

## Adsorption of Mercury(II) Ions by Poly(hydroxyethylmethacrylate) Adsorbents with Thiazolidine Groups

Ç. Arpa<sup>1</sup>, A. Sağlam<sup>1</sup>, S. Bektaş<sup>1</sup>, S. Patir<sup>2</sup>, Ö. Genç<sup>1</sup> and A. Denizli<sup>1\*</sup> (1) Department of Chemistry, Hacettepe University, 06532 Beytepe, Ankara, Turkey. (2) Department of Science Education, Hacettepe University, 06532 Beytepe, Ankara, Turkey.

(Received 30 August 2001; accepted 6 November 2001)

**ABSTRACT:** A wide variety of adsorbents has been reported in the literature for heavy metal adsorption. We have recently developed a new polymer system for the removal of contaminant heavy metal ions from aquatic systems. Thus, poly(hydroxyethylmethacrylate) (PHEMA) microbeads carrying thiazolidine (0.318 mmol/g) were prepared for the removal of different amounts of mercury(II) ions (50–900 mg/l) from aqueous solutions and at different pH values (3.0–7.0). Adsorption rates were high with adsorption equilibria being reached within 10 min. The adsorption of Hg(II) ions on to the thiazolidine-immobilized microbeads from single solutions amounted to 1.11 mmol/g. The formation constant of the thiazolidine–metal ion complex was investigated by the method of Ružić. The calculated value of the stability constant was  $9.11 \times 10^5$  l/mol for the Hg(II)–thiazolidine complex. PHEMA microbeads carrying thiazolidine may be regenerated by washing with a solution of hydrochloric acid (0.05 M). The maximum desorption ratio was as high as 99%. These PHEMA microbeads may be used repeatedly for more than three adsorption/desorption cycles without any considerable loss in adsorption capacity.

### INTRODUCTION

Mercury (Hg) is the only common metal that exists in a liquid form at room temperature. It is rare in the Earth's crust (0.1 ppm to 1 ppm). Although several forms occur, the principal ore is cinnabar, HgS. Elemental mercury is obtained when cinnabar is roasted and the resulting mercury vapour condensed. Some inorganic and organic mercury compounds are extremely toxic (Berlin 1986). A number of episodes leading to many fatalities have occurred in different countries in recent years as a result of exposure to the metal or its compounds.

Mercury contamination of the environment is caused both naturally and via man-made sources (WHO 1976). Natural sources include volcanic action and erosion of mercury-containing sediments. Some of the ways in which humans contaminate the environment with mercury are through mining, transportation and the processing of mercury ores; dumping industrial wastes into rivers and lakes; the combustion of fossil fuels (e.g. the mercury content of coal is ca. 1 ppm), pulp and paper; the use of mercury compounds as seed dressings in agriculture; and exhaust from metal smelters.

All plants appear to concentrate traces of mercury. The concentration of mercury in plants depends on deposits in the soil, plant species and the locality. Mercury can have a deleterious effect on different species of plants. It is particularly toxic to barley plants, more so than Pb, Cr, Cd, Ni and

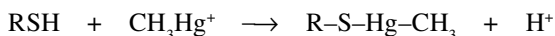
\*Author to whom all correspondence should be addressed. E-mail: denizli@hacettepe.edu.tr.

Zn (Oberlander and Roth 1978). Mercury impairs germination, as demonstrated by depressed root elongation and shoot growth (Allen and Brown 1995). Freshwater and marine organisms and their predators normally contain more mercury than terrestrial animals. Levels in top predatory fish are higher. Fish may accumulate mercury in excess of the 0.5 mg/g FDA guideline depending on various factors. This accumulation is part of a dynamic process in which an organism strives to maintain equilibrium between intake and elimination. There is no evidence that mercury compounds at the concentrations found in either the atmosphere or drinking water supplies contribute significantly to the methylmercury burden in the human body. The available data show that almost all the methylmercury in the human diet comes from fish, other seafood and possibly red meat.

The critical organ concentration may differ at different stages of the human life cycle. The developing foetal (and newborn) brain may be the most sensitive organ (i.e., critical organ) in terms of human methylmercury toxicity (Sumino *et al.* 1995).

Perhaps the greatest source of danger in industrial and research laboratories is the possible inhalation of mercury vapour. This can diffuse through the alveolar membrane and reach the brain, causing the vapour to interfere with coordination. The relative toxicity of various compounds towards tissue depends on the relative ease with which they form the Hg(II) ion (Sugiura *et al.* 1976).

