

# Dithiocarbamate-Incorporated Monodisperse Polystyrene Microspheres as Specific Sorbents: Adsorption of Cadmium Ions

ERHAN PIŞKIN,<sup>1,\*</sup> KEMAL KESENCI,<sup>1</sup> NURAY ŞATIROĞLU,<sup>2</sup> and ÖMER GENÇ<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering and Bioengineering Division and <sup>2</sup>Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

## SYNOPSIS

In this study, adsorption of cadmium ions from aqueous solutions by using dithiocarbamate-incorporated monodisperse crosslinked polystyrene (PS)-based sorbents was investigated. Monodisperse PS microspheres with a diameter of 2  $\mu\text{m}$  were produced by dispersion polymerization of styrene in isopropyl alcohol/water by using polyvinylpyrrolidone and azobisisobutyronitrile as stabilizer and initiator, respectively. These microspheres were then crosslinked by using divinylbenzene. In order to incorporate dithiocarbamate functional groups on the PS microsphere, first benzylamine was physically absorbed, then the amine groups were transformed into dithiocarbamate groups by interacting these microspheres with carbon disulphide. These PS-based sorbents carrying physically entrapped benzyl dithiocarbamate were characterized by scanning electron microscopy, optical microscopy, FTIR, and elemental analysis. Adsorption of cadmium ions on the PS-based sorbents were investigated in the batch equilibrium experiments by using atomic absorption spectrophotometer. Adsorption rates were very fast. Adsorption equilibria were achieved within 5–60 min. The highest adsorption capacity achieved was 154.1 mg cadmium/g sorbent. The most suitable pH was 6.0. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

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.<sup>1,2</sup> Specific sorbents consist of a ligand (e.g., ion-exchange material or chelating agents) that interacts with the metal ions specifically, and a carrier matrix that may be an inorganic material (e.g., aluminium oxide, silica or glass) or polymer microspheres (e.g., polystyrene, polymethylmeth-

acrylate, cellulose) have been considered for more specific removal.<sup>3–5</sup>

As carrier matrices, polymer microspheres have attracted the most attention because they may easily 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  $\mu\text{m}$  are used. These sorbents are usually used in fixed-bed columns (rarely in fluidized-bed columns). When the nonporous microspheres are used, only the outer surface of the microspheres are available for the incorporation of the ligands that will give the specificity of these sorbents. Low surface area means low adsorption capacity. Note that the surface area of these large size sorbent particles reported in the literature is an approximate value because these microspheres have always a size distribution, narrow or wide, de-

\* To whom correspondence should be addressed.

pending on the production process. The size distribution may even change from one batch to another in the same production process. This is, of course, an important disadvantage because we cannot define the adsorption capacities based on unit surface area, which means comparison of the adsorption capacities of these type of sorbents would be rather relative and poor.

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 that exhibit surface areas 200–500 m<sup>2</sup> 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, because of mainly the pore diffusion resistance. In addition, the high active surface area of these sorbents is 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.

Recently, we prepared monodisperse polystyrene (PS)-based polymer microspheres in the size range of 1–10 µm, and utilized them in diverse applications.<sup>6–12</sup> Here, we propose to use these polymer microspheres as the carrier matrix to prepare specific sorbents for separation and purification of metal ions. These microspheres exhibit a much higher outer surface area, which is available for ligand immobilization due to their size range. It is obvious that these sorbents do not exhibit diffusion limitation that the porous sorbents do. They are uniform in size (monodisperse); therefore, adsorption capacities can be easily calculated based on unit surface area. Due to their size they cannot be used in fixed-bed columns because the high pressure drop that will be developed in these columns. However, they can be utilized in fluidized beds, which are more effective than the fixed beds in most cases, from the mass transfer point of view. Note that this type of application is widely experienced in many chemical engineering applications, even on an industrial scale.

This study reports the results of our initial studies for the realization of the idea given above. Here, we first prepared monodisperse crosslinked PS microspheres with a diameter of 2 µm by phase inversion polymerization. We selected dithiocarbamate groups because they form very stable chelates with many metal ions of interest,<sup>13–16</sup> and incorporated into these microbeads by a very simple technique. Cadmium was chosen as the study heavy metal because

of its high solubility and widespread industrial use. We studied adsorption of cadmium ion these sorbents at different conditions.

## EXPERIMENTAL

### Preparation of PS-Based Microspheres

The monomer, i.e., styrene (S) (Yarpet A.S., Turkey) was treated with aqueous NaOH to remove the inhibitor and stored in a refrigerator until use. Divinylbenzene (DVB) (Fluka, Switzerland) was used as the crosslinker and purified by the same method. The initiator was 2,2'-azobisisobutyronitrile (AIBN) (BHD Chemicals Ltd., UK). As the dispersion medium, isopropanol (Merck, Germany)/water mixtures were used. Polyvinylpyrrolidone (PVP) (30K, Fluka, Switzerland) was used as a steric stabilizer.

