

Benzoylthiourea-Modified Mesoporous Silica for Mercury(II) Removal

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An incorporation of 1-benzoyl-3-propylthiourea groups into siliceous mesopores of MCM-41 afforded an ordered material with open porosity. This material was prepared via a two-step modification by attachment of an aminopropyl functionality and its subsequent conversion into a thiourea ligand. About 1.5 mmol/g of 1-benzoyl-3-propylthiourea groups was attached to the silica surface, which resulted in ca. 70% conversion of amino groups. Such material has a large surface area of 380 m²/g and accessible mesopores of 3.0 nm in diameter. The presence of several functional groups in the thiourea structure, able to coordinate metal ions, causes a significant enhancement of the maximum capacity of this material toward mercury ions. The maximum loading of mercury ions from aqueous solution for this material was ca. 1.0 g Hg²⁺/g or 5.0 mmol Hg²⁺/g, exceeding the capacity of the previously known samples by about twice. The fit of the mercury adsorption isotherm by a two-term Langmuir–Freundlich equation suggests a two-step adsorption process characterized by different adsorption constants. A relatively weak mercury interaction with 1-benzoyl-3-propylthiourea ligands made the adsorbent's regeneration possible under mild conditions via washing the mercury-loaded samples with slightly acidified aqueous thiourea solution. The regenerated material retained over 70% of the initial adsorption capacity.

Introduction

A serious environmental threat from heavy metal ion pollution, especially mercury, has generated a great deal of attention in recent years. The harmful effect of mercury toxicity is manifested by hindering the transport processes in living cells,¹ which is due to the high affinity of this element toward sulfur-containing biological molecules. This high affinity could be exploited for removal of mercury ions from aqueous media, for example, by designing materials with sulfur-containing groups. The recently discovered mesoporous silica MCM-41, having high surface area and large and accessible pores,^{2,3} is a good candidate as an insoluble matrix for the attachment of sulfur-containing groups, which possess the desired surface affinity toward mercury ions.^{4–6}

Targeting the achievement of high mercury adsorption capacity and the easiness of the adsorbent's regeneration drove our attention to thiourea surface ligands. These ligands, attached to a mesoporous silica support, are stable under typical regeneration conditions, which makes them perfectly suitable for environmental applications due to the presence of a sulfur-containing functionality that

exhibits high affinity toward mercury ions. Unlike the previously studied mercaptopropyl functionality,^{4–6} the thiourea ligands are expected to bind mercury ions less strongly, which should facilitate the adsorbent regeneration. While a simple thiourea ligand, 1-allyl-3-propylthiourea, after bonding to MCM-41 gave a promising material in terms of regeneration, its mercury adsorption capacity was not high enough.⁷ A logical strategy to increase the mercury adsorption capacity was the use of multifunctional ligands, which possess several "active" groups toward mercury ions. While the available surface area of the support would limit the total number of attached ligands per square meter, their multifunctional nature is expected to increase the mercury adsorption capacity. Our attention was directed to the attachment of the benzoylpropylthiourea functionality to the surface of ordered mesoporous silica, MCM-41.

Here we report the preparation of a new 1-benzoyl-3-propylthiourea-functionalized MCM-41 and characterization of its structural and adsorption properties. The experimental data demonstrate the high affinity of this material toward mercury ions, which is reflected by a high adsorption capacity approaching 5.0 mmol Hg²⁺ per gram of the adsorbent or ca. 1.0 g Hg²⁺/g. The nitrogen adsorption study and a successful regeneration of the mercury-loaded benzoylthiourea-modified MCM-41 demonstrate the accessibility of pores of this material to mercury ions. An efficient regeneration of this material was achieved with acidified aqueous thiourea solution. The regenerated material showed a significant mercury uptake (above 70% of the initial value).

Experimental Section

3-Aminopropyltrimethoxysilane and benzoyl isothiocyanate were from Fluka Chemical Corp. (St. Louis, MO). Diphenylthiocarbazon (dithizone, ACS reagent) was from Aldrich Chemi-

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(1) Manahan, S. E. *Environmental Chemistry*; Lewis Publishers: Boca Raton, FL, 1994.

(2) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(3) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(4) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923.

