mg) was dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (600 rpm) in a sealed pyrex polymerization reactor (volume, 250 mL). The reactor content was heated to polymerization temperature (i.e., 65°C) and the polymerization was conducted for 4 h with a 600 rpm stirring rate at 70°C. Then, temperature was increased to 90°C and the polymerization was conducted for 2 h. 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.

### Characterization studies

The specific surface area of the PHEMA and poly(HEMA-MALA) beads were determined in BET apparatus. The average size and size distribution of the poly(HEMA-MALA) beads were determined by screen analysis performed by using Tyler Standard Sieves. Water uptake ratios of the poly(HEMA-MALA) beads

were 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°C) for 2 h. The bead sample was taken out from the water, wiped using a filter paper, and weighed. The weight of dry and wet samples was recorded. The water content of the beads was calculated using the weights of beads before and after uptake of water. 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 for 2 min. The sample was then mounted in a scanning electron microscope (JEOL, JEM 1200 EX, Tokyo, Japan). The surface of the sample was then scanned at the desired magnification to study the morphology of the poly(HEMA–MALA) beads. To evaluate the degree of MALA incorporation into the polymer structure, the synthesized poly(HEMA–MALA) beads were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932).

### Hg<sup>2+</sup> adsorption studies

Adsorption of Hg<sup>2+</sup> from aqueous solutions was investigated in batch experiments. Effects of Hg<sup>2+</sup> concentration and pH of the medium on the adsorption rate and capacity were studied. Aliquots (100 mL) of aqueous solutions containing different amounts of Hg<sup>2+</sup> (in the range of 10–500 mg/L) were treated with the polymer beads at different pH (in the range of 2.0–7.0) (adjusted with HCl–NaOH). The polymer beads (50 mg) were stirred with a mercury nitrate salt solution at room temperature for 2 h. All glassware for adsorption experiments was washed with 1.0M HNO<sub>3</sub> and rinsed thoroughly with deionized water. The concentration of the Hg<sup>2+</sup> in the aqueous phase was measured by using an Atomic Absorption Spectrophotometer. A Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer (Japan) was used. 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 instrument response was periodically checked with a known Hg<sup>2+</sup> solution standard. The adsorption 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 adsorption capacity of the beads was calculated according to the mass balance on mercury ion.

### Competitive adsorption

Competitive heavy metal adsorption from aqueous solutions containing Hg<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Pb<sup>2+</sup> was also investigated in batch experimental system. A solution (100 mL) containing 50 mg/L of each metal ions was treated with the poly(HEMA–MALA) beads at a pH of 5.0 in the flasks stirred magnetically at 100 rpm. The temperature was maintained at 25°C. After a sufficient amount of time for equilibration, the solution was centrifuged, and the supernatant was removed and analyzed for remaining metal ions. The amounts of adsorbed heavy metal ions were then determined by difference. Equilibration time was relatively short; the adsorption experiment (from initial contact to final determination) was completed in 2 h.