The ultimate effects of mercury in the body are the inhibition of enzyme activity and cell damage. Inhibition of a large variety of enzyme systems by mercury has been reported (Boyer *et al.* 1959). The particular reactivity of mercury with thiol ligands has further confirmed the selective affinity of this metal to react with the SH group, as shown with methylmercury in the following equation:



Mercury is known to affect the metabolism of mineral elements such as Na and K by increasing the latter's permeability. Mercury also inhibits the active transport mechanism through dissipation of the normal cation gradient; destroys mitochondrial apparatus; causes swelling of cells leading to lysis; decreases  $\alpha$ - and  $\gamma$ -globulins whilst increasing  $\beta$ -globulin, suggesting liver dysfunction; decreases DNA content in cells; and adversely affects chromosomes and mitosis, leading to mutagenesis (Tephly *et al.* 1978).

A new and re-usable polymer system has been developed in our laboratories for the removal of contaminant heavy metal species from aquatic systems. The present study was dedicated to an investigation of the removal of Hg(II) ions by poly(hydroxyethylmethacrylate) microbeads carrying thiazolidine as a metal-complexing group.

## EXPERIMENTAL

### Materials

Thiazolidine was supplied by Sigma (St. Louis, MO, USA) and used as received. 2-Hydroxyethylmethacrylate (HEMA) was purchased from Sigma (St. Louis, MO, USA), purified by vacuum distillation under a nitrogen atmosphere and stored at 4°C until used. The co-monomer ethyleneglycoldimethacrylate (EGDMA) (Merck, Darmstadt, Germany) was used as the crosslinking agent. The polymerization initiator 2,2'-azobisisobutyronitrile (AIBN) was provided by Fluka, Switzerland. The dispersion medium was a saturated aqueous solution of magnesium oxide (Sigma). All other chemicals used were reagent grade from Merck AG (Darmstadt, Germany). The pH values of solutions were adjusted with nitric acid and sodium hydroxide, respectively.

## Preparation of poly(hydroxyethylmethacrylate) (PHEMA) microbeads

PHEMA microbeads were prepared using a suspension polymerization technique (Denizli and Pişkin 1995a). Polymerization was carried out in an aqueous dispersion medium containing magnesium oxide which was used to decrease the solubility of HEMA in the medium. The monomer phase containing HEMA, EGDMA and AIBN was added to the dispersion medium contained in a two-necked flask of 500 ml volume provided with a blade-type stirrer. In order to produce polymeric microbeads of ca. 200  $\mu\text{m}$  diameter with a narrow size distribution, the HEMA/EGDMA ratio, the monomer phase/dispersion phase ratio, the amounts of EGDMA and AIBN, and the agitation speed were maintained at 1:3 (v/v), 1:10 (v/v), 0.33 (mol EGDMA/mol HEMA), 0.0015 (mol AIBN/mol HEMA) and 600 rpm, respectively. Polymerization was carried out at 70°C for 3 h and then at 90°C for 1 h. After cooling, the polymeric microbeads were separated from the polymerization medium and the residual MgO removed by washing with a dilute HCl solution. The microbeads were also washed with water and ethanol, and then dried in a vacuum desiccator at room temperature.

## Thiazolidine immobilization

Thiazolidine was immobilized on the PHEMA microbeads via covalent coupling (Figure 1). Briefly, 1.0 g thiazolidine was dissolved in tetrahydrofuran and 0.5 g NaH added to this solution. The nucleophilic substitution reaction was started by adding 10 g dry PHEMA microbeads. The reaction was carried out at a constant temperature of 40°C for 24 h. The resulting thiazolidine-incorporated microbeads were first filtered and then washed several times with distilled water and methanol until all the physically adsorbed and/or absorbed thiazolidine molecules had been removed.

## Characterization of PHEMA microbeads

### *Swelling studies*

To determine the equilibrium water swelling ratio of PHEMA microbeads, ca. 3.0 g of a dry polymer sample was placed in a cylindrical tube. The height of the bed formed by the dry microbeads ( $H_d$ ) was measured and then 50 ml of a buffer solution of a known pH value and ionic strength was added to the tube. The sealed tube was shaken on a rotator for 24 h at 30 rpm. After this time, the height of the bed formed by the swollen PHEMA microbeads ( $H_s$ ) was recorded. The equilibrium water swelling ratio was calculated on the basis of the following expression:

