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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Competitive Adsorption of Heavy-Metal Ions on Monodisperse Polystyrene Microspheres Carrying Dithiocarbamate Groups

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To cite this Article Satiroglu, N. , Kesenci, K. , Bektas, S. , Genç, Ö. and Piskin, E.(1998) 'Competitive Adsorption of Heavy-Metal Ions on Monodisperse Polystyrene Microspheres Carrying Dithiocarbamate Groups', Journal of Macromolecular Science, Part A, 35: 1, 91 — 107

To link to this Article: DOI: 10.1080/10601329808001963

URL: http://dx.doi.org/10.1080/10601329808001963

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J.M.S.—PURE APPL. CHEM., A35(1), pp. 91–107 (1998)

COMPETITIVE ADSORPTION OF HEAVY-METAL IONS ON MONODISPERSE POLYSTYRENE MICROSPHERES CARRYING DITHIOCARBAMATE GROUPS

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Key Words: Monodisperse Polystyrene Microspheres, Dithiocarbamate Groups, Adsorption/Desorption, Heavy-metal Ions

ABSTRACT

Competitive adsorption of heavy-metal ions, i.e., Cd(II), Cu(II) and Pb(II), from aqueous media onto monodisperse polystyrene (PS) microspheres carrying dithiocarbamate groups were investigated. The crosslinked PS microspheres (2 μm in diameter) were produced by dispersion polymerization, and then dithiocarbamate groups were incorporated by a two-step procedure. The adsorption rate and capacity of these sorbents for selected heavy metal ions from aqueous media containing different amounts of these ions (0.05-600 ppm) and at different pH of 3.0-8.0 were investigated. Very high adsorption rates were observed at the beginning, and adsorption equilibria were then gradually achieved in about 5-90 minutes. The maximum adsorptions of metal ions onto the dithidcarbamate modified PS microsphere were 205.8 mg, 126.0 mg and 129.1 mg per gram of the sorbent microspheres for Pb(II), Cd(II) and Cu(II), respectively. When the metal ions competed (in

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the case of the adsorption from their mixture) the amounts of adsorption of metal ions were quite close. Desorption of metal ions were studied by using different eluent volume (20-200 ml) with 0.5 M NaCl. High desorption ratios (more than 90%) were achieved in all cases. Adsorption-desorption cycles showed the feasibility of repeated uses of this sorbent system.

INTRODUCTION

The presence of heavy-metals in the environment is a major concern due to their toxicities. Treatment of aqueous wastes containing soluble heavy-metals requires concentration of the metals into a smaller volume followed by recovery or secure disposal. Heavy-metals can be removed by adsorption on solid matrices. Nonspecific sorbents, such as activated carbon, metal oxides, and ion-exchange resins have been used [1, 2]. Specific sorbents consist of a ligand (e.g., ion-exchange material or chelating agents) which interacts with the metal ions specifically, and a carrier matrix which may be an inorganic material (e.g., aluminum oxide, silica or glass) or polymer microspheres (e.g., polystyrene, polymethylmethacrylate, cellulose) have been considered for more specific removal [3-6].

As carrier matrices, polymer microspheres have attracted the most attention because they may easily be produced in a wide variety of compositions, and modified into specific sorbents, by introducing a variety of ligands. Synthetic polymers have almost entirely displaced inorganic carriers, with few exceptions. In the conventional applications, nonporous or porous polymer microspheres with average diameters of usually more than 100 μm are used. When the nonporous microspheres are used, only the outer surface of the microspheres are available for the incorporation of the ligands which will give the specificity of these sorbents. Low surface area means low adsorption capacity. In order to increase the active surface area, porosity may be created within the microspheres. For instance, there are commercially available polymer based porous sorbents which exhibit surface areas 200-500 m^2 or even larger per unit mass of the sorbent. However, these type of sorbents have also important disadvantages. First of all, the adsorption rates are much slower, due mainly to pore diffusion resistance. In addition, the high active surface area of these sorbents is also mainly due to the fine pores in the matrix, which are not available for large solute molecules. In other words, large molecules cannot penetrate within these fine pores and therefore, cannot use the active surface area available, which means low adsorption capacities for large molecules.

