

Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions

Mahitti Puanggam, Fuangfa Unob*

Department of Chemistry, Faculty of Science, Chulalongkorn University, Payathai Road, Bangkok 10330, Thailand

Received 11 June 2007; received in revised form 17 October 2007; accepted 18 October 2007

Available online 30 October 2007

Abstract

Adsorbents for Hg(II) ion extraction were prepared using amorphous silica gel and ordered MCM-41. Grafting with 2-(3-(2-aminoethylthio)propylthio)ethanamine was used to functionalize the silica. The functionalized adsorbents were characterized by nitrogen adsorption, X-ray diffraction, ^{13}C MAS NMR spectroscopy and thermogravimetric analysis. The adsorption properties of the modified silica gel and MCM-41 were compared using batch method. The effect of pH, stirring time, ionic strength and foreign ions were studied. The extraction of Hg(II) ions occurred rapidly with the modified MCM-41 and the optimal pH range for the extraction by the modified materials was pH 4–7. Foreign ions, especially Cl^- had some effect on the extraction efficiency of the modified silica gel and the modified MCM-41. The adsorption behavior of both adsorbents could be described by a Langmuir model at 298 K, and the maximum adsorption capacity of the modified silica gel and MCM-41 at pH 3 was 0.79 and 0.70 mmol g^{-1} , respectively. The modified MCM-41 showed a larger Langmuir constant than that of the modified silica gel, indicating a better ability for Hg(II) ion adsorption. The results indicate that the structure of the materials affects the adsorption behavior. These materials show a potential for the application as effective and selective adsorbents for Hg(II) removal from water.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Silica gel; Mesoporous silica; MCM-41; Extraction; Mercuric ions

1. Introduction

The contamination by heavy metal pollutants, especially mercury ions, in water sources is an important environmental concern due to their high toxicity. The removal of inorganic mercury ions from contaminated water is required before discharging to the environment and adsorption processes are widely used for this purpose. Several materials such as activated carbon [1–7], resins [8–12], clays [13,14] and silica [15,16] have been studied for adsorption of Hg(II) ions. Moreover, the modification of adsorbents with organic functional groups has been shown to improve the selectivity of the adsorbents for binding desired metal ions and has recently drawn much attention. The high selectivity of such adsorbents is the main advantage over traditional adsorbents. Regarding mercury ions, the most effective modification is surface functionalization with coordinating ligands containing sulfur atoms [15–21].

Recently, surface functionalization of ordered mesoporous silica has garnered intense interest for use as solid supports due to its large surface area, fast adsorption kinetics and controllable pore size and pore arrangement in comparison to amorphous silica gel [15–19]. Several mesoporous silicas have been functionalized with different ligands and used for mercury removal from water. The modifications of SBA-15 and MCM-41 with 2-mercapto thiazoline, 2-mercaptopyridine, or 2-mercaptobenzothiazol and MCM-48 with benzoyl thiourea were recently reported [17,19–21]. Although mesoporous silica has several advantages over amorphous silica gel, it seems to be less suitable for some processes in water treatment such as column methods, due to smaller particle sizes. Moreover, there are few works that compared the adsorption behavior of the functionalized amorphous silica gel and ordered mesoporous silica.

The objective of this work is to compare the adsorption properties of functionalized amorphous silica gel to those of ordered mesoporous silica, aiming for future applications in water treatment. The adsorbents for Hg(II) were prepared using silica gel and MCM-41 as starting materials for surface modification. 2-

* Corresponding author. Tel.: +66 2 218 7609; fax: +66 2 254 1309.

E-mail address: Fuangfa.U@chula.ac.th (F. Unob).

(3-(2-aminoethylthio)propylthio)ethanamine [22] was chosen as the ligand due to the presence of sulfur and nitrogen donor atoms, the ease of preparation and the high yield of the reaction. The adsorption properties of the modified materials were investigated using a batch method.

2. Materials and methods

2.1. Materials and reagents

Silica gel used for modification was 70–230 mesh with a surface area of 480–540 m² g⁻¹ and was obtained from MERCK. Tetraethoxysilane (TEOS, 98%) and cetyltrimethyl ammonium bromide (CTAB) from ACROS Organics and MERCK, respectively were used to prepare MCM-41. The synthesis of the ligand was carried out using cystamine hydrochloride and 1,3-dibromopropane. 3-Aminopropyltriethoxysilane from MERCK and ethyl-2-bromo propionate from Sigma–Aldrich were employed in the modification of silica gel and MCM-41. Metal solutions for adsorption experiments were prepared by dissolving the appropriate amount of metal salts (Hg(NO₃)₃·H₂O, Cd(NO₃)₂·4H₂O, Ni(NO₃)₂·6H₂O or Co(NO₃)₂·6H₂O) with de-ionized water. The pH of the solutions was adjusted to the desired values using either NaOH or HNO₃ solutions. All reagents and organic solvents were of analytical grade and used without further purification.