The polymerizations were carried out in a magnetic-driven, sealed, cylindrical reactor equipped with a temperature-control system.<sup>9,11,17</sup> PVP (2 g) 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 the monomer. 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 h. The PS latex obtained was cleaned by using the serum replacement and ion-exchange methods described previously.<sup>9,11,17</sup>

The monodisperse PS microspheres were crosslinked by the following procedure: 3 mL of divinylbenzene 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 erlenmeyer flask and the resulting mixtures was stirred at a stirring rate of 600 rpm at room temperature for 24 h 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 h. The crosslinked PS microspheres were cleaned by using the serum replacement and ion-exchange methods.<sup>9,11,17</sup>

In order to incorporate dithiocarbamate functional groups on the crosslinked PS microspheres, a two-step procedure was applied. In a typical procedure, at the first step, 5 g of the PS microspheres were added into the mixtures of 50 mL water and benzylamine (Fluka, Switzerland) with different

amounts (i.e., 0.5–2.5 mL benzylamine for 50 mL distilled water), and the resulting suspensions were stirred at a stirring rate of 600 rpm at room temperature for 24 h. The swollen PS microspheres (i.e., swollen due to benzylamine adsorption) were washed with distilled water twice, and separated from the supernatant by filtration. At the second step, 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 N potassium hydroxide. Different amounts of carbon disulfide (Fluka, Switzerland) (i.e., 0.5–5.0 mL carbon disulfide for 50 mL distilled water) were then added to these media, and the resulting mixtures were stirred at a stirring rate of 600 rpm at room temperature for 24 h, in order to complete the reaction between benzylamine and carbon disulfide. These PS microspheres carrying physically entrapped benzyl dithiocarbamate (i.e., the so-called “dithiocarbamate-incorporated PS microspheres”) were cleaned by serum replacement technique.<sup>17</sup>

### Characterization of PS Based Microspheres

Average size and size distribution of the PS-based microspheres were evaluated by using micrographs obtained by a scanning electron microscopy (JEOL, JEM1200EX, Japan). A sample of the latex solution containing the PS microspheres was spread onto a metal disk and the solvent (i.e., water and alcohol) was evaporated. The dried beads were coated with a thin layer (about 100 Å) of gold in vacuum. Three separate micrographs containing 100–300 microspheres were taken with 2000–2600× magnification. The size of the microspheres was measured on photographs and checked using calibration samples.

Changes in size and agglomerations during the modification steps described before followed by taking optical photographs of the microspheres with an optical microscope (Nikon, Alphapot YS, Japan) equipped with a dark field phase-contrast attachment.

Bulk and surface chemistries of the PS-based microspheres were characterized by using FTIR and FTIR-DRS (Shimadzu, FTIR 8000 Series and DR-8001, Japan) spectra.

Atomic compositions of the PS based microspheres were evaluated from the elemental analysis data of the dried samples obtained by using an elemental analysis device (Leco, CHNS-932, USA).<sup>17</sup>

### Adsorption Studies

Adsorption of cadmium ions from aqueous solutions were investigated in batch systems. Cadmium adsorption rate and capacity of the microspheres were obtained. Cadmium solutions (20 mL) containing different amounts of cadmium ions (in the range of 0.05–1000 ppm) were incubated with 100 mg of the PS-based sorbents at different pH (3.0–9.0) (adjusted with 0.1 N NaOH or 0.1 N HNO<sub>3</sub>) at room temperature of 25°C for different time periods in simple erlenmeyer flasks agitated magnetically with an agitation speed of 600 rpm. The concentrations of the cadmium ions in the aqueous phases after the desired treatment periods were measured by using an Atomic Absorption Spectrophotometer (Unicam, 939 AAS, UK) with a graphite furnace atomizer. The amount of cadmium ions adsorbed per unit mass of the microspheres were evaluated by using the following expression.

$$Q = [(C_0 - C) \times V] / [m \times 1000] \quad (1)$$

Here,  $C_0$  and  $C$  are the concentrations of the cadmium ions in the initial solution and in the aqueous phase after treatment for certain period of time, respectively (ppm);  $V$  is the volume of the aqueous phase (mL); and  $m$  is the amount of the PS-based microspheres used (g).

## RESULTS AND DISCUSSION

### Preparation and Characterization of Sorbents

#### Monodisperse Polystyrene Microspheres

Monodisperse polystyrene (PS) microspheres were prepared by a phase inversion (dispersion) polymerization described in detail elsewhere.<sup>9,11</sup> The recipe to produce the monodisperse PS microspheres with a diameter of 2 μm is given in Table I. The solid content of the PS latex and the monomer conversion produced at these conditions were about 10% (w/w) and 80%, respectively.<sup>17</sup> Representative photographs (i.e., a SEM and an optical) of these microspheres are presented in Figure 1. These photographs clearly show that the microspheres are uniform in size (monodisperse) with very few exceptions.