(5) Mercier, L.; Pinnavaia, T. J. *Environ. Sci. Technol.* **1998**, *32*, 2749.

(6) Nooney, R. I.; Kalyanaraman, M.; Kennedy, G.; Maginn, E. J. *Langmuir* **2001**, *17*, 528.

cal Co. (Milwaukee, WI). Toluene (p.a., water content below 0.02%), *i*-propanol (anhydrous), and chloroform (HPLC grade, suitable for dithizone analysis) were from Fisher Scientific (Pittsburgh, PA). Mercury(II) nitrate volumetric standard, 0.145 N solution in water, was from Aldrich Chemical Co. Deionized water was from in-house purification on the Ionpure Plus 150 Service Deionization ion-exchange system (conductivity < 17.5 M Ω). All materials were used without additional purification.

The MCM-41 sample was synthesized according to the previously published procedure^{8,9} using the mixture of alkyltrimethylammonium and alkyltriethylammonium bromide surfactants. The as-synthesized material was washed with EtOH/HCl mixture and calcined as described elsewhere.⁹ The sample was designated as MCM-41C.

The MCM-41C sample was functionalized with 3-aminopropyltriethoxysilane in the toluene solution (refluxing for 24 h) according to the conventional procedure.¹⁰ After cooling, the modified mesoporous material was filtered out and washed several times with small portions of toluene and *i*-propanol to remove an excess of modifier and possible products of hydrolysis. Finally, the modified mesoporous material was dried overnight in an oven at 95–100 °C under a vacuum. The resulting material was designated as MCM-41NH₂.

The grafted 1-benzoyl-3-propylthiourea mesoporous silica was synthesized via reaction between aminopropyl-functionalized mesoporous silica (MCM-41NH₂) and benzoyl isothiocyanate, which normally proceeds completely.¹¹ A typical procedure included reaction of 2 g of aminopropylsilica with 0.50 mL of benzoyl isothiocyanate (25% excess) in toluene as a solvent. The resulting solid was filtered out, washed with 50 mL of toluene and 50 mL of *i*-propanol, and dried under a vacuum for 5 h at 90 °C. The final sample with the attached thiourea functionality had a light yellow color and was designated as MCM-41BTU.

Mercury adsorption was studied under static conditions from aqueous solutions. All Hg²⁺ solutions were prepared by dilution of the calculated amounts of mercury(II) nitrate volumetric standard, 0.145 N aqueous solution, up to 10 mL. In a typical determination, 0.05 g of the sample was equilibrated for 40 min with 10 mL of the solution containing mercury nitrate of known concentration (Hg²⁺: ligand ratios were in the range 5:1–1:5). After filtration, the adsorbent was washed with deionized water and the filtrate was collected and diluted to 25 mL. In a similar fashion, the mercury uptake experiments were done with regenerated adsorbents. For comparison purposes, adsorption experiments were performed for unfunctionalized mesostructured silica using the same amounts of the sample and solutions.

Mercury(II) concentration was measured spectrophotometrically with dithizone (diphenylthiocarbazone) as a complexing agent.¹² Mercury photometric determinations were performed on a Shimadzu-1601 spectrometer in a 1 cm quartz photocell (volume, ca. 5 mL). The amount of mercury was determined from the calibration curve that was prepared for the mercury concentration interval of 0–50 μ g per sample.¹³ The background correction was performed against pure chloroform. Each sample was analyzed at 490 nm.

Mercury desorption studies were performed for the samples loaded with mercury in adsorption experiments via treatment with 10% thiourea solution in aqueous 0.05 M HCl. The regeneration was performed under static conditions by soaking 0.05 g of mercury-loaded adsorbent for 15 min with 10 mL of thiourea solution followed by filtration and rinsing of the sample with an additional 10 mL of thiourea solution and 10 mL of deionized water. The samples were finally dried overnight under a vacuum at 65–70 °C.

Nitrogen adsorption measurements were performed using a Micromeritics model ASAP 2010 adsorption analyzer (Norcross,

GA). Adsorption isotherms were measured at –196 °C over the interval of relative pressures from 10^{–6} to 0.995 using nitrogen of 99.998% purity. Before each analysis, the sample was degassed for 2 h at 110 °C under a vacuum of about 10^{–3} Torr in the degas port of the adsorption apparatus. Such temperature was chosen on the basis of the thermogravimetric profile of the sample in order to avoid the degradation of the immobilized surface groups and at the same time to remove adsorbed gases and water.