2.2. Synthesis of MCM-41 mesoporous silica

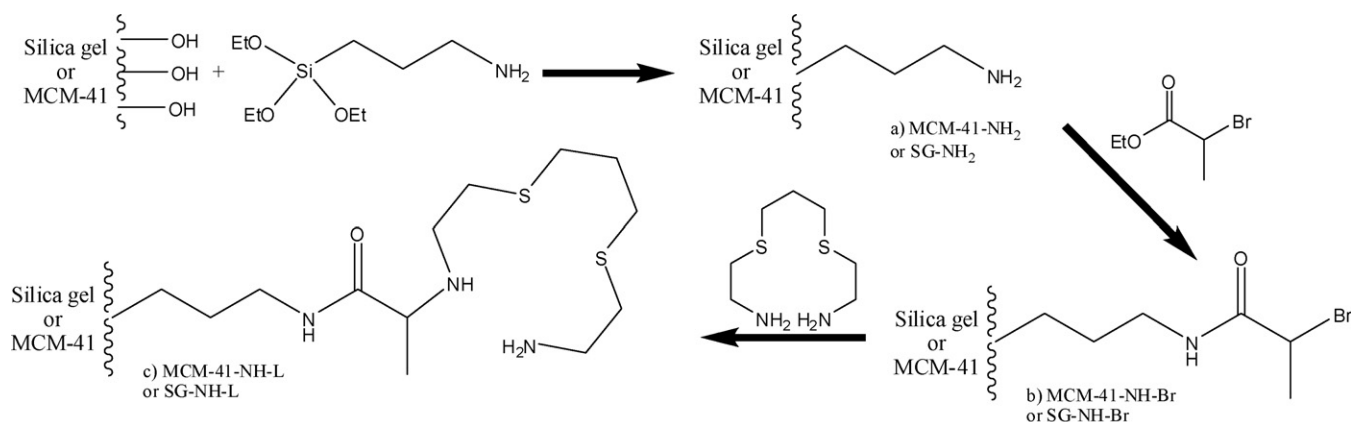
The source of silicon was TEOS and the structure directing agent was CTAB. MCM-41 was prepared by adding 5.78 g of TEOS (27.7 mmol) into a solution containing 1.01 g of CTAB (2.8 mmol) and 0.34 g of NaOH (8.5 mmol) in 30 mL of de-ionized water [23]. After stirring for 1 h at room temperature, the resulting homogeneous mixture was crystallized under static hydrothermal conditions at 110 °C in a Teflon bottle for 96 h. The molar composition of the initial gel mixture was 1.0:0.1:0.3:60 TEOS/CTAB/NaOH/H₂O. The solid product was obtained by filtration, washed with de-ionized water, ethanol and dichloromethane, and then dried in air at room temperature.

2.3. Synthesis of 2-(3-(2-aminoethylthio)propylthio)ethanamine

The synthesis of 2-(3-(2-aminoethylthio)propylthio)ethanamine [22]: sodium metal (1 g, 42.9 mmol) was dissolved in 20 mL of ethanol and the solution was kept at 10–20 °C. Cystamine hydrochloride (2.3 g, 20 mmol) was added to the solution. The mixture was stirred for 15 min before adding 1,3-dibromopropane (1.0 mL, 9.8 mmol) and stirring was continued for 4 h at 40 °C under nitrogen atmosphere. The solvent was subsequently removed by rotary evaporator. Sodium hydroxide solution (30%, w/v, 15 mL) was added to the residue and the resulting mixture was left to stand overnight. The ligand was extracted with dichloromethane (3 × 20 mL). The dichloromethane phase was separated and washed with de-ionized water. A yellow oil was obtained after evaporating the dichloromethane and characterized by ¹H NMR (400 MHz, CDCl₃) δ: 1.7 (q, 2H), 2.5 (t, 8H), 2.8 (t, 4H); ¹³C NMR (400 MHz, CDCl₃) δ: 29.5, 30.4, 36.2, 41.2.

2.4. Preparation of functionalized MCM-41 and silica gel

The method for functionalization of MCM-41 and amorphous silica gel is illustrated in Scheme 1. The first stage in the preparation was the reaction between the silylating agent and the silanol groups on the silica surface. Silica (25 g) was suspended in 200 mL of dry toluene before adding 10 mL of 3-aminopropyltriethoxysilane. The mixture was stirred and refluxed for 24 h under nitrogen atmosphere. The resulting product (Scheme 1, a) was filtered and washed with toluene (2 × 50 mL), ethanol (2 × 50 mL) and dichloromethane (4 × 50 mL). The product was dried for 6 h at room temperature under vacuum, and then immersed in 200 mL of toluene prior to adding 6.25 mL of ethyl-2-bromopropionate. The mixture was again stirred and refluxed for 24 h under nitrogen atmosphere. The resulting product (Scheme 1, b) was filtered and washed with toluene (2 × 50 mL), ethanol (4 × 50 mL) and dichloromethane (4 × 50 mL). The product was dried for 6 h at room temperature under vacuum, then dispersed in 200 mL of dry acetonitrile and 8.3 g of 2-(3-(2-aminoethylthio)propylthio)ethanamine was added. The mixture was stirred and refluxed for 24 h under nitro-



Scheme 1. Preparation of functionalized MCM-41 and silica gel.

gen atmosphere. The final product (Scheme 1, c) was filtered and washed with acetonitrile (2×50 mL), ethanol (6×50 mL) and dichloromethane (4×50 mL). This final product was dried for 10 h at room temperature under vacuum.

2.5. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 MHz nuclear magnetic resonance spectrometer. The ligand was dissolved in deuterated chloroform (CDCl_3). The characterization of all synthesized mesoporous silica MCM-41 was performed by powder X-ray diffraction (XRD) technique. The analysis was carried out with a Rigaku 1200 + series X-ray diffractometer, equipped with a monochromator, at $1.5\text{--}8^\circ 2\theta$ using a $\text{Cu K}\alpha$ radiation source accelerated at 40 kV and 30 mA. The surface area and pore size of the adsorbents were determined by nitrogen gas adsorption–desorption isotherms using a surface area analyzer (Quantachrome, Autosorb-1). The thermal stability of the modified silica gel and MCM-41 was investigated by thermogravimetric analysis (Netzsch STA 409 C/CD).