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Recently, we produced monodisperse polystyrene microspheres and also their functionalized forms in the size range of 1-10 μm, by phase inversion (or dispersion) polymerization [7-11], and proposed to use these polymer microspheres as the carrier matrix to prepare specific sorbents for separation and purification of heavy-metal ions

[12]. In our previous paper, we presented preparation and characterization of the monodisperse crosslinked PS microspheres carrying dithiocarbamate functional groups, and showed their metal chelating activities by using cadmium ions as an example. In this communication, we discuss competitive adsorption of some selected heavy-metal ions, namely, Cd(II), Cu(II) and Pb(II) on these new sorbent microspheres.

EXPERIMENTAL

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Preparation of Ps Microspheres Carrying Dithiocarbamate Groups

Details of production and characterization of the monosdisperse PS microspheres carrying dithiocarbamate groups were given elsewhere [12]. Briefly, at the first step, the monodisperse PS microspheres were prepared by a phase inverion polymerization, from styrene (Yarpet A. S., Turkey) by using 2,2'-azobisisobutyronitrile (AIBN) (BHD Chemicals Ltd., UK) as the initiator, and polyvinylpyrrolidone (PVP) (30K, Fluka, Switzerland) as the stabilizer, and in a dispersion medium composed of isopropanol (Merck, Germany)/water mixtures [7, 9, 12]. The polymerizations were carried out in a magnetic-driven, sealed, cylindirical reactor equipped with a temperature-control system. In order to obtain monodisperse PS microspheres in a diameter of 2 μm, 2 g of PVP was dissolved in the dispersion medium containing 180 ml of isopropanol and 20 ml of water. The monomer phase was prepared by dissolving 0.28 g AIBN in a 20 ml of styrene. These two phases were mixed and charged to the reactor agitated with an anchor-type agitator at a speed of 150 rpm, and the polymerization was conducted at 80°C for 24 hours. The PS latex obtained was cleaned by using the serum replacement and ion-exchange methods described previously [7, 9, 12].

At the second step, the monodisperse PS microspheres were crosslinked by using divinyl-benzene (DVB) (Fluka, Switzerland) as the crosslinker, by the following procedure [12]: 3 ml of DVB was mixed with 3 ml of styrene, and the 0.12 g AIBN was dissolved in this mixture. This monomer phase was added to the 200 ml of PS latex containing 20 g polymer in 400 ml of the latex. These two phases were charged to the erlenmayer flask and the resulting mixture was stirred at a stirring rate of 600 rpm at 20°C for 24 hours in order to allow the adsorption of the comonomers onto the PS microspheres. The adsorbed comonomers were then copolymerized in the reactor stirred at a stirring rate of 150 rpm at 80°C for 24 hours. The crosslinked PS microspheres were cleaned by using the serum replacement and ion-exchange methods [7, 9, 12].

In order to incorporate dithiocarbamate functional groups on the cross-linked PS microspheres, a two-step procedure was applied [12]. First, 5 g of the PS microspheres were added into the mixtures of 50 ml water and 1 ml benzylamine (Fluka, Switzerland), and the resulting suspensions were strirred at a stirring rate of 600 rpm at 20°C for 24 hours. The swollen PS microspheres were washed with distilled water twice, and separated from the supernatant by filtration. Then, the amine groups of benzylamine (physically-adsorbed within the PS microspheres) were transformed into dithiocarbamate groups by reacting with carbon disulfide. The PS microspheres containing benzylamine were added into the mixtures of 50 ml water and 2.5 ml of 1,4-dioxane (Merck, Germany), and the pH of the media were rapidly adjusted to 11.0 by using 1.0 M potassium hydroxide. 2.5 ml carbon disulfide (Fluka, Switzerland) was then added to these media, and the resulting mixture was stirred at a stirring rate of 600 rpm at 20°C for 24 hours, in order to complete the reaction between benzylamine and carbon disulfide. These PS microspheres carrying physically entrapped benzyl dithiocarbamate were cleaned by serum replacement technique [7, 9, 12]. Incorporation of dithiocarbamate groups were confirmed by using FTIR and elemental analysis [12].