### Regeneration studies

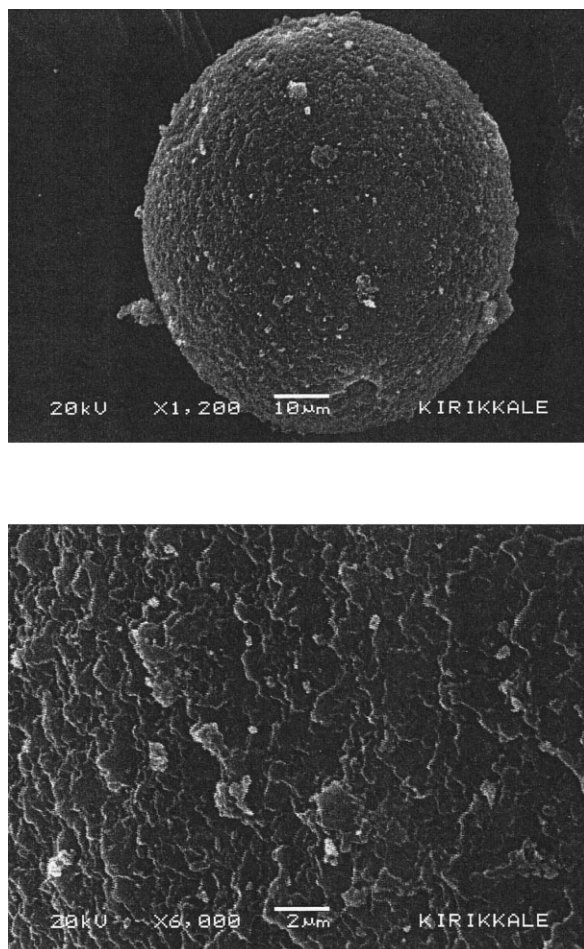
Elution of Hg<sup>2+</sup> was studied in 0.1M HNO<sub>3</sub> solution. The poly(HEMA–MALA) beads adsorbed with Hg<sup>2+</sup> were placed in this elution medium and stirred (at a stirring rate of 100 rpm) for 1 h at room temperature. Elution volume was 50 mL. The final concentration of Hg<sup>2+</sup> in the aqueous phase was determined by AAS. The elution ratio was calculated from the amount of Hg<sup>2+</sup> adsorbed on the beads and the final concentration of Hg<sup>2+</sup> in the elution medium. To show the reusability of the poly(HEMA–MALA) beads, adsorption–elution cycles were repeated 50 times by using the same metal-chelating beads.

## RESULTS AND DISCUSSION

### Properties of polymer beads

Suspension polymerization procedure provided crosslinked poly(HEMA–MALA) beads in the spherical form in the size range of 150–200 μm. The poly(HEMA–MALA) beads are crosslinked hydrophilic matrices. They do not dissolve in aqueous media, but do swell, depending on the degree of crosslinking. The equilibrium swelling ratio (the ratio of the volumes of the beads before and after swelling) of the beads is 63%. Compared with PHEMA (55%), the water uptake ratio of the poly(HEMA–MALA) beads increases (63%). Several possible factors may contribute to this result. First, incorporating MALA actually introduces more hydrophilic functional groups into the polymer chain, which can attract more water molecules into polymer matrices. Second, reacting MALA with HEMA could effectively decrease the molecular weight. Therefore, the water molecules penetrate into the polymer chains more easily, resulting in an improvement of polymer water uptake in aqueous solutions. To evaluate the degree of MALA incorporation into the polymer structure, elemental analysis of the





**Figure 1** Scanning electron microscopy of poly(HEMA-MALA) beads: (A) external part detail and (B) internal part detail.

synthesized poly(HEMA-MALA) was performed. The incorporation of the MALA was found to be 247  $\mu\text{mol/g}$  polymer from the nitrogen stoichiometry.

The surface and internal structures were verified by scanning electron microscopy (Fig. 1). The polymer beads have a spherical form and rough surface. The photograph in Figure 1(B) was taken with broken beads to observe the internal part of the polymer structure. The presence of pores within the bead internal part is clearly seen in this photograph. This result could be confirmed by the large surface area verified by the BET analysis. Specific surface area of the poly(HEMA-MALA) beads was found to be 68.5  $\text{m}^2/\text{g}$ . It can be concluded that the MALA incorporated beads have a microporous interior surrounded by a reasonably rough surface, in the dry state. The roughness of the bead surface should be considered as a factor providing an increase in the surface area. In addition, these micropores reduce diffusional resistance and facilitate mass transfer because of high internal surface area.