2.6. Adsorption of Hg(II) ions on the functionalized MCM-41 and amorphous silica gel

A batch method was employed to study the adsorption of Hg(II) ions from aqueous solution onto the functionalized MCM-41 and amorphous silica gel. The adsorbent (0.01 g) was added to 5 mL of metal solution. The mixture was stirred for 30 min at 600 rpm and the solid was separated. The concentration of Hg ions was determined using a cold vapor atomic absorption spectrometer (Perkin-Elmer, Analyst 300 coupled with FIAS 400 system). The reproducibility and repeatability of the analytical method for quantification of Hg(II) were evaluated. The inter-day precision of the slope of calibration curves (% R.S.D.) was 4.84% ($n = 10$). The intra-day precision was evaluated by injection of known standards and the value was 2.65% ($n = 10$). The initial concentration of Hg(II) ions was 20 and 100 mg L^{-1} for adsorption experiments using silica gel and MCM-41, respectively. The ionic strength of all solutions was controlled using 0.01 M NaNO_3 . The initial pH of the metal solutions was 5.0 ± 0.2 and did not exceed 7.5 at equilibrium. The precipitation of metal hydroxide was unlikely to occur. All adsorption experiments were carried out in triplicate. The effect of pH, ionic strength and interfering ions on adsorption of Hg(II) were investigated. The adsorption kinetics was also studied by varying stirring time of the adsorption experiments at room temperature.

3. Results and discussion

3.1. Characterization of adsorbents

The XRD pattern of MCM-41 and functionalized MCM-41 (Fig. 1) displayed a well-resolved pattern at low 2θ with a very sharp (100) diffraction peak at 2.12° and three additional higher order peaks (110, 200, 210) with lower intensities at 3.66° , 4.24° and 5.58° , respectively. The d -spacing values

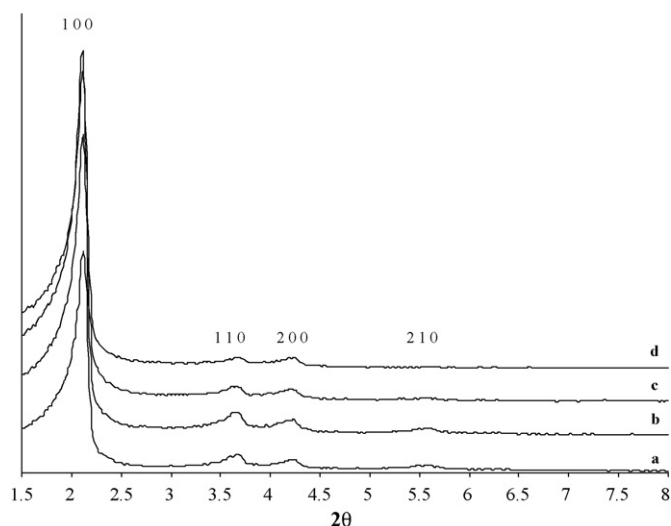


Fig. 1. XRD patterns of (a) MCM-41, (b) MCM-41-NH₂, (c) MCM-41-NH-Br and (d) MCM-41-NH-L.

for these XRD peaks were 41.65, 24.12, 20.83 and 15.82 Å, respectively. No change in the XRD pattern and d -spacing values was observed after functionalization. This indicates that the functionalization of MCM-41 did not lead to a structural change.

Thermogravimetric analyses of the modified silica gel and MCM-41 were performed (Fig. 2). The TGA and DTGA profiles indicate a difference in chemical composition of the adsorbent obtained from each step of the modification. For both silica gel and MCM-41, the DTGA profiles show a similar loss of moisture at $60\text{--}150^\circ\text{C}$. In the case of the modified silica gels (Fig. 2b–d), the profiles show a weight loss at $350\text{--}400^\circ\text{C}$ which could be attributed to the loss of aminopropyl groups from the silica gel surface. A difference in weight loss at $150\text{--}300^\circ\text{C}$ observed in the profiles of SG-NH-Br and SG-NH-L indicates a difference in composition of these adsorbents. The loss of water from the silica surface appeared at $400\text{--}850^\circ\text{C}$ [24]. Unfortunately, a difference in weight loss in TGA and DTGA profiles of unmodified and modified MCM-41 was not clearly observed. A dominant loss at $200\text{--}400^\circ\text{C}$ could be attributed to the loss of the remaining surfactant in its pores. Other techniques are required to confirm the functionalization of ligand onto the MCM-41 surface. The overall loading of organics on the functionalized silica gel was calculated using weight loss data of silica gel and functionalized silica gel [25,26]. The amount of 2-(3-(2-aminoethylthio)propylthio)ethanamine was found to be 0.36 mmol g^{-1} silica gel. On the other hand, the loading of organics on the functionalized MCM-41 could not be obtained due to the presence of the large amount of remaining surfactants on the unmodified and modified MCM-41.