#### Crosslinking

Monodisperse PS microspheres are soluble in benzylamine, which was used for the introduction of dithiocarbamate groups into the PS matrix. To ob-

**Table I** Recipe and Conditions for Production of Monodisperse PS Microspheres with a Diameter of 2  $\mu\text{m}$  by Phase Inversion Polymerization of Styrene

Monomer Phase	Dispersion Phase
Monomer: Styrene: 20 mL	Distilled Water: 20 mL
Initiator: AIBN: 0.28 g	Isopropanol: 180 mL
Polymerization Conditions	
Temperature: 80°C	
Stirring Rate: 150 rpm	
Time: 24 h	

tain swellable (not soluble) PS microspheres in benzylamine, we crosslinked the PS microspheres by coaxial copolymerization. The PS latex obtained at the first step were incubated with an aqueous phase containing the comonomers, styrene, and divinyl benzene. Then, the adsorbed comonomers were copolymerized. The recipe for crosslinking is given in Table II. As seen in the representative optical photograph given in Figure 2, these formulation and copolymerization conditions allowed us to achieve the crosslinked structure without any noticeable size change (without losing their original monodispersity), and without any significant agglomeration, which was the case in most of other conditions studied.<sup>17</sup>

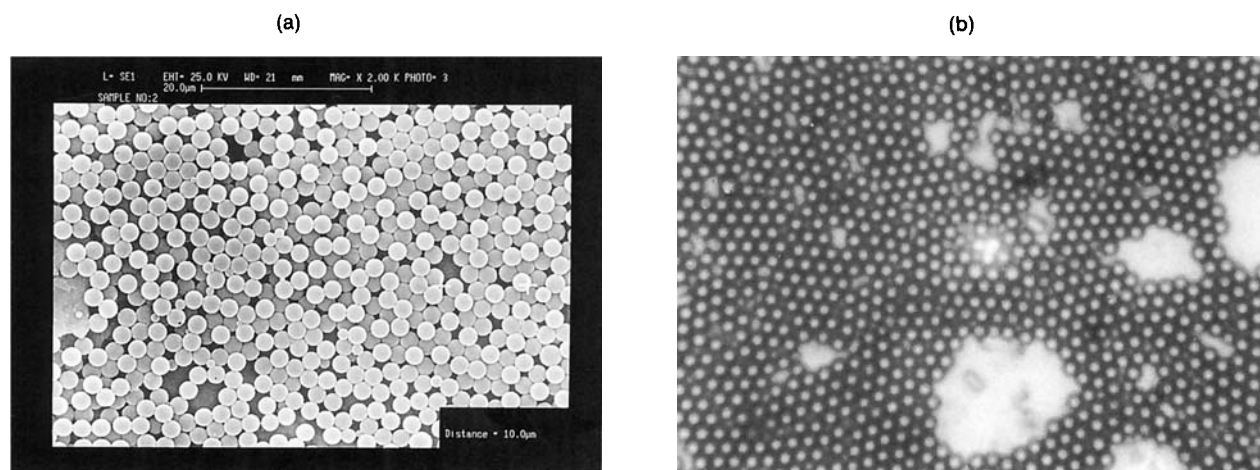
### Dithiocarbamate Incorporation

For incorporation of dithiocarbamate functional groups into the crosslinked PS microspheres, a two-step procedure was applied. At the first step, the

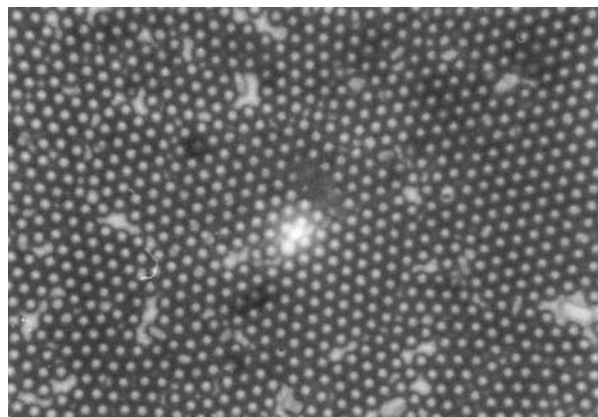
**Table II** Recipe and Conditions for Production of the Crosslinked PS Microspheres by Coaxial Copolymerization of Styrene and Divinylbenzene