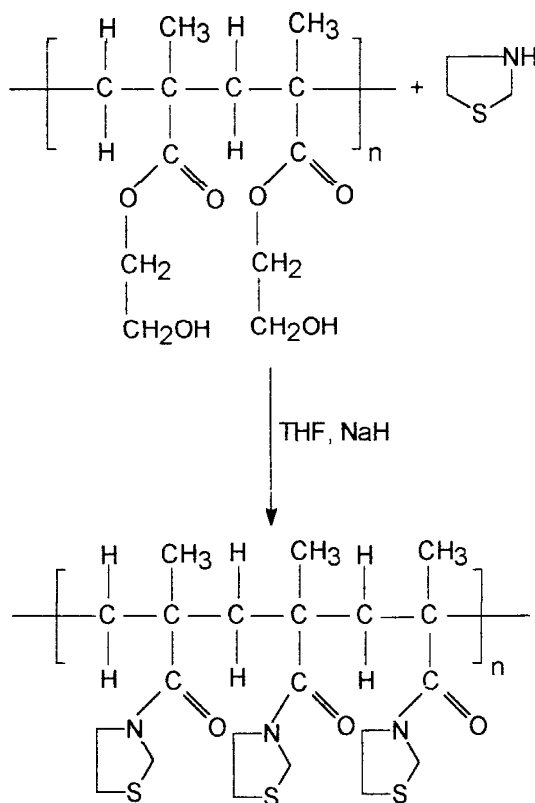
$$\text{Equilibrium water swelling ratio} = (H_s/H_d) \times 100 \quad (1)$$

### *Elemental analysis*

The amount of thiazolidine immobilized on the PHEMA microbeads was determined from elemental analysis employing a Leco (USA) CHNS-932 instrument.

### *FT-IR spectroscopic studies*

FT-IR spectra of the PHEMA and PHEMA–thiazolidine microbeads were obtained using an FT-IR spectrophotometer (FT-IR 8000 Series, Shimadzu, Japan).



**Figure 1.** Coupling of thiazolidine on to PHEMA microbeads.

### Adsorption studies

The adsorption of Hg(II) ions from aqueous solution was studied using batch systems. The nitrate salt of the mercury ion was used. Aqueous solutions (20 ml) containing different amounts of Hg(II) ions (50–900 mg/l) were incubated with 50 mg of the thiazolidine-immobilized PHEMA sample at different pH values (within the range 3.0–7.0, obtained by adjusting with HCl or NaOH at the beginning of the experiment and not controlled thereafter) at room temperature in a flask agitated magnetically at 600 rpm. After the desired incubation period (up to 60 min), the aqueous phases were separated from the polymers by centrifugation (4000 rpm for 10 min) and the concentrations of metal ions in these phases measured using an atomic absorption spectrophotometer (Shimadzu AA 6800, Japan) equipped with a mercury vapour unit (MVU-1A). Deuterium background correction was used. The working conditions were as follows: wavelength: 253.6 nm; bandpass: 1.0 nm; lamp current: 6.0 mA. Conditions for MVU:  $\text{SnCl}_2$  concentration, 1 w/v%;  $\text{KMnO}_4$  concentration, 0.5 w/v%; and  $\text{H}_2\text{SO}_4$  concentration, 5 w/v%.

The quantities of metal ions adsorbed per unit mass of the polymer (mmol metal ions/g polymer) were calculated using the following expression:

$$\text{Metal ions adsorbed} = [(C_0 - C) \times V]/[m \times 1000] \quad (2)$$

where  $C_0$  and  $C$  are the metal ion concentrations in the aqueous phase before and after incubation, respectively (mg/l),  $V$  is the volume of the aqueous phase (ml) and  $m$  is the amount of polymer used (g).

### Desorption and re-use

Desorption of Hg(II) ions was achieved using 25 ml of eluent, i.e., 0.05 M HCl. The polymer was saturated with Hg(II) ions under the following conditions: initial concentration of Hg(II) ions, 50 mg/l; amount of polymer, 50 mg; volume of adsorption medium, 25 ml; temperature, 20°C; adsorption time, 30 min. The polymer was then placed in the desorption medium and stirred at a rate of 600 rpm for up to 30 min. The concentration of the Hg(II) ions in the aqueous phase was measured as described above. The desorption ratio was calculated using the following expression:

$$\text{Desorption ratio} = \frac{\text{Quantity of Hg(II) ions desorbed to the elution medium}}{\text{Quantity of Hg(II) ions adsorbed on to the sorbent}} \times 100 \quad (3)$$

In order to define the possible re-usability of the cysteine-attached PHEMA, the adsorption/desorption cycle was repeated five times using the same sorbent.