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Adsorption/Desorption/Reuse

Adsorption Studies

Adsorption of heavy-metal ions (i.e., Cd(II), Cu(II) and Pb(II)) from aqueous solutions were studied in batch systems. Adsorption rate and capacities were investigated. Nitrates of the respective metal ions were used. Aqueous solutions (20 ml) containing different amounts of heavy-metal ions (0.05-600 ppm) were incubated both with 25 mg of the unmodified (plain) or dithiocarbamate-carrying PS microspheres at different pH (in the range of 3.0-8.0, which was adjusted with HNO_3 or NaOH at the beginning of the experiment and not controlled afterwards) at 20°C (performed in a temperature-control chamber), in the flasks agitated magnetically at an agitation speed of 600 rpm. After the desired incubation periods (up to 120 minutes), the aqueous phases were separated from the microspheres by centrifugation (4000 rpm for 30 minutes), and the concentrations of the metal ions in these phases were measured by using an Atomic Absorption

Spectrophotometer (Unicam, 939 AAS, UK) with a graphite furnace atomizer. The respective hollow cathode lamps (Unicam, UK) for each metal ions were used. The spectral band with was 0.5 nm. The working currents/wave lengths for Cd(II), Cu(II) and Pb(II) were 8 mA/228.8 nm, 5 mA/324.8 nm, and 10 mA/283.3 nm, respectively. The amounts of metal ions adsorbed per unit mass of the microspheres (mg metal ions/g polymer) were evaluated by using the following expression.

$$\text{Metal ions adsorbed} = [(C_0\text{-}C) \times V] / [m \times 1000] \qquad (1)$$

Here, C_0 and C are the concentrations of the metal ions in the aqueous phase before and after the incubation period, respectively (ppm); V is the volume of the aqueous phase (ml); and m is the amount of the microspheres used (g).

Competitive heavy-metal adsorption from aqueous solutions containing Cd(II), Cu(II) and Pb(II) were investigated by following a similar procedure described above. These studies were performed at a constant pH [5.0 or 6.0 for Cu(II) and 6.0 for Cd(II) and Pb(II)], and at 20°C using solutions containing different amounts of the respective ions.

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Desorption and Reuse

Desorption of heavy-metal ions was achieved by using different volumes (20 ml, 100 ml and 200 ml) of the eluent, i.e., 0.5 M NaCl. The microspheres adsorbed with the heavy-metal ions in the following conditions: initial concentration of the metal ions: 100 ppm; amount of the microspheres: 25 mg; volume of the adsorption medium: 20 ml; pH: 6.0; temperature: 20°C; and adsorption time: 30 minutes. Then, these microspheres were placed in this desorption medium and stirred at a stirring rate of 600 rpm up to 120 minutes. pH and temperature of the medium were 6.63 (the original pH of the 0.5 M NaCl in deionized water, not buffered) and 20°C, respectively. The concentrations of metal ions in the aqueous phase were followed bas mentioned before. Desorption ratio was calculated from the following expression.

$$\text{Desorption ratio} = \frac{(\text{Amount of metal ions desorbed to the elution medium})}{(\text{Amount of metal ions adsorbed onto the sorbent microspheres})} \times 100 \qquad (2)$$

In order to obtain the reusability of the dithiocarbamate-carrying PS microspheres, adsorption-desorption cycle was repeated three times by using the same sorbent. Adsorption conditions were as follows: initial concentration of the metal

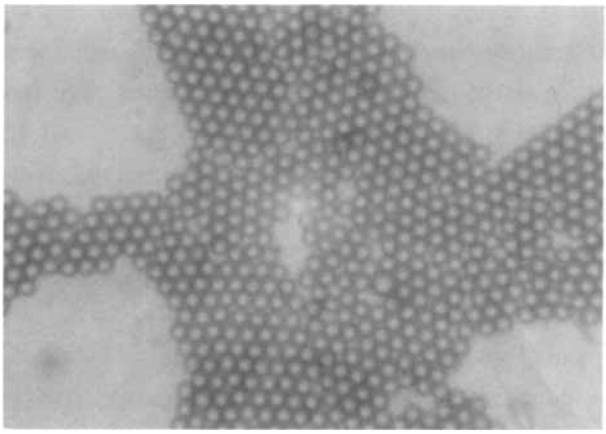

Figure 1. A representative optical photograph of the dithiocarbamate-carrying PS sorbent microspheres (taken with 1000x magnification and reduced at a proper ratio to place the figure).

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ions: 100 ppm from the adsorption of single metal ion solutions, and 150 ppm from the adsorption of ternary metal ion solutions (equal amounts of the metal ions were used); amount of the microspheres: 25 mg; volume of the adsorption medium: 20 ml; temperature: 20°C; and adsorption time: 30 minutes. The microspheres were washed few times with 0.5 M NaCl and demineralized water and reloaded.