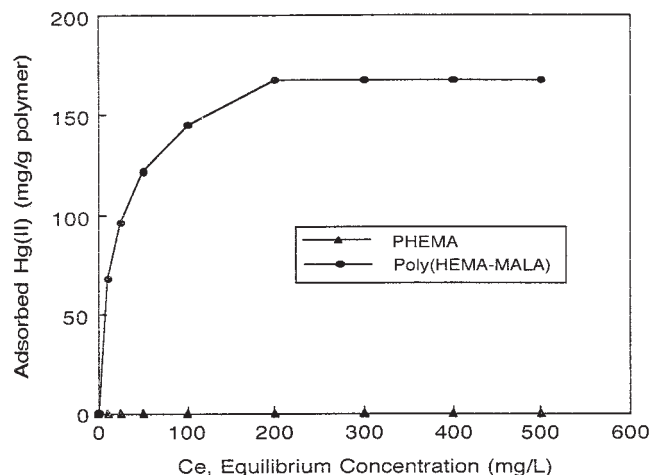
## Metal ion adsorption on polymer beads

### Effect of $\text{Hg}^{2+}$ concentration

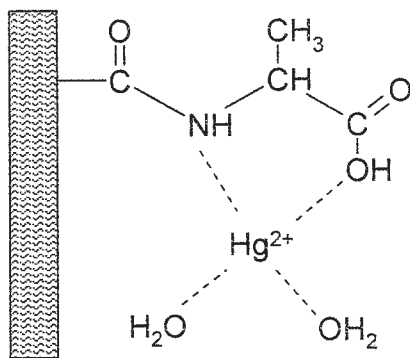
Figure 2 shows the equilibrium concentration of  $\text{Hg}^{2+}$  dependence of the adsorbed amount of the  $\text{Hg}^{2+}$  onto the both PHEMA and poly(HEMA-MALA) beads. Adsorption of  $\text{Hg}^{2+}$  onto the PHEMA beads was very low, about 0.3  $\text{mg/g}$ , because PHEMA beads do not contain any binding sites for complexation of  $\text{Hg}^{2+}$ . This very low adsorption value of  $\text{Hg}^{2+}$  may be due to diffusion of  $\text{Hg}^{2+}$  into the pores of the swollen matrix of the beads and weak interactions between  $\text{Hg}^{2+}$  and hydroxyl groups on the surface of the PHEMA beads. However, MALA incorporation into the polymer structure significantly increased the adsorption capacity to 168  $\text{mg/g}$ . The adsorption values increased with increasing equilibrium concentration of  $\text{Hg}^{2+}$ , and a saturation value is achieved at ion concentration of 200  $\text{mg/L}$ , which represents saturation of the active binding sites on the poly(HEMA-MALA) beads.

MALA content of the adsorbent beads used in this group of experiments was 247  $\mu\text{mol/g}$ . The maximum  $\text{Hg}^{2+}$  adsorption capacity achieved in the studied range is around 221.8  $\mu\text{mol}$  per unit mass of the beads. This seems to give a stoichiometry of one MALA groups per one mercury ion. MALA molecules were thought to be incorporated to the backbone through copolymerization and the pendant carboxyl groups in the MALA are postulated to be responsible for mercury binding as shown in Figure 3.

Different polymeric adsorbents carrying metal-chelating ligands with a wide range of adsorption capacities for mercury ions have been reported (Table I). Comparing the maximum adsorption capacities, it seems that the adsorption capacity achieved with the novel MALA-incorporated PHEMA beads are rather satisfactory.



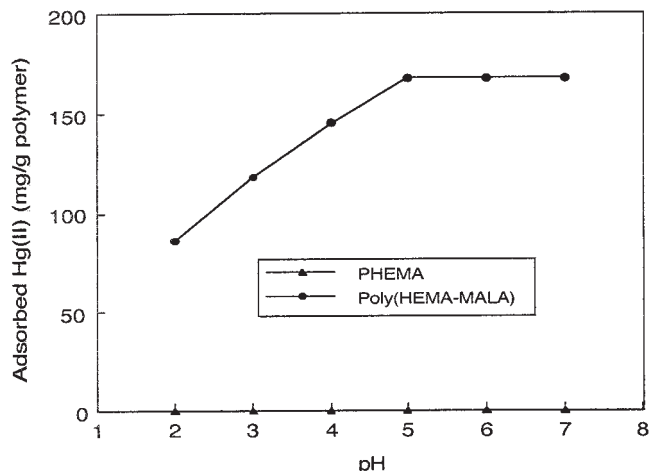
**Figure 2** Effect of  $\text{Hg}^{2+}$  concentration on adsorption of  $\text{Hg}^{2+}$  on the PHEMA and poly(HEMA-MALA) beads, pH 6.0.