Incubation Medium	
PS Latex: (with a solid content of 10% w/w): 200 mL	
Styrene: 3 mL	
Divinylbenzene: 3 mL	
Incubation Conditions	
Temperature: 20°C	
Stirring Rate: 600 rpm	
Time: 24 h	
Polymerization Medium	
Swollen PS Latex: 200 mL	
Distilled Water: 200 mL	
Initiator: AIBN: 0.12 g	
Polymerization Conditions	
Temperature: 80°C	
Stirring Rate: 150 rpm	
Time: 24 h	

crosslinked PS microspheres were incubated with benzylamine aqueous solutions containing different amounts of benzylamine (i.e., 0.5–2.5 mL benzylamine with 50 mL distilled water). Here, we aimed to adsorb benzylamine as much as possible for unit mass of the microspheres, but without causing any significant size change and agglomeration of the microspheres. As exemplified in Figure 3, the particle shapes were disordered when we used benzylamine more than 1 mL (for example, 2.5 mL benzylamine with 50 mL water) for 5 g of the PS microspheres (with a diameter of 2  $\mu\text{m}$ ). Benzylamine (1 mL) for 5 g of the PS microspheres was safe (we assumed as the optimal) for preparation of the benzylamine



**Figure 1** Photographs of the PS microspheres (diameter: 2  $\mu\text{m}$ ): (A) a SEM (magnification: 2000 $\times$ ); (B) an optical (magnification: 1000 $\times$ ) (reduced at a proper ratio to place the figure).



**Figure 2** Optical photograph of the crosslinked PS microspheres ( $2\ \mu\text{m}$ ) taken with  $1000\times$  magnification and reduced at a proper ratio to place the figure.

adsorbed PS microspheres without causing the undesired changes noted above. The optimal recipe for adsorption of benzylamine into the crosslinked PS microspheres is given in Table III with the other adsorption conditions.

FTIR and FTIR-DSR spectra of the crosslinked PS and the benzylamine adsorbed PS microspheres are given in Figure 4. The most specific bands are at  $3000\ \text{cm}^{-1}$  and  $1500\ \text{cm}^{-1}$ , which belong to aliphatic carbon-hydrogen and aromatic carbon-hydrogen bands, respectively, which represent the styrene structure. There is no clear band indicating the existence carbon-nitrogen representing benzylamine, most probably due to intensity of the other bands.