RESULTS AND DISCUSSION

Sorbent Microspheres

In this study, we attempted to prepare a new metal chelating sorbent system, i.e., monodisperse polystyrene (PS) microspheres carrying dithiocarbamate functional groups. We selected dithiocarbamate groups because they do form chelates with many metal ions of interest [6, 13-19]. These PS based sorbent microspheres were prepared by a three-step procedure, which were described in detail in our previous paper [12]. A representative optical photograph of these monodisperse dithiocarbamate-carrying PS microspheres is given in Figure 1. This photograph clearly shows that the microspheres are uniform in size (monodisperse) with very few exceptions.

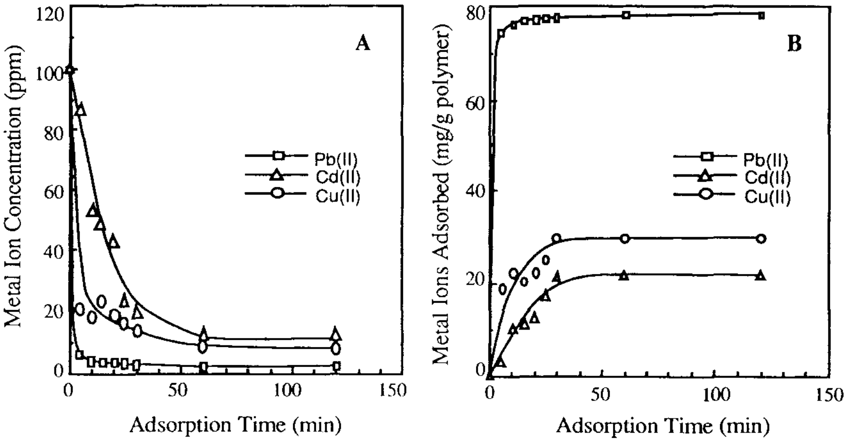

Figure 2. Adsorption rates of heavy-metal ions by dithiocarbamate-carrying PS sorbent microspheres: (A) changes in the metal ions concentrations in the adsorption medium, and (B) changes in the amount of metal ions adsorbed. Adsorption conditions: initial concentration of the metal ions: 100 ppm; amount of the microspheres: 25 mg; volume of the adsorption medium: 20 ml; pH: 6.0; and temperature: 20°C.

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Adsorption of Heavy-metal Ions

Adsorption Rate

Figure 2 exemplifies adsorption rates of heavy-metal ions by dithiocarbamate-carrying PS microspheres as a function of time. Note that these batch experiments were performed by using single (not together) solutions of the interested ions. Figure 2A gives the decreases in the concentrations metal ions in the adsorption medium with time. While Figure 2B shows the changes of the amounts with metal ions adsorbed with time which were calculated by using the expression given in Equation 1. Adsorption conditions are given in the figure legend. The slopes of these curves reflect the adsorption rates. It should be noted that there was no precipitation in these group of experiments because the initial concentrations of the metal ions and pH were 100 ppm and 6.0, respectively (as seen in Table 1). As seen here, high adsorption rates are observed at the beginning, and then plateau values (i.e., adsorption equilibrium) are gradually reached within 5-30 minutes.

Several experimental data on the adsorption kinetics of heavy-metal ions by various sorbents have shown a wide range of adsorption rates [2, 20-28]. For

TABLE 1. Precipitation Concentrations of Pb(II),Cd(II) and Cu(II) Hydroxides at Different pH's

pH*	Precipitation Concentrations** (ppm)		
	Cd(II)	Cu(II)	Pb(II)
3	$6.63\text{x}10^{12}$	$1.02\text{x}10^{8}$	$5.18\text{x}10^{11}$
4	$6.63\text{x}10^{10}$	$1.02\text{x}10^{6}$	$5.18\text{x}10^{9}$
5	$6.63\text{x}10^{8}$	$1.02\text{x}10^{4}$	$5.18\text{x}10^{7}$
6	$6.63\text{x}10^{6}$	102	$5.18\text{x}10^{5}$
7	$6.63\text{x}10^{4}$	1.02	$5.18\text{x}10^{3}$
8	663	$1.02\text{x}10^{-2}$	51.8
9	6.63	$1.02\text{x}10^{-4}$	0.518

*Adjusted by using NaOH or HNO_3

**The K_{sp} values for $Cd(OH)_2$, $Cu(OH)_2$ and $Pb(OH)_2$ are $5.9\text{x}10^{-15}$, $1.6\text{x}10^{-19}$, and $2.5\text{x}10^{-16}$, respectively.