The specific surface area of the materials under study was calculated using the Brunauer–Emmett–Teller (BET) method.^{14,15} The adsorption data in a narrow range of relative pressures ($p/p_0 = 0.04–0.20$) were used to calculate the BET surface area (S_{BET} , m²/g). The total pore volume (V_{tot} , cm³/g) was evaluated from the total volume of nitrogen adsorbed at the relative pressure $p/p_0 = 0.995$. Differential pore size distributions were evaluated from adsorption branches of nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) method¹⁶ with the corrected form of the Kelvin equation for capillary condensation in cylindrical pores.¹⁷ The position of the peak maximum on the pore size distribution is referred to as the pore width (d_{BJH} , nm).

The content of carbon, nitrogen, and hydrogen in all samples was determined using a LECO model CHNS-932 elemental analyzer (St. Joseph, MI). For each sample, three measurements were performed with a relative error of less than 0.1%. The carbon, hydrogen, and nitrogen contents from elemental analysis as well as the BET specific surface area from nitrogen adsorption data were used to estimate the concentrations of attached ligands. Similarly as in refs 7 and 10 the ligand concentration (C_{lig} , mmol/g) was related to 1 g of unmodified MCM-41 material. Since all ligand concentrations were related to 1 g of unmodified silica (MCM-41), the concentration of unreacted amino groups was determined by subtracting the amount of benzoylthiourea ligands attached during the second modification step from the total amount of amino groups attached during the first modification step.

A TA Instruments model TA 2950 (New Castle, DE) analyzer was used to carry out high-resolution thermogravimetric analysis (TGA). All thermogravimetric measurements were done in a nitrogen atmosphere. The maximum heating rate in all cases was 5 °C/min over a temperature range from 25 to 1000 °C. The accuracy in the weight change measurements was 0.1%.

Results and Discussion

Introduction of benzoylpropylthiourea on the silica surface via postsynthesis modification of MCM-41 afforded material with a large number of potential coordination centers per attached ligand. An increase in the adsorption capacity is anticipated because of the multifunctional nature of the 1-benzoyl-3-propylthiourea ligand (see Figure 1). Also, the expected thiol and enol tautomeric forms of this ligand¹⁸ are susceptible to the deprotonation that would greatly enhance coordination of metal ions. Both these factors are expected to cause a considerably high adsorption capacity of the 1-benzoyl-3-propylthiourea-modified MCM-41 material.

Previous experimental data^{7,19} demonstrated that the pore structure of the mesostructured silica support is of great importance for the total adsorption capacity as well as for the transport properties of the adsorbent. In this work, we decided to use a large-pore MCM-41 in order to obtain the resulting material of good transport and

(14) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(15) Roquerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes, J. H.; Pernicone, N.; Ramsay, J. D. F.; Sing, K. S. W.; Unger, K. K. *Pure Appl. Chem.* **1994**, *66*, 1739.

(16) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.

(17) Kruk, M.; Jaroniec, M.; Sayari, A. *Langmuir* **1997**, *13*, 6267.

(18) *Comprehensive Organic Chemistry*; Barton, D., Ollis, D. W., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, Chapter 5, and Vol. 3, Chapter 11.

(19) Antochshuk, V.; Jaroniec, M.; Joo, S. H.; Ryoo, R. *Stud. Surf. Sci. Catal.* **2002**, *141*, 258.

(8) Ryoo, R.; Ko, C. H.; Park, I.-S. *Chem. Commun.* **1999**, 1413.

(9) Jaroniec, M.; Kruk, M.; Shin, H. J.; Ryoo, R.; Sakamoto, Y.; Terasaki, O. *Microporous Mesoporous Mater.* **2001**, *48*, 127.

(10) Antochshuk, V.; Jaroniec, M. *J. Phys. Chem. B* **1999**, *103*, 6252.

(11) *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: New York, 1995; Vol. 6, Chapter 18.