## RESULTS AND DISCUSSION

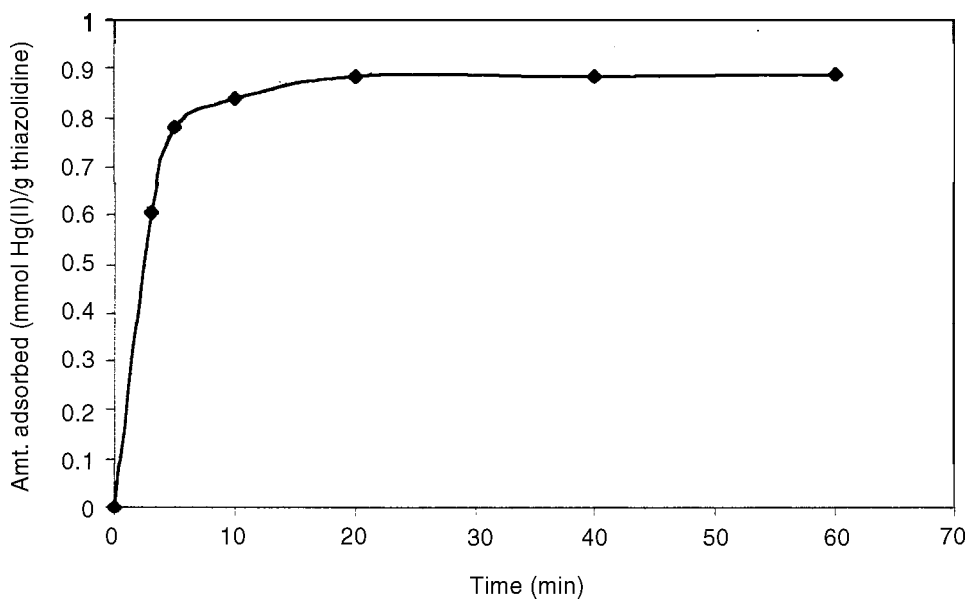
The PHEMA microbeads used in this study were prepared and characterized as in our earlier studies (Denizli and Pişkin 1995b; Arica *et al.* 1998; Denizli *et al.* 1995c). The microbeads were crosslinked hydrogels which did not dissolve in aqueous media but were swollen in water to an extent depending on the degree of crosslinking and on the hydrophilicity of the polymeric matrix. The PHEMA microbeads prepared in this study had a rather hydrophilic structure with the equilibrium water swelling ratio being ca. 50% on a weight basis. The size range obtained from the optical micrographs was 150–200  $\mu\text{m}$  (in the swollen form). It should also be noted that these microbeads were quite rigid and strong due to their highly crosslinked structure, and were therefore suitable for fixed bed or fluidized bed continuous column applications for heavy metal ion removal from aqueous solutions or wastewaters.

To explain the nature of the interaction between the thiazolidine and PHEMA microbeads, FT-IR spectra of the plain PHEMA and thiazolidine-immobilized PHEMA beads were obtained. The FT-IR spectra of the thiazolidine-immobilized PHEMA microbeads exhibited some absorption bands which were different from those of PHEMA. These occurred at 1745  $\text{cm}^{-1}$ , 1625  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  and corresponded to C=O stretching of the ester, the amide I band and the amide II band, respectively.

### Adsorption of Hg(II) ions

#### Adsorption rate

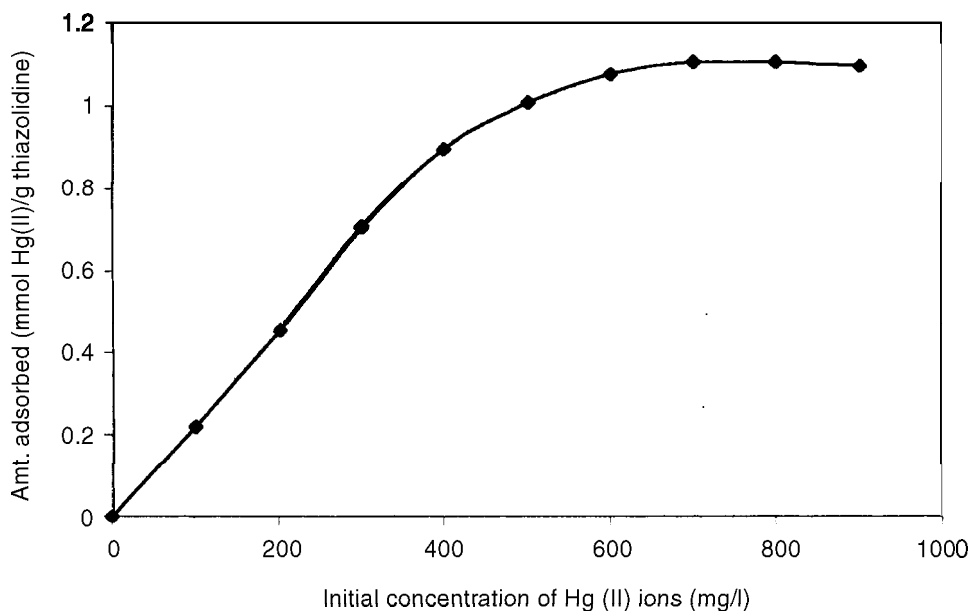
Figure 2 depicts the changes in the amounts of Hg(II) ions adsorbed with time as calculated using the expression given in equation (2). The adsorption conditions are listed in the figure caption. The initial slope of the curve reflects the adsorption rate. It should be noted that no precipitation was observed in this group of experiments. As seen, a high adsorption rate was observed initially followed



**Figure 2.** Adsorption rate of Hg(II) ions by thiazolidine-immobilized PHEMA. Adsorption conditions: initial concentration of Hg(II) ions, 400 mg/l; pH, 6.5; temperature, 20°C.

by a plateau value (i.e., adsorption equilibrium) which was attained gradually over a period of 20 min.