**Table III** Recipe and Conditions for Adsorption of Benzylamine into the Crosslinked PS Microspheres

Incubation Medium

The Crosslinked PS Microspheres: 5 g

Distilled Water: 50 mL

Benzylamine: 1 mL

Incubation Conditions

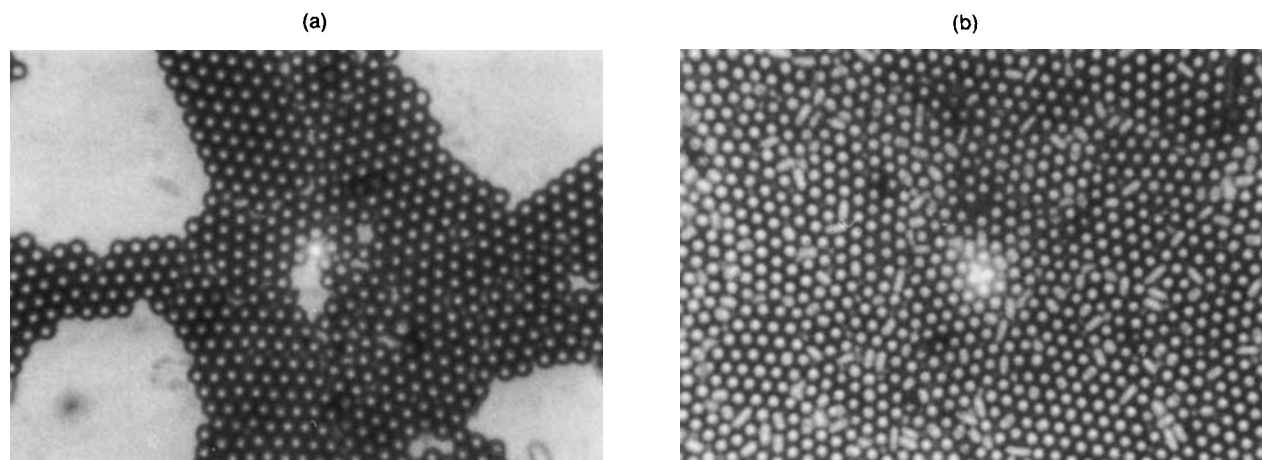
Temperature:  $20^\circ\text{C}$

Stirring Rate: 600 rpm

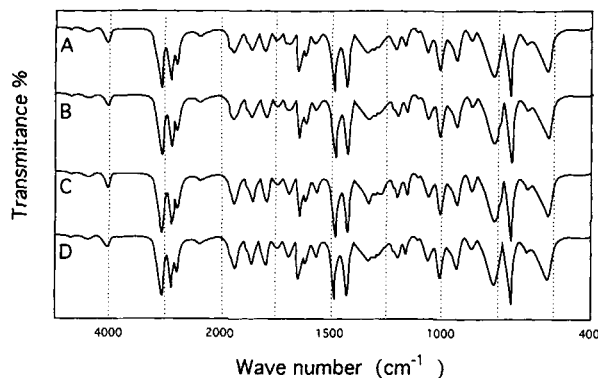
Time: 24 h

At the second step, in order to form the dithiocarbamate groups, benzylamine, which was physically adsorbed into the PS microspheres, was allowed to react with carbon disulphide in aqueous media containing dioxane. Note that the reaction between benzylamine and carbon disulphide was very rapid, and the product of this reaction is benzyl dithiocarbamate, which was physically entrapped within the crosslinked PS microspheres. In order to change the degree of dithiocarbamate incorporation, we varied the amount of carbon disulphide used in the range of 0.5–5.0 mL for 5 g of the microspheres. Table IV gives the sulphur content of the PS microspheres modified by using different amounts of carbon disulphide. This table shows that we may increase the sulphur content (means higher degrees of dithiocarbamate incorporation) by increasing the amount of carbon disulphide used.

The  $\text{C}=\text{S}$  bands at  $2000\ \text{cm}^{-1}$  on the FTIR and FTIR spectra given in Figure 5 may be considered



**Figure 3** Optical photograph of the crosslinked PS microspheres incubated with aqueous benzylamine solutions containing: (A) 1 mL benzylamine (with 50 mL water) for 5 g of PS; (B) 2.5 mL benzylamine (with 50 mL water) for 5 g of PS (taken with  $1000\times$  magnification and reduced at a proper ratio to place the figure).



**Figure 4** FTIR and FTIR-DSR spectra: (A) FTIR spectrum of the crosslinked PS; (B) FTIR-DSR spectrum of the crosslinked PS; (C) FTIR spectrum of the benzylamine adsorbed PS; (D) FTIR-DSR spectrum of the benzylamine adsorbed PS.

as another indication of the incorporation of dithiocarbamate groups to the PS microspheres. The relative intensity of the C=S band is stronger in the FTIR-DSR spectrum of the PS microspheres, which may be due to localization of the dithiocarbamate groups at the outer surfaces of the microspheres.

When the benzylamine concentration was constant, the sulphur content of the microspheres was significantly increased with the increase in the amount of carbon disulfide used, as mentioned above. However, increase in the concentration of carbon disulfide caused coagulation and agglomeration of the PS microspheres, as seen Figure 6. The recipe given in Table V was concluded as the best recipe for transformation of amine groups into dithiocarbamate groups on the benzylamine adsorbed PS microspheres without losing monodispersity of the microspheres, and without causing any coagulation. Note that the sulphur content of these microspheres was 1.52 (%), and they were utilized in the cadmium adsorption studies discussed in the following section.

### Adsorption of Cadmium Ions on PS Based Sorbents

#### Adsorption Rate

Figure 7 shows adsorption rates of  $\text{Cd}^{2+}$  ions onto the dithiocarbamate-incorporated PS microspheres from aqueous solutions containing different amounts of  $\text{Cd}^{2+}$  ions (in the range of 0.05–100 ppm) at a constant pH of 6.0. Note that the ordinate values on this figure were calculated by using the expression given eq. (1). As seen here, high adsorption rates are observed at the beginning, and then plateau val-

**Table IV** Sulphur Content of the PS Microspheres Modified by Using Different Amounts of Carbon Disulphide, Obtained by Elemental Analysis

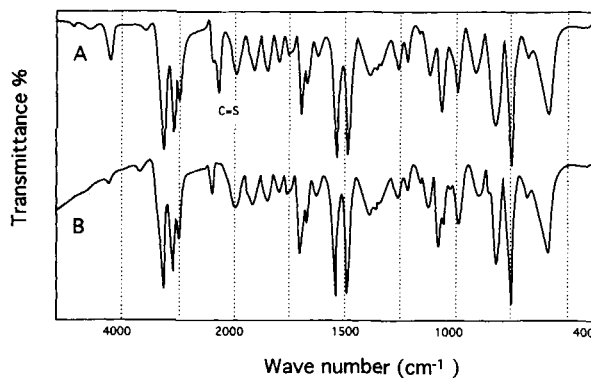
$\text{CS}_2$ (mL)	% S
0.5	0.24
1.25	0.67
2.5	1.52
5.0	1.63

ues (i.e., adsorption equilibrium) are gradually reached within 5–60 min. Equilibrium was achieved in few minutes, especially when the cadmium concentration was low.