**Figure 3** Complex formation of poly(HEMA-MALA) bead and mercury ion.

### Effect of pH

pH is the most critical parameter for metal adsorption as it influences both the polymer surface chemistry as well as the solution chemistry of soluble metal ions. Because of the deprotonation of the acidic groups of the metal complexing ligand (MALA group), its adsorption behavior for metal ions is influenced by the pH value, which affects the surface structure of adsorbents, the formation of metal hydroxides, and the interaction between adsorbents and metal ions. Therefore, to establish the effect of pH on the adsorption of  $\text{Hg}^{2+}$  onto the both PHEMA and poly(HEMA-MALA) beads, we repeated the batch adsorption equilibrium studies at different pHs in the range of 2.0–7.0. In this group of experiments, the initial concentration of  $\text{Hg}^{2+}$  and the adsorption equilibrium time were 300



**Figure 4** Effect of pH on adsorption of  $\text{Hg}^{2+}$  on the PHEMA and poly(HEMA-MALA) beads. Initial concentration of  $\text{Hg}^{2+}$  is 300 mg/L.

mg/L and 2 h, respectively. The pH dependence of adsorption values of  $\text{Hg}^{2+}$  is shown in Figure 4. In the case of PHEMA beads, adsorption is pH independent. But, it is indicated that the adsorption of  $\text{Hg}^{2+}$  onto the poly(HEMA-MALA) beads was pH dependent. The results show that mercury adsorption by the poly(HEMA-MALA) beads was very low at pH 2.0, but increased rapidly with increasing pH and then reached the maximum at pH 5.0.  $\text{Hg}^{2+}$  adsorption around pH 3.0–4.0 was also low. This can be explained by the fact that, at this pH, most of pendant carboxyl groups are protonated. It is well known in

**TABLE I**  
Comparison of Adsorption Capacities of Different Adsorbents

Adsorbent	Chelating ligand	Capacity (mg/g)	Reference
Styrene-divinylbenzene	Thiol	20	17
PMMA	Ethylenediamine	30	18
Polystyrene	Dithiocarbamate	32	19
Poly(glycidyl methacrylate-divinyl benzene)	Phosphoric acid	40	20
PHEMA	Dithizone	42	21
Polystyrene	Sulfur-chlorinated jajoba wax	50	22
PEGDMA	Acrylamide	54	23
Soy protein hydrogel	Ethylenediamine tetraacetic acid	60	24
Poly(vinyl alcohol)	Procion Blue MX-3G	69	25
<i>N</i> -hydroxymethyl thioamide	Thioamide	72	26
Poly(vinyl pyridine)	Dithizone	144	27
Silica	3-trimethoxysilyl-1-propanethiol	184	28
Silica Gel	Polyethyleneimine	200	29
Poly( <i>N</i> -vinylimidazole)	Imidazole	200	30
PHEMA	Thiazolidine	222	31
Cellulose	Polyethyleneimine	288	32
PHEMA	Polyethyleneimine	334	33
Amberlite IRC 718	Iminodiacetic acid	360	34
Poly(GMA-DVB)	Thiol	400	35
PHEMA	<i>N</i> -methacryloyl-(L)-cysteine	1018	36
PHEMA	<i>N</i> -methacryloyl-(L)-histidine	1234	37
PHEMA	<i>N</i> -methacryloyl-(L)-alanine	168	In this study

adsorption mechanisms, that a decrease in solubility favors an improvement in adsorption performance.