Data on the adsorption kinetics of heavy metal ions by various sorbents have shown a wide range of adsorption rates. Dev and Rao (1996) studied the sorption of different metal ions including Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Zn(II) and Mn(II) using a poly(styrene-co-divinylbenzene)-based macroreticular resin functionalized with bis(*N,N'*-salicylidene) 1,3-propanediamine ligands and reported that the kinetics of the resin-metal interaction were sufficiently rapid for most of the metal ions concerned. Equilibrium sorption was reached within 60 min. Roozmond *et al.* (1988) studied copper and cadmium ion uptake by 3,5-dimethyl-1-hydroxymethylpyrazole-attached *p*-aminomethyl-substituted poly(styrene-co-divinylbenzene) chelating polymer. They showed that adsorption was rather slow with the resin only appearing to reach equilibrium after 2 d. Ebraheem and Hamdi (1997) studied the adsorption of various divalent ions including Ni(II), Cu(II), Zn(II) and Cd(II) on phenol-formaldehyde polymer containing poly(salicylaldoxime 3,5-diylmethylene) and reported a 10 h equilibrium adsorption time. Latha *et al.* (1991) studied ethylenediamine-functionalized polyacrylamide resin for the extraction of several metal ions such as Fe(III), Fe(II), Cu(II) and Ni(II) and reported that the complexation reaction proceeded very slowly (equilibrium time, 5 h). Konishi *et al.* (1993) studied the sorption of zinc, cadmium and lanthanum ions by biopolymer gel beads of alginic acid and reported high adsorption rates in which equilibrium was achieved after ca. 2 h. Note that a lot of experimental and structural parameters determine the adsorption rate, such as the stirring rate in the aqueous phase, the structural properties of the sorbent (e.g., hydrated ionic radius, coordination complex number), the initial concentration of heavy metal ions, the chelate-formation rate between the complex ligand and the metal ions, and, of course, the presence of other metal ions which may compete with the metal ions of interest for



**Figure 3.** Adsorption capacity of thiazolidine-immobilized PHEMA for Hg(II) ions. Adsorption conditions: amount of polymer, 50 mg; volume of adsorption medium, 20 ml; pH, 6.5; temperature, 20°C; adsorption time, 60 min.

the same active complexation sites. Hence, it is difficult to compare the adsorption rates reported. However, the adsorption rates obtained with the thiazolidine-immobilized PHEMA microbeads in this study were sufficiently high to allow the effective removal of Hg(II) ions from aquatic systems.

#### Adsorption capacity

*Effect of the initial concentration of Hg(II) ions:* Adsorption capacities for Hg(II) ions by the thiazolidine-immobilized PHEMA are given as a function of the initial concentration of Hg(II) ions within the aqueous phase in Figure 3. It is interesting to note that the non-specific adsorption of Hg(II) ions on to the plain microbeads was approximately zero. The adsorption capacity of the thiazolidine-immobilized microbeads towards Hg(II) ions initially increased with increasing initial concentration of Hg(II) and then reached a saturation level at an initial Hg(II) concentration of ca. 600 mg/l. The maximum Hg(II) adsorption capacity was 1.11 mmol/g (222.6 mg/g). Elemental analysis showed that unit mass of the PHEMA microbeads carried 0.318 mmol thiazolidine. From mass stoichiometry, it would appear that one immobilized thiazolidine molecule interacted with approximately four Hg(II) ions.

A wide variety of polymers having a wide range of adsorption capacities towards Hg(II) ions has been reported. Shah and Devi (1996) used a dithizone-anchored poly(vinyl pyridine) support and reported a specific mercury adsorption capacity up to 144 mg/g. Liu *et al.* (1990) achieved 72.2 mg/g Hg(II) ion adsorption capacity with *N*-hydroxymethyl thioamide resin while Cestari and Airoldi (1997) determined a value of 186 mg/g for adsorption of the same metal ion by 3-trimethoxysilyl-1-propanethiol-immobilized silica. Binman *et al.* (1997) used sulphur chlorinated jajoba wax-attached polystyrene beads and found that the maximum adsorption capacity