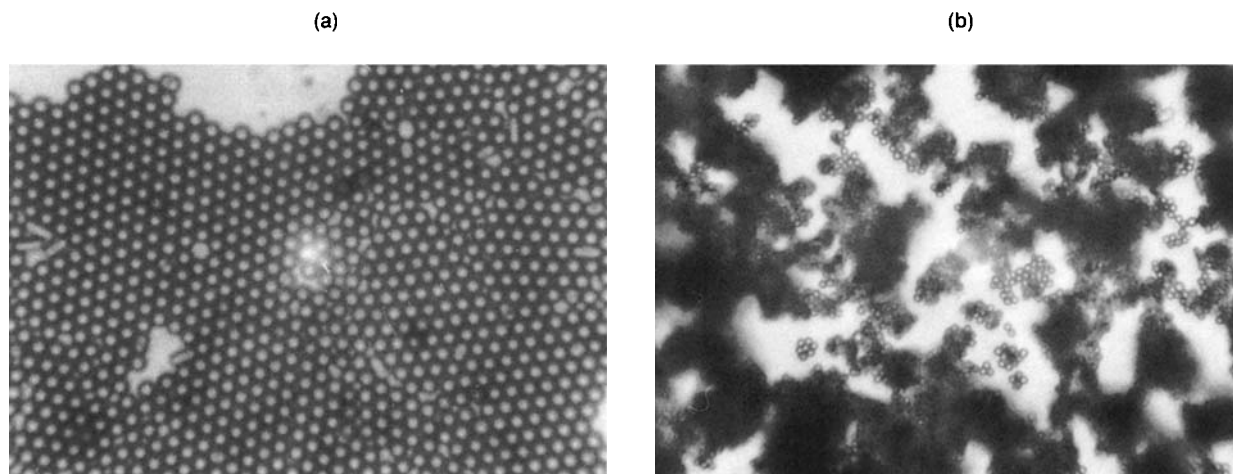
Several experimental data on the adsorption kinetics of cadmium by various sorbents have shown a wide range of adsorption rates.<sup>2,18–25</sup> For example, recently, Reed and Matsumoto have considered 6 h as a short equilibrium time in their cadmium adsorption kinetic studies, in which they have used activated carbon as sorbent.<sup>2</sup> Konishi et al. have investigated recovery of zinc, cadmium, and lanthanum by biopolymer gel particles of alginic acid. In their recent article, they reported much faster adsorption rates for lanthanum by alginic acid, in which equilibrium was achieved in about 60–90 min.<sup>23</sup> By comparing these literature data with our results, 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

Figure 8 shows effects of initial concentration of  $\text{Cd}^{2+}$  ions onto the adsorption capacity of the



**Figure 5** FTIR and FTIR-DSR spectra of the dithiocarbamate incorporated PS: (A) FTIR spectrum; and (B) FTIR-DSR spectrum.



**Figure 6** Optical photograph of the benzylamine adsorbed PS microspheres interacted with aqueous solutions (pH: 11) containing 2.5 mL dioxane and (A) 2.5 mL carbon disulfide (with 50 mL water) for 5 g of PS; (B) 5 mL carbon disulfide (with 50 mL water) for 5 g of PS (taken with 1000× and 400× magnification and reduced at a proper ratio to place the figure).

dithiocarbamate-incorporated PS microspheres at pH 6.0. Note that this graph was obtained by using the plateau values of the adsorption rate curves discussed above. The amount of Cd<sup>2+</sup> ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased first with the initial concentration of Cd<sup>2+</sup> ions then reached almost a plateau value at about an initial Cd<sup>2+</sup> ions concentrations of 400 ppm. The maximum adsorption (corresponding a 1000 ppm Cd<sup>2+</sup> ion initial concentration), which represents saturation of the active points (which are available for Cd<sup>2+</sup> ions) on the microspheres, was 154.1 mg Cd<sup>2+</sup>/g polymer.

Some previous data on the sorption equilibria of cadmium for aqueous solutions by natural and synthetic polymers and other sorbents were again in a very wide range (4.8–96.3 mg cadmium/g sorbent), in which initial concentration of the cadmium in

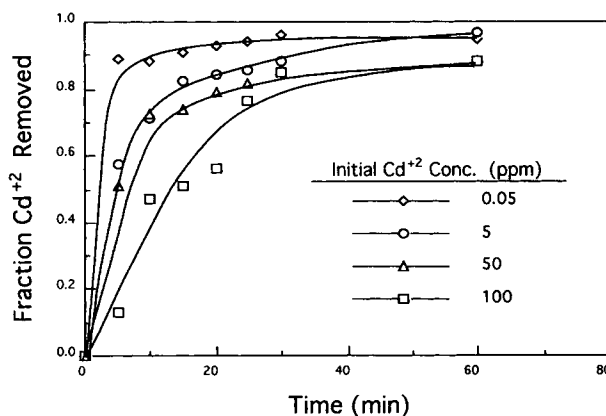
solution was in the range of 0.056–2.81 mg/L.<sup>2,18–25</sup> By comparing these literature data with our results, our approach presented here may be considered as an important improvement also in adsorption capacities in addition to adsorption kinetics.