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example, Reed and Matsumoto have considered 6 hours as a short equilibrium time in their metal ions adsorption kinetic studies, in which they have used activated carbon as sorbent [2, 20]. Konishi *et al.* have investigated recovery of zinc, cadmium, and lanthanum by biopolymer gel particles of alginic acid. In their recent paper, they reported very high adsorption/desorption rates for lanthanum by alginic acid, in which equilibrium was achieved in about 60-90 minutes [21]. Shreedhara-Murty and Ryan have investigated mercury, copper, cadmium, lead and uranium adsorption on cellulose-dithiocarbamate resins and reported that the adsorption rates were slow, but they were able to use a 30 minute equilibrium time reproducibly [29]. Egawa has studied uranium adsorption on polyacryonitile fibers containing amidoxime groups and reported 7 hour equilibrium adsorption time [30]. Recently, our group was able to shorten the equilibrium times (5-90 minutes) for heavy-metal adsorption by using dye-attached swellable poly(EGDMA-HEMA) microspheres [31-33].

Note, that in such an adsorption process, there are several parameters which determine the adsorption rate, such as agitation (or flow) rate in the aqueous phase, sorbent structural properties (e.g., size, porosity, surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, pH, temperature, chelate-formation rate, and of course existence of other ions which may compete with the ions interest for active adsorption sites. All individual experimental studies published in the literature have been performed at different conditions. Consequently, it is not reasonable to make a healthy comparison of the adsorption rates reported. However, by only considering adsorption equilibrium times, we can say that, the approach proposed in this study in which microspheres in micron size range are used, may be considered as an important improvement in the adsorption kinetics.

Adsorption capacity

Heavy-metal ion adsorption capacities of the dithiocarbamate-carrying PS sorbent microspheres are presented as a function of the initial concentration of metal ions within the aqueous adsorption medium in Figure 3. This figure was prepared by using the plateau values of the adsorption rate-curves (examples are given in Figure 2B). These batch experiments were performed by using single solutions of the interested ions. Adsorption conditions are given in the Figure Legend.

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Note that in the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species [2, 20-34]. The solubility of metal ion is governed by hydroxide or carbonate concentration. As discussed in detail by Boomhover [34] and Reed and Matsumoto [2, 20], hydrolysis of metal ions becomes significant at approximately pH 8.5, pH 6.5 and pH 7.5 for Cd(II), Cu(II) and Pb(II), respectively. We have also estimated the theoretical precipitation concentrations of hydroxides of the respective metal ions at different pH by using K_{sp} values given by Skoog and West [35]. Table 1 shows these values. By considering these data, in order to eliminate the effects of precipitation we performed these group of experiments at pH: 5.0 for Cu(II) and 6.0 for Pb(II) and Cd(II).

The amount of metal ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased with the initial concentration of metal ions, as expected. In order to reach the plateau values which represent saturation of the active points (which are available for specific interaction with metal ions) on the microspheres, in other terms to obtain the maximum adsorption capacities of the dithiocarbamate-carrying PS microspheres for the interested metal ions, we increased initial concentration of the metal ions up to 600 ppm. The maximum adsorption capacities of the dithiocarbamate-carrying PS microspheres (corres-

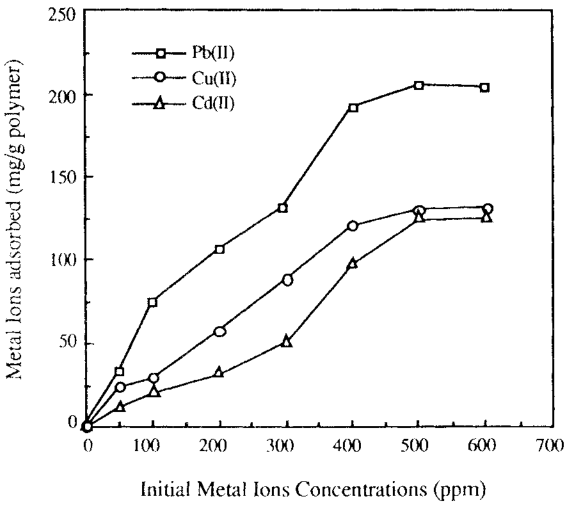

Figure 3. Adsorption capacities of dithiocarbamate-carrying PS sorbent microspheres for heavy-metal ions. Adsorption conditions: amount of the microspheres: 25 mg; volume of the adsorption medium: 20 ml; pH: 5.0 for Cu(II) and 6.0 for Pb(II) and Cd(II); temperature: 20°C; and adsorption time: 30 minutes.