Solid state ^{13}C NMR spectra of SG-NH-L and MCM-41-NH-L are shown in Fig. 3. Solid state ^{13}C NMR spectra of SG-NH-L and MCM-41-NH-L are shown in Fig. 3. The methylene groups, labeled (a) and (b), gave signals at 7.3 and 19.1 ppm, respectively. The signal at 38.2 ppm was assigned to the methylene groups (labeled (c), (g), (m)) and the methyl group (labeled (f)). The signals belonging to the carbonyl and methylene group, labeled (d) and (e), appeared at 172.5 and 119.3 ppm, respec-

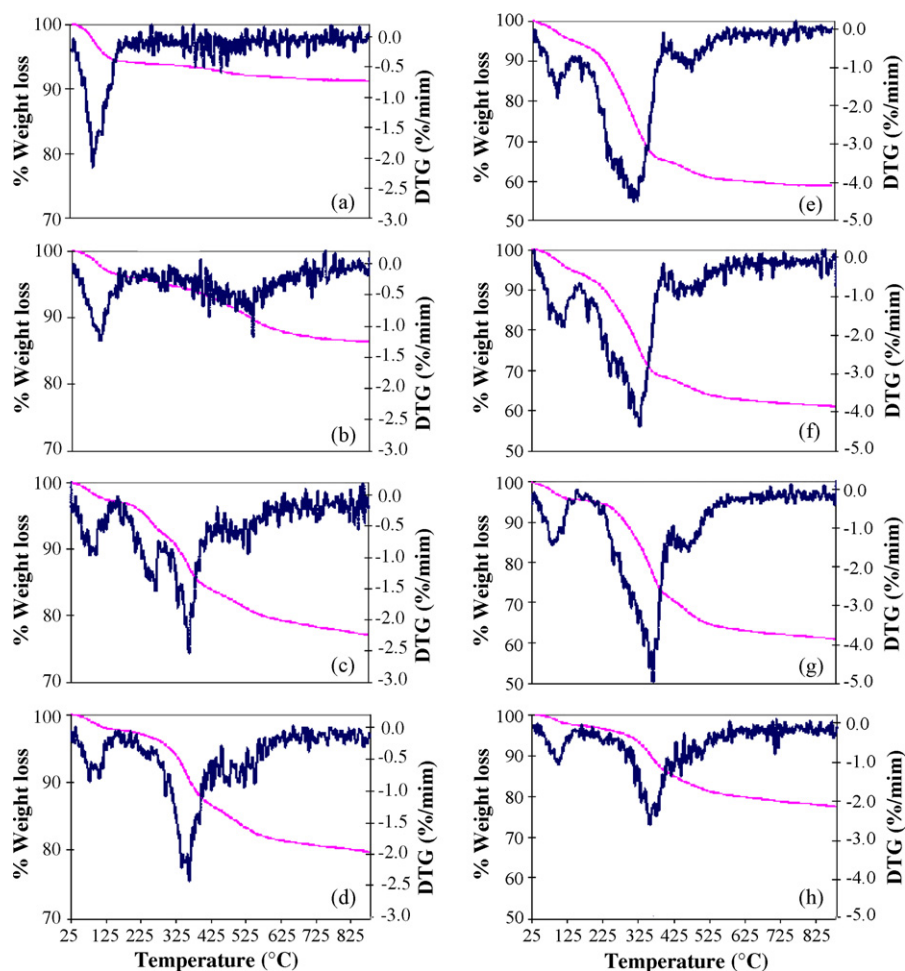


Fig. 2. TGA and DTGA curves of (a) SG, (b) SG-NH₂, (c) SG-NH-Br, (d) SG-NH-L, (e) MCM-41, (f) MCM-41-NH₂, (g) MCM-41-NH-Br and (h) MCM-41-NH-L.

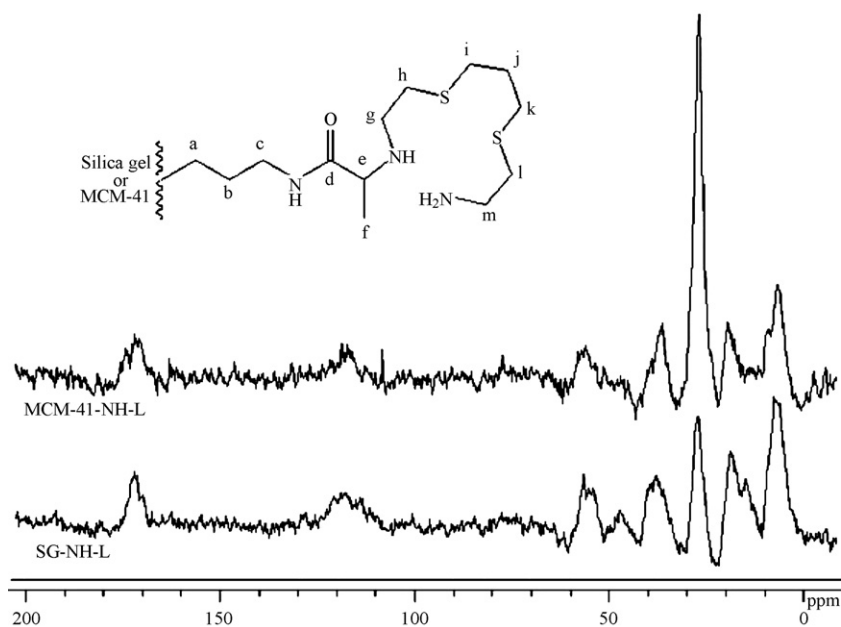


Fig. 3. ¹³C MAS NMR spectra of the SG-NH-L and MCM-41-NH-L.