**Effect of pH**

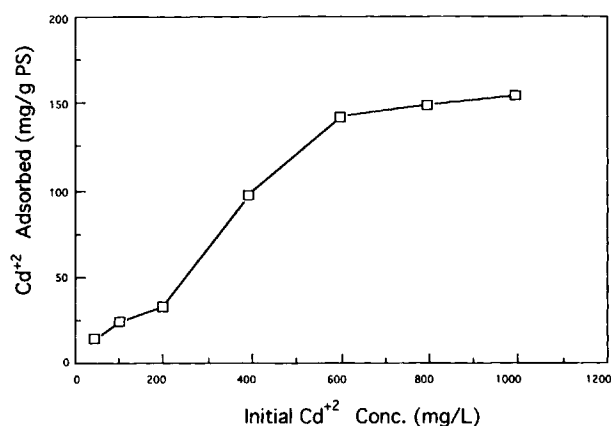
It is well known that cadmium adsorption both on nonspecific and specific sorbents is pH dependent.<sup>2,18–25</sup> In the absence of complexing agents, the hydrolysis and precipitation of the metal ion are affected by the concentration and form of soluble metal species. The solubility of cadmium is governed by hydroxide or carbonate concentration. As dis-

**Table V** Recipe for Transformation of Amine Groups into Dithiocarbamate Groups on the Benzylamine Adsorbed PS Microspheres

<b>Reaction Medium</b>	
The Benzylamine Adsorbed PS Microspheres:	5 g
Aqueous Phase:	50 mL water + 2.5 mL dioxane
Carbon Disulfide:	2.5 mL
<b>Reaction Conditions</b>	
pH:	11.0
Temperature:	20°C
Stirring Rate:	600 rpm
Time:	24 h



**Figure 7** Adsorption rate curves of cadmium ions on dithiocarbamate incorporated PS microspheres at pH 6.0.



**Figure 8** Effects of initial concentration of cadmium ions on adsorption capacity of the dithiocarbamate incorporated PS microspheres at pH 6.0.

cussed in detail by Boomhove<sup>26</sup> and Reed and Matsumoto,<sup>23</sup> hydrolysis of cadmium becomes significant at approximately pH 8.0. For example, the theoretical and experimental precipitation curves indicated that precipitation begins at pH values of 9.2 and 8.6 for cadmium concentrations of 5 mg/L and 50 mg/L, respectively.<sup>2</sup> Therefore, in our study, in order to establish the effect of pH on the adsorption of Cd<sup>2+</sup> ions onto the dithiocarbamate-incorporated PS microspheres, we repeated the batch equilibrium studies at different pH in the range of 3.0–9.0. Note that we did not attempt to study below

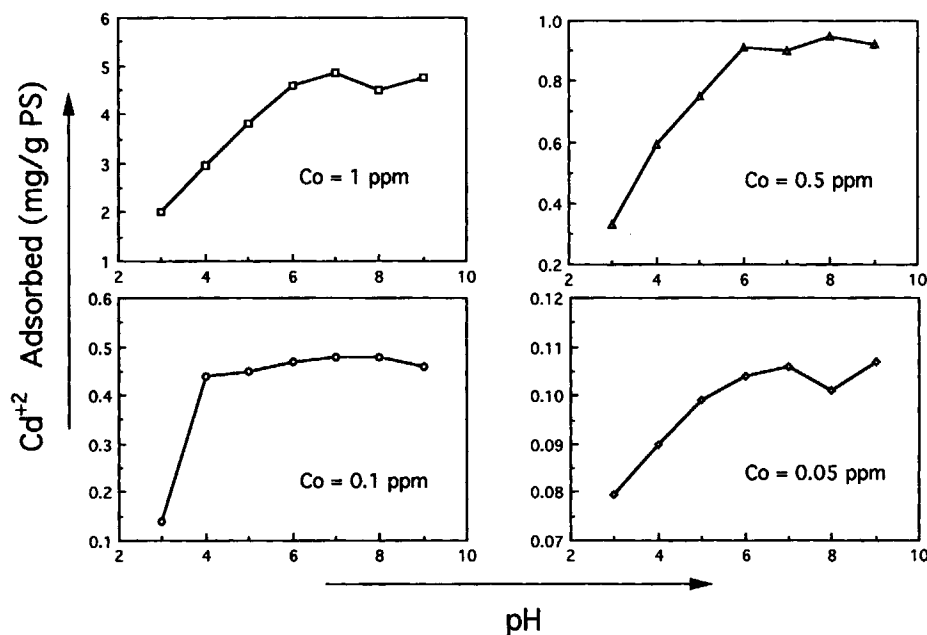
pH 3.0 by considering possible decomposition of dithiocarbamate groups.<sup>27</sup>