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ponding a 600 ppm metal ion initial concentration) are 205.8 mg, 126.0 mg and 129.1 mg per gram of the sorbent for Pb(II), Cd(II) and Cu(II), respectively. The order of affinity based on a weight uptake by the dithiocarbamate-carrying PS sorbent microsphere is as follows: Pb(II)>Cu(II)> Cd(II). Note that the maximum adsorption capacities (in molar basis) of the microspheres are 0.99 mmol, 1.12 mmol, and 2.03 mmol per gram of the sorbent for Pb(II), Cd(II) and Cu(II), respectively. Therefore, the order of affinity is as follows: Cu(II)>Cd(II)>Pb(II). Note that comparing with the adsorption capacities of several sorbents for different heavy-metal ions reported in the related literature [2, 19-34], which are usually in the range of 1-100 mg/g sorbent, our approach (using monodisperse micron-size sorbents) may be considered as an important improvement in addition to adsorption kinetics.

It should be noted that the nonspecific adsorption (adsorption on the plain PS microspheres) of heavy-metal ions are relatively low, but were still significant, which were 51.4 mg, 35.8 mg, and 18.5 mg per gram of the sorbent microspheres for Pb(II), Cd(II) and Cu(II), respectively. These adsorptions may be due to the residuals of the surfactant molecules (i.e., polyvinyl-pyrrolidone) on the PS

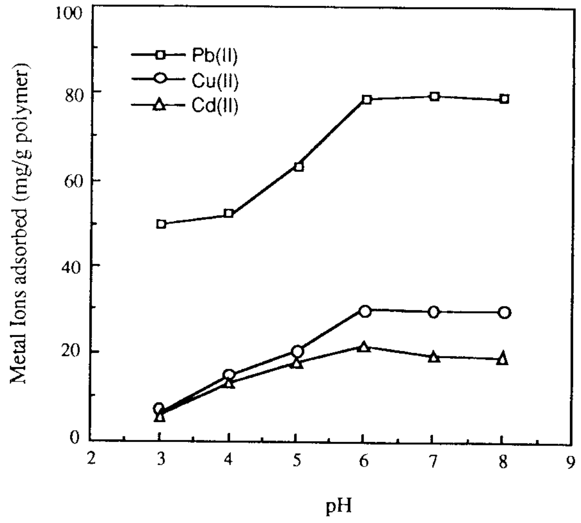

Figure 4. Adsorption capacities of dithiocarbamate-carrying PS microspheres for heavy-metal ions at different pH. Adsorption conditions: initial concentration of the metal ions: 100 ppm; amount of the microspheres: 25 mg; volume of the adsorption medium: 20 ml; temperature: 20°C; and adsorption time: 30 minutes.

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microspheres entrapped during the phase inversion polymerization. It was a surprising result that without any further modification, the polystyrene microspheres prepared with polyvinylpyrrolidone (as surfactant) may be used as sorbent for the removal of heavy-metal ions. Optimization of the adsorption properties of these microspheres is under investigation.

It is well-known that metal ion adsorption both on non-specific and specific sorbents is pH dependent [2, 20-34]. Therefore, in this study, in order to establish the effect of pH on the adsorption of metal ions onto the dithiocarbamate-carrying PS microspheres, we repeated the batch equilibrium studies at different pH values in the range of 3.0-8.0. Note that we did not attempt to study below pH 3.0 by considering possible decomposition of dithiocarbamate groups [36].

Figure 4 exemplifies the effects of pH on adsorption. Adsorption conditions are given in the Figure Legend. As seen here, adsorption of all heavy-metal ions evaluated in this study first increased with pH, and then almost reached a plateau value around pH 6.0. High adsorption at higher pH values implies that metal ions interact with dithiocarbamate (unprotonated) by chelating, as also stated in the related literature [2, 19-33].