(12) *Comprehensive Analytical Chemistry*; Svehla, G., Ed.; Elsevier: Amsterdam, 1985; Vol. XX, Chapter 6.

(13) *AOAC Official Methods of Analysis*; Helrich, K., Ed.; The Association of Official Analytical Chemists: Arlington, 1990.

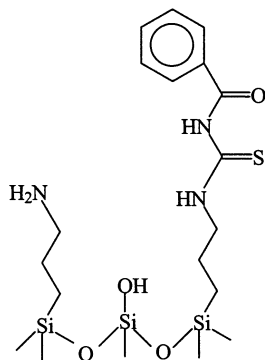


Figure 1. Schematic illustration of the surface groups present in the modified MCM-41 material.

Table 1. Parameters of the Parent and Modified MCM-41 Samples^a

sample	S_{BET} (m^2/g)	d_{BJH} (nm)	V_{tot} (cm^3/g)	C_{lig} (mmol/g)
MCM-41C	1040	4.8	1.42	
MCM-41NH ₂	665	4.2	0.94	2.15
MCM-41BTU	380	3.0	0.45	1.50

^a S_{BET} , BET specific surface area; d_{BJH} , primary mesopore diameter; V_{tot} , total pore volume; C_{lig} , surface coverage of bonded ligands expressed in relation to 1 g of unmodified MCM-41.

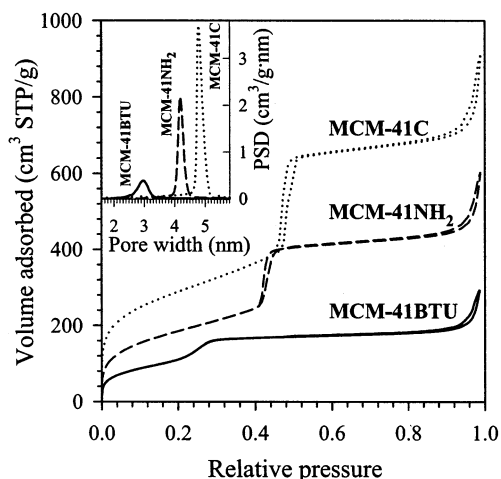


Figure 2. Nitrogen adsorption isotherms for calcined mesoporous silica, MCM-41 (dotted line), and materials modified with aminopropyl (dashed line) and 1-benzoyl-3-propylthiourea (solid line) groups, respectively. The insert shows the corresponding differential pore size distributions.

adsorption properties. The parameters of the starting and functionalized materials and the corresponding adsorption isotherms are shown in Table 1 and Figure 2, respectively. The extremely narrow step on the nitrogen adsorption isotherm and the narrow peak of the corresponding pore size distribution prove a high uniformity of the starting MCM-41 material (Figure 2). This uniformity was preserved during both steps of modification, which is evident from the narrowness of the pore size distributions for the modified samples.

The two-step modification process was chosen to ensure better control of the modification process and to avoid unnecessary pore blockage. The first modification step, reaction with aminopropyl silane, gave materials with a large amount of the incorporated amino groups (2.15 mmol/g), causing the surface area to decrease by less than 400 m^2/g (Table 1). The subsequent reaction with benzoylthiocyanate led to the formation of the benzoylthiourea functionality immobilized on the silica walls of MCM-41

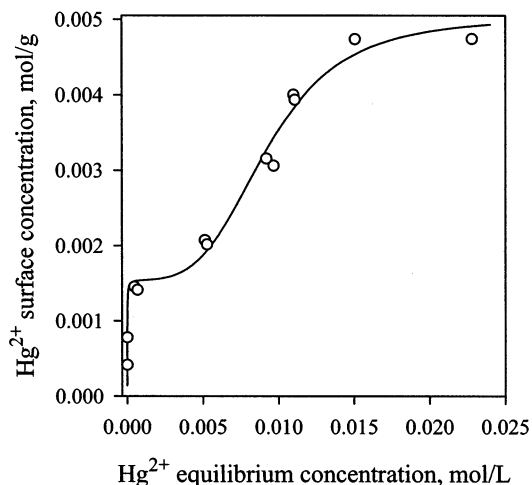


Figure 3. Mercury adsorption isotherm for the 1-benzoyl-3-propylthiourea-modified material, MCM-41BTU (open circles denote experimental data), and its fit to a two-term Langmuir–Freundlich equation (solid line). The calculated constants, $K_1 = 1.41 \times 10^5$ and $K_2 = 1.08 \times 10^2$ L/mol, demonstrate that there are two types of adsorption sites on the surface of significantly different interaction energies.