Table 1
Physical parameters of the adsorbents measured by nitrogen adsorption–desorption isotherms

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (\AA)	Pore size range (\AA)
SG	515.67	0.69	53.54	20–100
SG-NH-L	201.93	0.30	59.05	20–100
MCM-41	852.60	0.75	35.31	20–40
MCM-41-NH-L	670.15	0.49	29.33	20–35

tively. The signal at 27.5 ppm was assigned to the six carbon atoms of the ligand molecule, labeled (h)–(l). The signals at 56.8 and 19.1 ppm belong to the methylene and the terminal methyl of the remaining ethoxy groups on the silicon of the silylating agent (i.e. tetraethoxysilane), respectively [27]. These results confirm the successful modification of the silica gel and MCM-41 with the desired molecule. The spectra of unmodified silica gel and MCM-41 were also recorded. It was found that there was no carbonaceous compound on the unmodified silica gel, while the signals of the residual surfactant template were observed in the spectrum of unmodified MCM-41 (21.1, 24.6, 28.3, 30.4, 51.7 and 64.9 ppm). Nevertheless, these signals disappeared from the spectrum of the modified MCM-41, except for the peak at 27.5 ppm, revealing that some of the template was washed out during the modification.

Furthermore, the surface area, pore volume and the average pore size of the modified adsorbents were determined and compared to those of unmodified adsorbents (Table 1). The results show that the surface properties of the modified adsorbents (SG-NH-L and MCM-41-NH-L) are clearly different from those of the unmodified adsorbents (SG and MCM-41). The modification leads to a reduction in surface area and pore volume. This is probably due to the occupation of the functionalized molecules on the surface and inside the pores of the adsorbents.

The results of pore size distribution (Fig. 4) indicate that the modification of silica gel did not change the range of pore size of the adsorbent, while the pore size of the modified MCM-41 clearly shifted to a smaller size compared to the unmodified MCM-41. This is likely because amorphous silica gel has a wide range of pore sizes, therefore changes in pore size are difficult to observe. On the other hand, MCM-41 has a uniform and a narrow range of pore sizes. When this material is modified, the pore surface was coated with the organic molecules and a significant change could be observed.

3.2. Adsorption of Hg(II) ions from aqueous solution

3.2.1. Effect of pH on Hg(II) ion adsorption

The solution pH is one of the major factors that influences the adsorption of metal ions. In this study, the effect of pH on the extraction of Hg(II) ions was investigated and the results of extraction as a function of initial pH are shown in Fig. 5. It was observed that the pH of the solution at equilibrium increased to 7.1–7.3 when the initial pH was 4 and higher. A possible

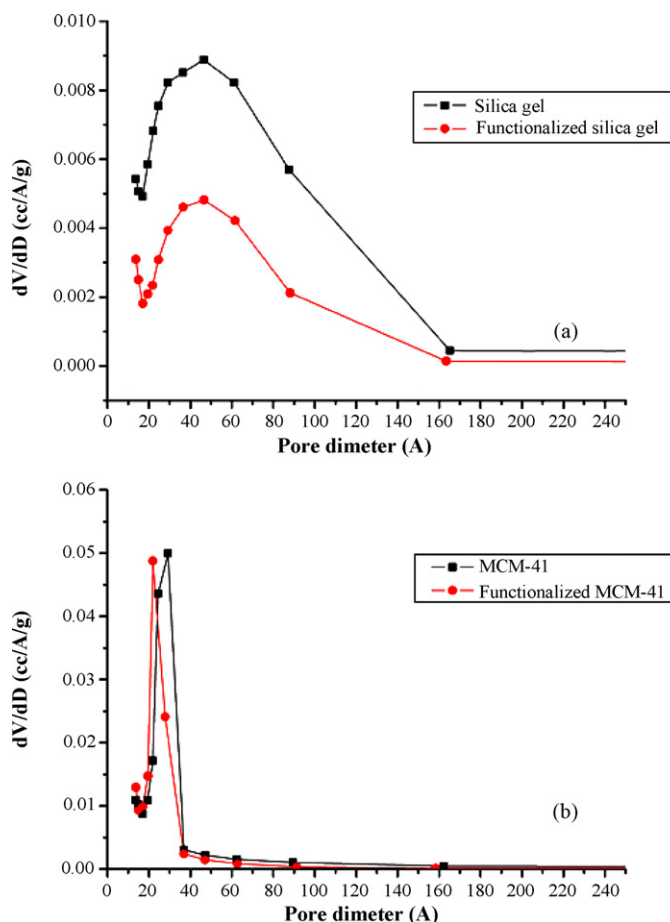


Fig. 4. Pore size distribution of (a) SG and SG-NH-L and (b) MCM-41 and MCM-41-NH-L.

explanation for this pH increase is that the ligand has basic properties.

The results show that the adsorption behavior of adsorbents for Hg(II) ions was strongly affected by changes in pH and a similar behavior for SG-NH-L and MCM-41-NH-L was observed. At low pH values (pH 2–3), low extraction efficiencies were observed, while the efficiency increased by increasing the pH of the solutions. The optimal pH for Hg(II) ion adsorption ranged from 4 to 7. Moreover, the extent of decrease in adsorption efficiency was more pronounced with amorphous silica (SG-NH-L).

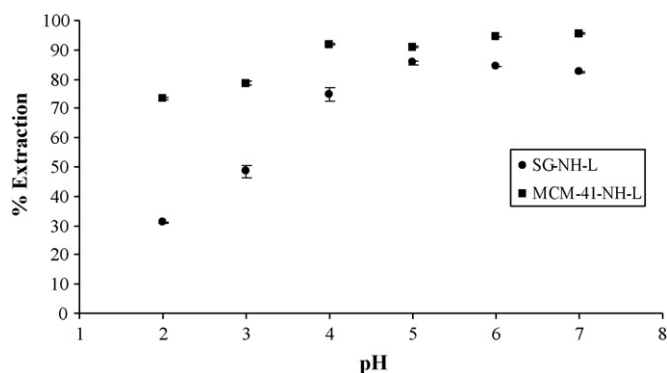


Fig. 5. Effect of pH on the adsorption of Hg(II) ions by SG-NH-L and MCM-41-NH-L.