Figure 9 exemplifies the effects of pH adsorption of Cd<sup>2+</sup> ions from aqueous solution with four different cadmium initial concentrations. As seen here, adsorption of cadmium increased with pH and reached almost a plateau value around pH 6.0. High adsorption at higher pH values implies that Cd<sup>2+</sup> ions interact with dithiocarbamate (unprotonated) by chelating, as also stated in the related literature.<sup>2,18–25</sup>

## CONCLUSIONS

From the data presented here, it can be concluded that the dithiocarbamate-incorporated PS microspheres may effectively (means with high adsorption rates and capacities) be used for removal of cadmium ions from aqueous solutions. Our studies related to adsorption/desorption of other heavy metal ions (e.g., Pb<sup>++</sup>, Hg<sup>++</sup>) from different matrix systems (i.e., different aqueous media) are still under investigation.

We would like to thank Assoc. Prof. Ali Tuncel from Hacettepe University, Chemical Engineering Department for his supervision in the preparation of polymeric microspheres and Assoc. Prof. Bekir Salih from Hacettepe Uni-



**Figure 9** Effects of pH on adsorption capacity of the dithiocarbamate incorporated PS microspheres.



versity, Department of Chemistry for his contributions in the elemental analysis studies.

## REFERENCES

1. A. E. Rodrigues, Ed., *Ion Exchange: Science and Technology*, Martinus Nijhoff, Dordrecht, 1986.
2. B. E. Reed and M. R. Matsumoto, *Sep. Sci. Technol.*, **28**, 2179 (1993).
3. M. Kaneko and E. Tsuchida, *J. Polym. Sci., Macromol. Rev.*, **16**, 397 (1981).
4. G. V. Myasoediva and S. B. Savvin, *Crit. Rev. Anal. Chem.*, **17**, 1 (1986).
5. C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta*, **37**, 491 (1990).
6. A. Tuncel and E. Pişkin, Turkish Pat. 24125 (1991).
7. A. Tuncel and E. Pişkin, Turkish Pat. 24126 (1991).
8. M. T. Ercan, A. Tuncel, B. E. Ercan, M. Mutlu, and E. Pişkin, *Nucl. Med. Biol.*, **18**, 253 (1991).
9. A. Tuncel, R. Kahraman, and E. Pişkin, *J. Appl. Polym. Sci.*, **50**, 303 (1993).
10. A. Tuncel, A. Denizli, D. Purvis, C. R. Lowe, and E. Pişkin, *J. Chromatogr.*, **634**, 161 (1993).
11. A. Tuncel, R. Kahraman, and E. Pişkin, *J. Appl. Polym. Sci.*, **51**, 303 (1994).
12. E. Pişkin, A. Tuncel, A. Denizli, and H. Ayhan, *J. Biomater. Sci.: Polym. Ed.*, **5**, 451 (1994).
13. J. Sary and K. Kratzer, *Anal. Chim. Acta*, **40**, 93 (1968).
14. D. M. Hercules, L. E. Cox, S. Onisick, G. D. Nicholas, and J. C. Carver, *Anal. Chem.*, **45**, 1973 (1973).
15. D. E. Lyden and G. H. Luttrell, *Anal. Chem.*, **47**, 1612 (1975).
16. C. K. Wagner, G. Hall, B. Riegel, J. Virgilio, V. Kamath, and G. Germann, *J. Appl. Polym. Sci.*, **31**, 1797 (1986).
17. K. Kesenci, M.S. Thesis, Hacettepe University, Ankara, Turkey, 1994.
18. M. S. Masri, W. Reuter, and M. Fiedman, *J. Appl. Polym. Sci.*, **18**, 675 (1974).
19. J. M. Randall, R. L. Bermann, V. Garret, and A. C. Waiss, *Forest Prod.*, **24**, 80 (1974).
20. J. M. Randall, *Forest Prod.*, **27**, 51 (1977).
21. T. C. Yang and R. R. Zall, *Ind. Eng. Chem., Prod. Res. Dev.*, **23**, 168 (1984).
22. T. Saegusa, S. Kobayashi, and A. Yamada, *J. Appl. Polym. Sci.*, **21**, 2481 (1977).
23. Y. Konishi, S. Asai, Y. Midoh, and M. Oku, *Sep. Sci. Technol.*, **28**, 2179 (1993).
24. U. Hoins, L. Charlet, and H. Sticher, *Water Air Soil Poll.*, **68**, 241 (1993).
25. A. Syamal and M. M. Singh, *Reac. Polym.*, **21**, 149 (1993).
26. A. E. Boomhower, M.S. Thesis, University of Delaware, 1982.
27. S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *Anal. Chem.*, **41**, 11 (1969).

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