TABLE 2. Competitive Adsorption of Pb(II),Cd(II) and Cu(II) Ions from their Ternary Solutions onto Dithiocarbamate-Carrying PS Sorbent Microspheres

Metal ions conc.* (ppm)	Metal ions adsorbed** (mg/g polymer)			
	Total***	Cd(II)	Cu(II)	Pb(II)
9	3.43	0.083 (0.7mmol)	1.12 (17.6μmol)	2.23 (10.7μmol)
15	5.85	0.800 (7.1mmol)	1.72 (27.1μmol)	3.33 (16.0μmol)
30	13.78	2.260 (20.1mmol)	4.31 (67.9μmol)	7.21 (34.8μmol)
90	31.68	3.040 (27.0mmol)	7.42 (116.8μmol)	21.22 (102.4μmol)
150	57.05	8.990 (80.0mmol)	17.0 (267.7μmol)	31.06 (150.0μmol)

*Total metal ions initial concentaration in the adsorption medium. Equal amounts of the metal ions were used

**Adsorption values in molar basis are given in the paranthesis

***Total amount of metal ions adsorbed as mg metal ions/gram polymer

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Competitive Adsorption

In this group of experiments, competitive adsorption of Cd(II), Cu(II) and Pb(II) ions from their ternary solutions was investigated. Solutions (20 ml) containing different amounts of metal ions were incubated with 25 mg of the dithiocarbamate-carrying PS microspheres for 30 minutes at pH: 6.0, and at a temperature of 20°C. Note that in each experiment the total amount of metal ions were changed, but the relative ratios (in ppm units) were the same (1/1/1). Table 2 gives the results of a set of experiments as an example. As seen in this table, amounts of the adsorbed Pb(II) ions are higher than those obtained for Cd(II) and Cu(II) ions, not only in weight basis but also in molar basis (opposite to the adsorption of the ions from their single metal ions solutions). These results may be considered as an indication of higher specificity of the dithiocarbamate-carrying PS microspheres for the Pb(II) ions comparing to other ions. It should be noted that the extent of adsorption of each type of metal ion is strongly dependent upon its relative concentration within the mixture. Therefore, it is almost impossible to generalize the order of adsorption or to define the extent of adsorption for each metal ion when they compete.

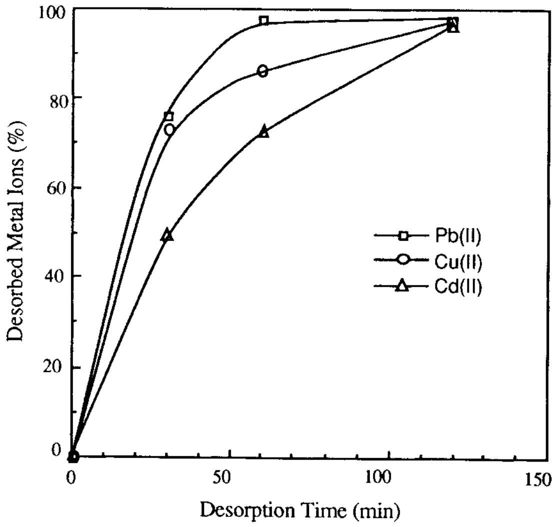

Figure 5. Desorption of heavy-metal ions from sorbent microspheres. Adsorption conditions: initial concentration of the metal ions: 100 ppm; amount of the micro-spheres: 25 mg; volume of the adsorption medium: 20 ml; temperature: 20°C; and adsorption time: 30 minutes. Desorption conditions: desorption medium: 0.5 M NaCl; volume of the desorption medium: 200 ml; amount of the sorbent microspheres: 25 mg; pH: 6.63; and temperature: 20°C.

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Desorption and Reuse

Desorption

Desorption of the adsorbed metal ions from the dithiocarbamate-carrying PS sorbent microspheres was also studied in a batch experimental set-up. In the first group of experiments, desorption rates of heavy-metal ions from the sorbent microspheres loaded with the maximum amounts of the respective metal ions (loaded from their single metal ions solutions) were obtained. The change in the amount of metal ions desorbed (i.e., desorption rate curves) are given in Figure 5. Desorption conditions are given in the Figure Legend. The slowest desorption was observed for Cd(II) ions. Even in that case, it was possible to remove almost all the adsorbed metal ions (more than 95%) from the sorbent in about two hours,which was seleceted as the desorption time in the second part of the experiments.