Similar results were also observed by Walcarius and Delacote when using mesoporous amorphous and ordered silica functionalized with thiol groups [28]. In this study, the effect of pH on extraction efficiency seems to be related to the protonation of the ligand and speciation of Hg(II) ions in the solution. Theoretically, Hg(II) ions in solution exist as different species depending on the pH of the solution. At pH values lower than four, the major species of Hg(II) ions are Hg^{2+} cations, while $\text{Hg}(\text{OH})_2$ species dominate at pH values higher than four. Moreover, at pH values lower than four, protonation of the amine group on the ligand is expected. The binding ability of the protonated ligand with Hg^{2+} cations is believed to be lower than that of the non-protonated molecule with $\text{Hg}(\text{OH})_2$ at pH values higher than four. Therefore, a low extraction efficiency of Hg(II) ions by the adsorbents was observed at pH 2 and 3.

Furthermore, the extent of ligand protonation could be different depending on the structure of the silica. When the ligands on mesoporous ordered silica were protonated, these positive charge bearing ligands may act as an electrostatic barrier inside the mesopores thus causing an electrostatic repulsion with the entering proton [29]. This effect would be less pronounced in amorphous silica because the positive charge is randomly distributed resulting in less electrostatic repulsion. It was found by Walcarius et al. that 100% protonation could be achieved with amorphous silica functionalized with aminopropyl, while lower degrees of protonation were observed with MCM-41 bearing the same functional group [29,30]. In our study, it is possible that SG-NH-L could be protonated to a higher extent in comparison to MCM-41-NH-L. As a result, the extraction efficiency of SG-NH-L decreased more remarkably than that of MCM-41-NH-L due to the decreased complexation ability of the protonated ligands towards Hg(II) ions as proposed earlier.

3.2.2. Effect of stirring time

The effect of stirring time on the extraction of Hg(II) ions was studied (Fig. 6). The results show that the adsorption of Hg(II) ions onto SG-NH-L and MCM-41-NH-L occurred rapidly and reached equilibrium after ca. 5 min. It appears that the adsorption kinetics of modified MCM-41 was faster than for the modified amorphous silica in the first 5 min. This is likely due to higher accessibility of analyte through the ordered structure compared

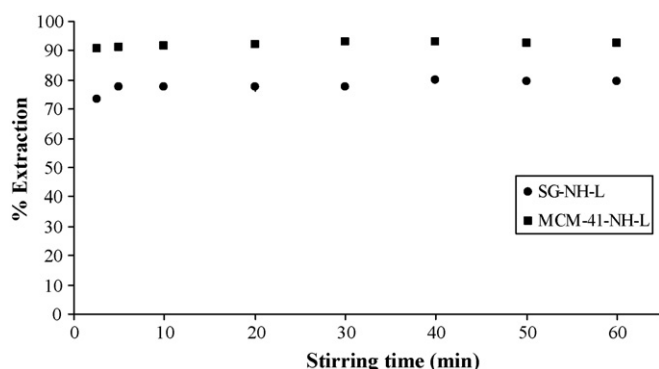


Fig. 6. Effect of stirring time on the extraction of Hg(II) ions at pH 5 by SG-NH-L and MCM-41-NH-L.

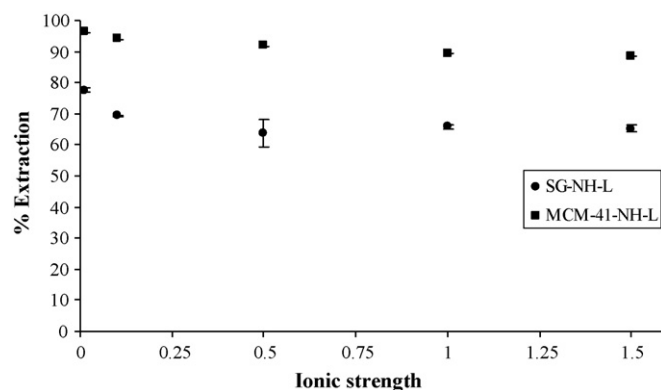


Fig. 7. Effect of ionic strength on the extraction of Hg(II) ions at pH 5 by SG-NH-L and MCM-41-NH-L.

to the amorphous structure [31]. Further adsorption batch experiments of SG-NH-L and MCM-41-NH-L were performed using a stirring time of 30 min to assure that the adsorption equilibrium was reached.

3.2.3. Effect of ionic strength

In general, natural water and wastewater have different ion concentrations depending on the water source. The presence of ions at different concentrations may affect the adsorption efficiency of the adsorbents. In this study, the effect of ionic strength on Hg(II) ion adsorption was investigated using NaNO_3 (Fig. 7). In both cases (SG-NH-L and MCM-41-NH-L), an increase of ionic strength from 0.01 to 0.1 at pH 5 resulted in a slight decrease in extraction efficiency. The ionic strength seems to have no significant effect on the extraction efficiency at higher ionic strength (using the two-tailed paired *t*-test at the 95% confidence level). This reveals that the adsorption of Hg(II) ions on the adsorbents occurred via specific complex formation with the functionalized ligand rather than by ion exchange.

3.2.4. Effect of interfering ions

The presence of ions other than Hg(II) ions may influence the adsorption of Hg(II) ions due to: (i) the competition for the adsorption sites between Hg(II) ions and other ions, (ii) the complex formation of Hg(II) ions with certain anions, and (iii) the formation of insoluble compounds (i.e. precipitation). In order to evaluate the selectivity of adsorbents towards Hg(II) ions, the extraction of Hg(II) ions was carried out in the presence of several cations, anions and heavy metal ions.