achieved was 50 mg/g. Jyo *et al.* (1997) used phosphoric acid-functionalized poly(glycidyl methacrylate-co-divinylbenzene) beads and reported 40 mg/g Hg(II) ion adsorption capacity. Becker and Eldridge (1993) used an iminodiacetic acid chelating ion-exchanger (Amberlite IRC 718) and achieved an adsorption value of 135 mg Hg(II) ion/g wet polymer. Rivas *et al.* (1998) analyzed the applicability of poly(*N*-vinylimidazole) hydrogels to metal-cation binding from aqueous solutions and obtained an adsorption capacity of ca. 200 mg Hg(II) ion/g while Hwang and Damodaran (1997) used ethylenediamine tetraacetic acid dianhydride-modified soy protein hydrogel sorbents in which the maximum adsorption capacity was 62.1 mg Hg(II) ion/g dry gel. Lezzi *et al.* (1994) synthesized a series of chelating resins derived from macroreticular styrene–divinylbenzene copolymer beads grafted with various poly(ethylene glycols) and reported a maximum adsorption capacity of 20 mg Hg(II) ion/g. Salih *et al.* (1998) developed dithizone-anchored poly(ethylene glycol dimethacrylate-co-hydroxyethylmethacrylate) microspheres and achieved 43.1 mg Hg(II) ion/g. Say *et al.* (1998) used dithiocarbamate-incorporated monosize polystyrene microspheres for the adsorption of organomercury species and reported maximum adsorption capacities of 122.4 mg/g for CH<sub>3</sub>HgCl, 114.3 mg/g for C<sub>2</sub>H<sub>5</sub>HgCl and 20.1 mg/g for C<sub>6</sub>H<sub>5</sub>HgCl.

From the results obtained in this study, it may be concluded that the new polymeric sorbent presented is promising for the adsorption of Hg(II) ions from aqueous media.

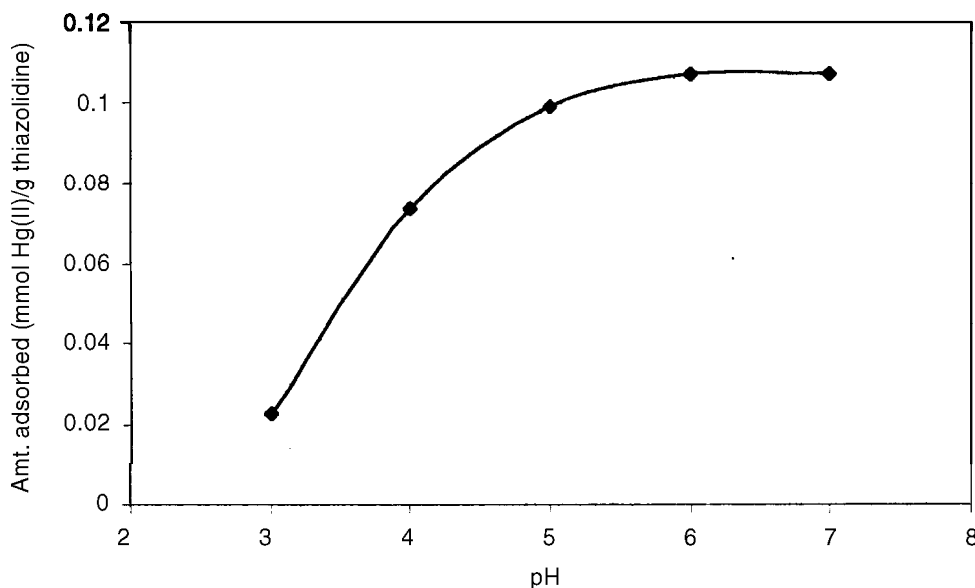
*Effect of the pH value:* The adsorption of heavy metal ions by resins is strongly dependent on the pH value. In the absence of complexing chemical substances, the precipitation of the heavy metal ion is affected by the concentration. As discussed in the literature (Reed and Matsumoto 1993), precipitation of Hg(II) ions becomes significant at ca. pH 8.0. Both the theoretical and experimental precipitation curves showed that precipitation begins above this pH value, which also depends on the concentration of Hg(II) ions in the medium. In the present study, in order to establish the effect of pH on the adsorption of Hg(II) ions on to the thiazolidine-immobilized PHEMA, the batch equilibrium studies were repeated at different pH values in the range 3.0–7.0. Figure 4 shows the effect of pH on the adsorption under the conditions listed in the figure caption. As can be seen from the figure, the adsorption of Hg(II) ions increased with increasing pH and then reached an almost plateau value at ca. pH 6.0. The thiazolidine-immobilized microbeads exhibited a low affinity for Hg(II) ions under acidic conditions (pH < 4.0), a somewhat higher affinity between pH 4.0 and 5.0, and an increase in adsorption above pH 5.0. Increasing the pH value of the solution favoured complex formation between the thiazolidine groups and the Hg(II) ions. The specific adsorption of Hg(II) ions via thiazolidine groups, which was pH-dependent, was much higher (up to 222.6 mg/g) than the non-specific adsorption.