In the second group of experiments, desorption ratios for heavy-metal ions from the sorbent microspheres loaded with the maximum amounts of the respective metal ions (loaded from their single and/or ternary metal ions solutions) were

TABLE 3. Desorption of heavy-metal ions from sorbent microspheres. Adsorption conditions: initial concentration of the metal ions: 100 ppm from the adsorption of single metal ion solutions, and 150 ppm from the adsorption of ternary metal ion solutions (equal amounts of the metal ions were used); amount of the microspheres: 25 mg; volume of the adsorption medium: 20 ml; temperature: 20°C; and adsorption time: 30 minutes. Desorption conditions: desorption medium: 0.5 M NaCl; volume of the desorption medium: 20, 100 or 200 ml; desorption time 120 minutes; amount of the sorbent microspheres: 25 mg; pH: 6.63; and temperature: 20°C

Metal ions	Desorption ratio (%)		
	Volume of desorption medium (ml)		
	20	100	200
Desorption from sorbent microspheres (loaded from single metal ions solutions			
Pb(II)	16	33	98
Cd(II)	24	85	97
Cu(II)	18	50	98
Desorption from sorbent microspheres (loaded from ternary metal ions solutions)			
Pb(II)	65	85	97
Cd(II)	75	80	98
Cu(II)	70	82	95

obtained. The desorption conditions are given in the Table Legend. The desorption ratios were calculated by using the expession given in Equation 2 and given in Table 3.

As seen in Table 3, the desorption ratio is strongly dependent on the desorption medium volume. The desorption ratios obtained with a desorption volume of 20 ml were very low, while almost all of the adsorbed metal ions were removed in 120 min when the desorption volume was 200 ml.

Reuse

In order to obtain the reusability of the dithiocarbamate-carrying PS microspheres, adsorption-desorption cycle was repeated 3 times by using the same sor-

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TABLE 4. Reusebility of the dithiocarbamate-carrying PS microspheres. Adsorption/desorption of heavy-metal ions from sorbent microspheres. Adsorption conditions: initial concentration of the metal ions: 100 ppm; amount of the microspheres: 25 mg; volume of the adsorption medium: 20 ml; pH: 6.0; temperature: 20°C; and adsorption time: 30 minutes. Desorption conditions: desorption medium: 0.5 M NaCl; volume of the desorption medium: 200 ml; amount of the sorbent microspheres: 25 mg; pH: 6.63; temperature: 20°C, and desorption time: 120 minutes

Metal Ions	Metal ions adsorbed (mg/g polymer)			Desorption Ratio (%)		
	First	Second	Third	First	Second	Third
Cd (II)	21.64	20.96	20.83	97.3	97.8	98.2
Cu (II)	30.12	30.12	29.70	97.0	97.7	98.1
Pb (II)	78.66	77.52	78.20	97.6	98.3	97.9

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bent. Note that adsorptions were achieved from the single metal ion solutions. The data is presented in Table 4. Both the adsorption and desorption conditions are given in the table. As seen here, resorption capacity of the sorbent for all metal ions did not change significantly during repeated adsorption-desorption operations.

CONCLUSION

In this study, we attempted to prepare a new sorbent system, i.e., monodisperse polystyrene (PS) microspheres carrying dithiocarbamate functional groups for removal of heavy-metal ions from aqueous solutions. Crosslinked PS microspheres (2 μm in diameter) were produced by dispersion polymerization and used as the carrier matrix. In order to include functionality, dithiocarbamate groups were incorporated to these microspheres by a simple two-step procedure. Adsorption rate and capacity of these sorbents for selected heavy metal ions from aqueous media containing different amounts of these ions (0.05-600ppm) and at different pH of 3.0-8.0 were investigated. Very high adsorption rates (in other terms, very short adsorption equilibrium times), much better than have been reported by others were achieved. Adsorptions rates were very fast at the beginning, and adsorption equilibria were then gradually achived in about 5-90 minutes. Adsorption capacities of this novel sorbents for different heavy-metal ions were superior to the existing similar sorbents. The maximum adsorptions of metal ions onto the dithiocarbamate modified PS microsphere were 205.8 mg, 126.0 mg and 129.1 mg per gram of the sorbent microspheres for Pb(II), Cd(II) and Cu(II), respectively. Metal ions were desorbed successfully by using 0.5 M NaCl as the eluant, therefore it was posible to use the same sorbent microspheres in repeated adsorption-desorption cycles. Further studies with continuous use of the sorbents in adsorption columns for removal of heavy-metal ions from polluted water are under investigation.

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Received April 30, 1997
Final revision received August 1, 1997

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