through a propyl tether. The latter reaction normally proceeds completely,¹¹ but in the case of confined geometry (curvature of the walls) and a relatively large ligand to be attached, the achieved yield of derivatization of aminopropyl groups was ca. 70%. The surface concentration of 1-benzoyl-3-propylthiourea was 1.5 mmol/g, and the amount of residual (unreacted) aminopropyl groups was ca. 0.65 mmol/g (note that all ligand concentrations are expressed per gram of unmodified MCM-41).

As demonstrated by nitrogen adsorption studies (Figure 2), the thiourea-modified MCM-41 materials have accessible porosity of a significant pore volume (0.45 cm^3/g) and large surface area (380 m^2/g) (see Table 1). The two-step functionalization resulted in a decrease in the pore size by about 0.6 nm for the smaller aminopropylsilyl tether and ca. 1.2 nm for the larger benzoylthiourea functionality, giving the total decrease in the pore size of about 1.8 nm. The resulting material with the pore width of ca. 3.0 nm was well suited for mercury adsorption–desorption experiments. The thermogravimetric study (see Supporting Information) confirmed the two-step functionalization and demonstrated that the 1-benzoyl-3-propylthiourea-functionalized samples are thermally stable up to ca. 170 °C.

The mercury adsorption on the 1-benzoyl-3-propylthiourea-functionalized mesoporous silica, performed under static conditions, demonstrated superiority of this ligand over the smaller mercaptopropyl^{4–6} and allylthiourea⁷ ligands. Despite the similar or even lower surface coverage,^{4–6} the 1-benzoyl-3-propylthiourea-functionalized material had much higher maximum adsorption capacity toward mercury ions (ca. 5.0 mmol Hg^{2+}/g or 1.0 g Hg^{2+}/g) in comparison to the previously reported data.^{4–7} At the same time, the mercury adsorption on the unmodified mesoporous MCM-41 was undetectable. The equilibration time of 40 min used in the experiments was enough for quantitative mercury adsorption with the residual concentration below 0.8 ppm.

The mercury adsorption isotherm for the 1-benzoyl-3-propylthiourea-modified mesoporous silica (Figure 3) exhibits initially a very steep increase, which indicates high adsorption at lower concentrations. Later this isotherm shows a kink, which indicates a change in adsorption mechanism. The data of the mercury adsorp-

tion (Figure 3) were successfully fitted by a two-term Langmuir–Freundlich equation:²⁰

$$a = \frac{a_1}{1 + \frac{1}{K_1 C_{\text{Hg}}}} + \frac{a_2}{1 + \frac{1}{(K_2 C_{\text{Hg}})^m}}$$

where a is the amount of mercury adsorbed at a given equilibrium concentration, m is a heterogeneity parameter, a_1 and a_2 are the maximum amounts adsorbed on the first and second types of adsorption sites, respectively, K_1 and K_2 are the Langmuir type constants characterizing the interaction of ions with attached ligands, and C_{Hg} is the mercury(II) equilibrium concentration. The sum of the values of a_1 and a_2 would correspond to the total amount of mercury(II) ions adsorbed on the surface of 1-benzoyl-3-propylthiourea-functionalized material. The first part of this equation (Langmuir equation) describes adsorption of mercury ions on the strongly binding sites that are initially available on the benzoylthiourea-functionalized material. The second half of the equation (Langmuir–Freundlich equation) takes into account the heterogeneity effects of the system (the heterogeneity parameter m was equal to 3.7) and describes mercury adsorption on the weakly binding sites. The latter sites interact with mercury much more weakly, which is reflected by a significant difference in the interaction constants, $K_1 = 1.41 \times 10^5$ versus $K_2 = 1.08 \times 10^2$ L/mol, respectively. The amount of mercury adsorbed on the strongly binding sites was 1.55 mmol/g, and this value is in excellent agreement with the total amount of the attached benzoylthiourea functionality of ca. 1.50 mmol/g (Table 1). The weaker binding sites were responsible for adsorption of ca. 3.48 mmol/g.