### The stability constant of the Hg(II) ion–thiazolidine complex

In order to understand the affinities of heavy metal ions towards dye molecules, it is of great importance to know the formation constants of thiazolidine–metal ion complexes. The formation constant for the Hg(II) ion–thiazolidine complex has been investigated using the Ružić method (Ružić 1982). According to this method, on plotting  $[M]_{\text{ionic}}/(M_{\text{T}} - [M]_{\text{ionic}})$  versus  $[M]_{\text{ionic}}$  a straight line should be obtained if one type of complex is predominant ( $M_{\text{T}}$  being the total metal concentration and  $[M]_{\text{ionic}}$  the concentration of the labile metal species). From the slope, it is possible to determine the metal-binding capacity of the ligand ( $C_{\text{L}}$ ). According to equation (4), the intercept should give the apparent stability constant ( $K_{\text{stability}}$ ):

$$\{[M]_{\text{ionic}}/(M_{\text{T}} - [M]_{\text{ionic}})\} = 1/K_{\text{stability}} C_{\text{L}} \quad (4)$$





**Figure 4.** Effect of pH on the adsorption capacity of thiazolidine-immobilized PHEMA for Hg(II) ions. Adsorption conditions: initial concentration of Hg(II) ions, 50 mg/l; amount of polymer, 50 mg; volume of adsorption medium, 20 ml; temperature, 20°C; adsorption time, 30 min.

In the present work, use of this method gave a straight line, thereby indicating that the interaction of metal ions with thiazolidine occurs via one type of functional group. The value of  $K_{\text{stability}}$  for the Hg(II)–thiazolidine complex was calculated as  $9.11 \times 10^5$  l/mol.

### Desorption and re-use

Desorption of the adsorbed Hg(II) ions from the thiazolidine-immobilized PHEMA was also studied using a batch experimental set-up. The desorption ratios of the Hg(II) ions thereby obtained are listed in Table 1. The desorption conditions employed are listed in the footnote to the table. The desorption ratios were calculated using the expression given in equation (3).

**TABLE 1.** Desorption of Hg(II) Ions from Thiazolidine-immobilized PHEMA Microbeads<sup>a</sup>

	Hg(II) ions adsorbed (mg/g)	Desorption ratio (%)
First cycle	222.8	100.0
Second cycle	221.3	99.5
Third cycle	222.1	99.3
Fourth cycle	220.6	99.7
Fifth cycle	219.8	98.9

<sup>a</sup>Adsorption conditions: initial concentration of Hg(II) ions, 700 mg/l; amount of polymer employed, 50 mg; adsorption time, 10 min; pH, 6.5. Desorption conditions: desorption medium, 0.05 M HCl; desorption time, 60 min; temperature, 20°C.

### Regeneration of microbeads

To be useful in metal-ion recycling processes, the chelated metal ions should be readily desorbed under suitable conditions. Desorption experiments were performed using 0.05 M HCl solution as the desorption agent. Thus, the PHEMA microbeads loaded with the maximum amounts of Hg(II) ions were placed in the desorption medium and the amount of metal ions desorbed within 5 min measured. Table 1 shows the adsorption/desorption values of Hg(II) ions by PHEMA–thiazolidine microbeads after several cycles of consecutive adsorption and desorption. When HCl was used as the desorption agent, the coordination spheres of the chelated mercury ions were disrupted so that the metal ions were released from the polymer surface into the desorption medium. The data given in the table clearly show that the thiazolidine-immobilized PHEMA microbeads could be used repeatedly without losing their adsorption capacities for the metal ions studied to any significant extent.

### CONCLUSIONS

Thiazolidine-immobilized PHEMA microbeads were used for the adsorption/desorption of Hg(II) ions from aqueous solution under different experimental conditions. High adsorption rates were observed at the beginning of the adsorption process, followed by plateau values (i.e., adsorption equilibrium) which were attained gradually over ca. 20 min. The maximum Hg(II) adsorption capacity of the thiazolidine-immobilized PHEMA microbeads was 1.11 mmol/g (222.6 mg/g). The amount of adsorbed Hg(II) ions increased with increasing pH and reached a virtual plateau value at ca. pH 6.0. The formation constant for the thiazolidine–Hg(II) ion complex has been calculated by Ružić's method, the value of the calculated stability constant being  $9.11 \times 10^5$  l/mol.

We have also investigated the adsorption of Cd(II) and Pb(II) ions by thiazolidine-immobilized PHEMA microbeads in a recent study (Sağlam *et al.* 2001). In this case, the adsorption capacities were found to be 0.397 mmol/g (44.6 mg/g) and 0.336 mmol/g (69.6 mg/g) for Cd(II) and Pb(II) ions, respectively. Taken together with the results obtained in the present study, these data may be considered an indication of the higher specificity of the thiazolidine-immobilized PHEMA microbeads for the Hg(II) ion. On a molar basis the affinity order [Hg(II) > Cd(II) > Pb(II)] may be interpreted using Pearson's HSAB (Hard and Soft Acids and Bases) theory (Pearson 1963). Sulphur-containing ligands, which are usually considered as soft bases, can coordinate soft acids such as Hg(II) ions quite strongly. The Hg(II) ion may be classified as a softer acid than the Cd(II) or Pb(II) ion because of its larger size and greater deformability of its electron cloud.