### Competitive adsorption

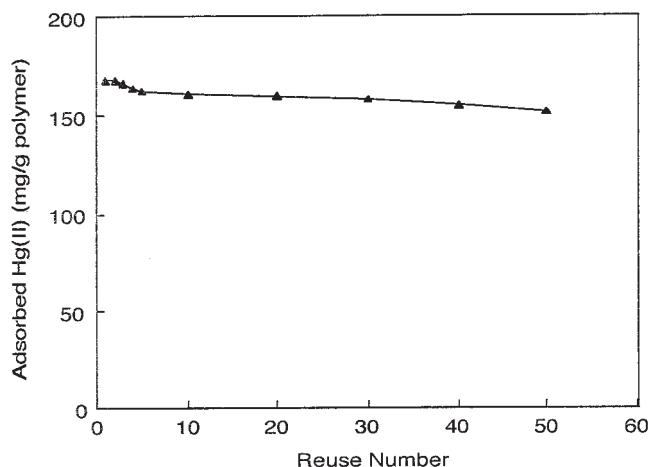
As seen in Table II, adsorbed amounts of  $\text{Hg}^{2+}$  ions are higher than those obtained for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ , not only in weight basis but also in molar basis. The adsorption capacities are 44.5 mg/g for  $\text{Hg}^{2+}$ , 6.4 mg/g for  $\text{Cd}^{2+}$ , 2.9 mg/g for  $\text{Pb}^{2+}$ , and 2.0 mg/g for  $\text{Cu}^{2+}$  ions. From these results the order of affinity is  $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+}$ . This trend is presented on the basis of mass (mg) metal adsorption per gram adsorbent 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 adsorption on a molar basis; this gives a measure of the total number of metal ions adsorbed, as opposed to total weight, and is an indication of the total number of binding sites available on the adsorbent matrix, to each metal. Additionally, the molar basis of measurement is the only accurate way of investigating competition in multi-component metal mixtures. Molar basis units are measured as  $\mu\text{mol}$  per gram of dry-adsorbent. It is evident from Table II that the order of capacity of poly(HEMA-MALA) beads is as follows:  $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ . It is clear from Table II that the poly(HEMA-MALA) beads showed more affinity to  $\text{Hg}^{2+}$  ions.

### Behavior of the elution

The regeneration of the adsorbent is likely to be a key factor in improving process economics. To be useful in metal remediation processes, metal ions should be easily eluted under suitable conditions. Elution of the  $\text{Hg}^{2+}$  from the metal-chelating beads was performed in a batch experimental set-up. Various factors are probably involved in determining rates of  $\text{Hg}^{2+}$  elution, such as the extent of hydration of the metal ions and polymer microstructure. However, an important factor appears to be binding strength. When  $\text{HNO}_3$  is used as the elution agent, the coordination spheres of chelated  $\text{Hg}^{2+}$  ions is disrupted and, subsequently,

**TABLE II**  
Competitive Adsorption of  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  from Their Mixture onto Poly(HEMA-MALA) Beads

Metal Ions	Metal Ions Adsorbed	
	(mg/g polymer)	( $\mu\text{mol}$ /g polymer)
$\text{Hg}^{2+}$	44.5	221.8
$\text{Cd}^{2+}$	6.4	56.9
$\text{Pb}^{2+}$	2.9	14.0
$\text{Cu}^{2+}$	2.0	31.5



**Figure 5** Adsorption–elution cycles for  $\text{Hg}^{2+}$ . Adsorption conditions:  $\text{Hg}^{2+}$  initial concentration, 300 mg/L; pH, 6.0.

$\text{Hg}^{2+}$  ions are released from the polymer surface into the desorption medium. In this study, the elution time was found to be 30 min. Elution ratios are very high (up to 99%). The ability to reuse the poly(HEMA-MALA) beads was shown in Figure 5. The adsorption behavior is stable for fifty cycles of use and it could be used at least 50 times. The adsorption capacity of the recycled beads can be maintained at 96% level at the 50th cycle. This means that the newly synthesized polymeric beads have great potential for industrial applications.

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