3.2.4.1. Cations. The effect of Na^+ , K^+ , Mg^{2+} and Ca^{2+} on the extraction efficiency for Hg(II) ions was investigated using nitrate salts with two concentrations (0.1 and 1.0 M). The results are shown in Table 2. It is clearly seen that these cations, with the concentrations used, have little effect on extraction of Hg(II) ions onto both functionalized amorphous silica gel and MCM-41. When comparing the effect of these cations at the same concentration, the extraction of Hg(II) ions did not change significantly in the presence of different cations. This confirms that the extraction of Hg(II) ions by the adsorbents occurred via complex formation with the ligand, which is more selective towards

Table 2
Effect of cations on the extraction of Hg(II) ions by SG-NH-L and MCM-41-NH-L

Salts	Concentration (M)	% Extraction ^a	
		SG-NH-L	MCM-41-NH-L
NaNO ₃	0.1	81.69 ± 0.40	92.13 ± 0.16
	1.0	75.00 ± 0.83	88.96 ± 0.12
KNO ₃	0.1	78.15 ± 0.99	91.87 ± 0.24
	1.0	75.00 ± 0.69	88.58 ± 0.17
Mg(NO ₃) ₂	0.1	77.30 ± 0.77	89.27 ± 0.24
	1.0	74.99 ± 0.63	85.42 ± 0.62
Ca(NO ₃) ₂	0.1	76.29 ± 0.96	88.23 ± 0.30
	1.0	72.63 ± 0.13	86.30 ± 0.14

^a Mean ± S.D. (n = 3).

Table 3
Effect of anions on the extraction of Hg(II) ions by SG-NH-L and MCM-41-NH-L

Salts	Concentration (M)	% Extraction ^a	
		SG-NH-L	MCM-41-NH-L
NaNO ₃	0.1	73.83 ± 1.25	94.03 ± 0.66
	1.0	69.99 ± 0.15	88.88 ± 0.77
Na ₂ SO ₄	0.1	70.45 ± 0.27	90.04 ± 0.97
	1.0	68.76 ± 0.25	89.55 ± 0.40
NaCl	0.1	87.83 ± 1.01	61.45 ± 1.81
	1.0	65.52 ± 1.81	39.22 ± 0.64

^a Mean ± S.D. (n = 3).

Hg(II) ions over alkaline and alkaline earth metals due to the hard/soft acid/base principle [32].

3.2.4.2. Anions. The effect of anions (i.e. NO₃⁻, SO₄²⁻, Cl⁻) on Hg(II) ion extraction was studied. The sodium salt of these anions was added to the Hg(II) ion solutions with a concentration of 0.1 or 1.0 M. The results are listed in Table 3. These anions can act as ligands to form different Hg(II) ion species in solution with formation constants shown in Table 4. The results show that the extraction efficiency of the adsorbents was not affected by the presence of either NO₃⁻ or SO₄²⁻. On the other hand, the presence of Cl⁻ had a significant effect on the extraction efficiency of Hg(II) ions. Moreover, the effect seems to be dependent on the concentration of Cl⁻ and the type of adsorbent. Regarding

Table 4
Aqueous speciation reactions and equilibrium constants of Hg(II) ions [33,36]

Reaction	log K
Hg ²⁺ + H ₂ O ⇌ HgOH ⁺ + H ⁺	-2.70
Hg ²⁺ + 2H ₂ O ⇌ Hg(OH) ₂ + 2H ⁺	-6.19
Hg ²⁺ + NO ₃ ⁻ ⇌ HgNO ₃ ⁺	0.45
Hg ²⁺ + Cl ⁻ ⇌ HgCl ⁺	6.74
Hg ²⁺ + 2Cl ⁻ ⇌ HgCl ₂	13.22
Hg ²⁺ + 3Cl ⁻ ⇌ HgCl ₃ ⁻	14.07
HgCl ₃ ⁻ ⇌ HgCl ₄ ²⁻	15.07
Hg ²⁺ + Cl ⁻ + H ₂ O ⇌ HgClOH + H ⁺	3.23
Hg ²⁺ + SO ₄ ²⁻ ⇌ HgSO ₄	1.39
Hg ²⁺ + SO ₄ ²⁻ + 2H ₂ O ⇌ Hg(OH) ₂ SO ₄ ²⁻ + 2H ⁺	-4.83 ^a

^a Conditional equilibrium constant (log K, ionic strength = 0.1) optimized using the Hg(II)-SO₄-quartz and Hg(II)-PO₄-quartz system data.