Desorption of the adsorbed Hg(II) ions was performed by using 0.05 M HCl solution, with up to 99% adsorption ratios being achieved. From the results presented in this paper, it may be concluded that thiazolidine-immobilized PHEMA microbeads may be used effectively (i.e. with high adsorption rates and capacities) for the specific removal of Hg(II) ions from aqueous solutions.

### REFERENCES

- Allen, S.J. and Brown, P.A. (1995) *J. Chem. Technol. Biotechnol.* **62**, 17.
- Arica, M.Y., Testereci, H.M. and Denizli, A. (1998) *J. Chromatogr. A* **799**, 83.
- Becker, N.S.C. and Eldridge, R.J. (1993) *React. Polym.* **21**, 5.
- Berlin, M. (1986) *Handbook on the Toxicology of Metals*, Friberg, L., Nordberg, G.F., Vouk, E.B., Eds, 2nd Edn, Elsevier/North Holland, New York.
- Binman, S., Belfer, S. and Shani, A. (1997) *J. Appl. Polym. Sci.* **63**, 625.

- Boyer, P.D., Lardy, H. and Myrback, K. (Eds) (1959) *The Enzymes*, 2nd Edn, Vol. 1, Academic Press, New York.
- Cestari, A.R. and Airoidi, C. (1997) *J. Colloid Interface Sci.* **195**, 338.
- Denizli, A. and Pişkin, E. (1995a) *J. Chromatogr. B* **670**, 157.
- Denizli, A. and Pişkin, E. (1995b) *J. Chromatogr. B* **666**, 13.
- Denizli, A., Rad, A.Y. and Pişkin, E. (1995c) *J. Chromatogr. B* **668**, 13.
- Dev, K. and Rao, G.N. (1996) *Talanta* **43**, 451.
- Ebraheem, K.A.A. and Hamdi, S.T. (1997) *React. Funct. Polym.* **34**, 5.
- Hwang, D.C. and Damodaran, S. (1997) *J. Appl. Polym. Sci.* **64**, 891.
- Jyo, A., Matsufune, S., Ono, H. and Egawa, H. (1997) *J. Appl. Polym. Sci.* **63**, 1327.
- Konishi, Y., Asai, S.S., Midoh, Y. and Oku, M. (1993) *Sep. Sci. Technol.* **28**, 1691.
- Latha, A.G., George, B.K., Kannon, K.G. and Ninan, K.N. (1991) *J. Appl. Polym. Sci.* **43**, 1159.
- Lezzi, A., Cobianco, S. and Roggrero, A. (1994) *J. Polym. Sci., A* **32**, 1877.
- Liu, C.Y., Chang, H.T. and Hu, C.C. (1990) *Inorg. Chim. Acta* **172**, 151.
- Oberlander, H.E. and Roth, K. (1978) *Soil Sci.* **141**, 107.
- Pearson, R.G. (1963) *J. Am. Chem. Soc.* **85**, 3533.
- Reed, B.E. and Matsumoto, M.R. (1993) *Sep. Sci. Technol.* **28**, 2179.
- Rivas, B.L., Maturana, H.A., Molina, M.J., Gomez-Anton, M.R. and Pierola, I.F. (1998) *J. Appl. Polym. Sci.* **67**, 1109.
- Roosmond, D.A., Hond, F.D., Veldhuis, J.B., Strasdeit, H. and Driessen, W.L. (1988) *Eur. Polym. J.* **24**, 867.
- Ružić, I. (1982) *Anal. Chim. Acta* **140**, 99.
- Salih, B., Denizli, A., Kavakli, C., Say, R. and Pişkin, E. (1998) *Talanta* **46**, 1205.
- Say, R., Şatiroğlu, N., Pişkin, E., Bektaş, S. and Genç, Ö. (1998) *Anal. Lett.* **31**, 511.
- Shah, R. and Devi, S. (1996) *React. Funct. Polym.* **31**, 1.
- Sugiura, Y., Hojo, Y., Tamai, Y. and Tanaka, H. (1976) *J. Am. Chem. Soc.* **98**, 2339.
- Sumino, K., Yamamoto, R. and Kitamura, S. (1995) *Nature (London)* **268**, 17.
- Tephly, T.R., Wagner, G. and Sedman, R.W.P. (1978) *Fed. Proc.* **37**, 35.
- World Health Organization (WHO) (1976) *Mercury, Environmental Health Criteria 1*, Geneva, Switzerland.