While the amount of grafted sulfur-containing groups was ca. 1.5 mmol/g, the total amount of adsorbed mercury was equal to ca. 5.0 mmol of Hg^{2+} per gram of the modified material, which indicates that the 1-benzoyl-3-propylthiourea material adsorbed on average three mercury ions per attached ligand. The total capacity of such material exceeds by about twice the values reported elsewhere.^{4–6} The presence of different functionalities in the structure of 1-benzoyl-3-propylthiourea (see Figure 1) and the ability to deprotonate into the thiol and enol tautomeric forms of the benzoylthiourea ligand makes the assumption of multiple binding very plausible. The deprotonation of 1-benzoyl-3-propylthiourea ligands is further enhanced by adsorption of mercury ions.

The observed difference in the binding constants ($K_1 = 1.41 \times 10^5$ vs $K_2 = 1.08 \times 10^2$ L/mol), obtained by fitting the mercury adsorption data to the Langmuir–Freundlich equation (Figure 3), further supports the idea of multiple interactions. It can be assumed that the most strongly bound mercury ions would be the ions that interact with the 1-benzoyl-3-propylthiourea ligands through the sulfur-containing groups. After saturation of all strongly binding

sites, mercury ions would adsorb on available nitrogen- and oxygen-donor sites.

Despite the mercury(II) preference to form bonds with sulfur-containing ligands, there are numerous examples of mercury–nitrogen and mercury–oxygen bonding.^{21,22} In the solid state, such compounds tend to form extended polymeric chains due to the binding of one ligand to two adjacent mercury ions.²¹ Also, as is evident from the elemental analysis data (Table 1), the sample of 1-benzoyl-3-propylthiourea-modified material contains some residual aminopropyl groups (ca. 0.6 mmol/g). These groups have the ability to interact with mercury and would give some additional mercury binding capacity.

The regeneration of the mercury-loaded 1-benzoyl-3-propylthiourea-modified mesoporous silica was performed similarly to that of the previously studied allylpropylthiourea-modified materials.^{7,19} The washing of the mercury-containing MCM-41BTU samples with slightly acidified aqueous thiourea solution was enough to restore more than 70% of the material's initial capacity.

Our results demonstrate that the proper selection of the multifunctional ligand attached to a large-pore MCM-41 leads to a significant increase in the adsorption capacity of functionalized material toward mercury ions. Despite the large size of 1-benzoyl-3-propylthiourea ligands, the pore diameter of the mesoporous silica MCM-41 decreased less than 1.8 nm. At the same time, the resulting material exhibited a narrow pore size distribution. A relatively large surface area (380 m²/g), the large surface concentration of the attached 1-benzoyl-3-propylthiourea groups in the sample (1.5 mmol/g), and the presence of several functional groups in the thiourea structure caused a significant enhancement in the adsorption capacity of the synthesized material with respect to mercury ions. The 1-benzoyl-3-propylthiourea-functionalized MCM-41 exhibited the maximum loading of mercury of ca. 5.0 mmol Hg^{2+} /g or 1.0 g Hg^{2+} /g. The residual concentration of mercury in aqueous solution after one-time treatment with 1-benzoyl-3-propylthiourea-functionalized material can be as low as 0.8 ppm. The two-step adsorption process characterized by two different Langmuir type constants was suggested because the mercury adsorption data can be fitted by a two-term Langmuir–Freundlich equation. The regeneration of the mercury-loaded adsorbent was achieved under mild conditions via washing the mercury-loaded samples with slightly acidified aqueous thiourea solution. The regenerated material retained more than 70% of the initial adsorption capacity.

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Supporting Information Available: Figures 1S and 2S containing high-resolution TGA data for the samples studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 5.
(22) Hiremath, A. C.; Murthy, A. S. R. *Indian J. Chem.* **1977**, *15A*, 55.

(20) Jaroniec, M.; Madey, R. *Physical Adsorption on Heterogeneous Solids*; Elsevier: Amsterdam, 1988.