the formation constants and the results observed, a hypothesis to rationalize these results is proposed. It is possible that the ligand can reduce Hg(II) to Hg(I) ions which can precipitate with Cl⁻ as Hg₂Cl₂ (K_{sp} , 1.3×10^{-18} , [33]). The extraction of the metal in this case is due to both complexation with the ligand and also precipitation. This would result in the observed high extraction efficiency of SG-NH-L in the presence of 0.1 M Cl⁻. On the other hand, in the presence of other anions, precipitation did not occur and the extraction observed was only the result of complexation of Hg species with the ligand. To test this hypothesis, free ligand solution (in MeOH) was added to a HgCl₂ solution and Hg(II) ion solutions containing NaCl or NaNO₃ with concentrations similar to those used in the extraction experiments. A white precipitate was obtained immediately after adding the ligand solution to both the HgCl₂ solution and the Hg(II) ion solution containing NaCl, while no precipitation was observed in the Hg(II) ion solution containing NaNO₃. The precipitate is proposed to be Hg₂Cl₂. This result suggests that Hg(II) ions can be reduced by the ligand. Nevertheless, it was found that the extraction efficiency decreased by increasing the Cl⁻ concentration from 0.1 to 1.0 M. In solutions containing different concentration of Cl⁻, the dominant Hg species are also different. Using the formation constants in Table 4, in 0.1 M NaCl, the dominant species are HgCl₂, HgCl₃⁻ and HgCl₄²⁻ with a distribution of 42%, 29% and 29%, respectively while the major species found in the 1.0 M NaCl solution was only HgCl₄²⁻. Regarding the standard reduction potential of these Hg species, the standard reduction potential of Hg²⁺, HgCl₂ and HgCl₄²⁻ are 0.91, 0.63 and 0.54 V, respectively [34]. Therefore, HgCl₂ could be reduced more readily than HgCl₄²⁻ to yield Hg₂²⁺ or Hg₂Cl₂ precipitate, resulting in the greater extraction efficiency observed in the 0.1 M NaCl solution and the poor extraction efficiency observed in the 1.0 M NaCl solution.

In the case of MCM-41-NH-L, the presence of Cl⁻ markedly reduced the extraction efficiency of Hg(II) ions, possibly due to the restricted access of different species of Hg-Cl complexes through the small and uniform pore size of the adsorbent. Therefore, the extraction efficiency of Hg(II) ions in the presence of Cl⁻ was found to be less than those of the other anions.

3.2.4.3. Heavy metal ions. The effect of heavy metal ions other than Hg(II) ions on extraction efficiency was studied. Ni(II), Cd(II) and Co(II) ions were added separately to solutions containing Hg(II) ions at two different concentrations. The results are summarized in Table 5. It was found that the extraction of Hg(II) ions by the adsorbents was not affected by the presence of the foreign ions with concentrations equal to or 10 times higher than that of the Hg(II) ions. This indicates that both functionalized amorphous silica gel and MCM-41 have high selectivity towards Hg(II) ions.

3.2.5. Adsorption isotherm

The distribution of metal ions between the liquid and solid phase at equilibrium can be expressed by adsorption isotherms. The Langmuir and Freundlich isotherm are widely used to describe the adsorption phenomena at the solid-liquid interface. The Langmuir relation assumes monolayer sorption onto

Table 5
Selectivity of SG-NH-L and MCM-41-NH-L on the extraction of Hg(II) ions in the presence of other heavy metal ions

Metals	Concentration (mM)	% Extraction ^a	
		SG-NH-L	MCM-41-NH-L
NaNO ₃ (blank)	0.1 × 10 ³	79.20 ± 0.04	87.38 ± 0.10
Ni(II)	0.01	81.39 ± 0.43	–
	0.10	81.46 ± 0.51	–
	0.05	–	87.05 ± 0.51
	0.50	–	86.63 ± 0.26
Cd(II)	0.01	80.01 ± 0.39	–
	0.10	82.01 ± 1.36	–
	0.05	–	85.87 ± 0.31
	0.50 ^b	–	–
Co(II)	0.01	79.44 ± 1.26	–
	0.10	79.59 ± 1.15	–
	0.05	–	87.14 ± 0.29
	0.50	–	85.08 ± 0.10

Initial concentration of Hg(II) ions was 0.01 mM for SG-NH-L and 0.05 mM for MCM-41-NH-L.

^a Mean ± S.D. (*n* = 3).

^b Cadmium precipitated as cadmium hydroxide.

the homogeneous surface with a specific number of equivalent sites. The Langmuir equation [35] governs the amount of metal sorbed and its concentration in solution is given in Eq. (1):

$$\frac{C}{N_f} = \frac{C}{N_f^s} + \frac{1}{bN_f^s} \quad (1)$$

where N_f is the amount of metal ion per gram of adsorbent, C the equilibrium concentration of metal ion, $b = K_{eq}/a$ (where a represents the activity of the solvent in solution, K_{eq} is the equilibrium constant) and N_f^s is the maximum sorption capacity of the sorbent.

The Freundlich relation [35] describes multilayer sorption and can be expressed as

$$\log N_f = \log K_f + \left(\frac{1}{n}\right) \log C \quad (2)$$

where n and K_f are Freundlich constants. The values of $1/n$ and K_f can be obtained from the slope and the intercept of the linear plot of $\log N_f$ versus $\log C$, respectively.

The experiments were carried out at 298 K using a batch method. The results were collected from the extraction of Hg(II) ions at pH 3. The initial concentration of Hg(II) ions ranged from 0.50 to 4.0 mM and the stirring time was 30 min to assure that the adsorption equilibrium was reached. The capacity of the functionalized adsorbents increased first by increasing initial concentration of metal ions, and finally reached a saturation level at high initial concentrations. From the Langmuir and Freundlich plots, the results of MCM-41-NH-L and SG-NH-L fit well with the Langmuir model and under the conditions used in this study, the results of SG-NH-L also fit the Freundlich model. The Langmuir and Freundlich parameters are summarized in Table 6.

The monolayer coverage of the metal ions on the MCM-41-NH-L occurred with a maximum adsorption capacity of 0.70 mmol g⁻¹. On the other hand, in the case of SG-NH-L,

Table 6
Thermodynamic parameters of Langmuir and Freundlich adsorption isotherms at 298 K

Phases	Langmuir constants			Freundlich constants		
	N_f^s (mmol g ⁻¹)	b (L mol ⁻¹)	R^2	K_f	n	R^2
SG-NH-L	0.79	1955.7	0.9927	9150	4.66	0.9860
MCM-41-NH-L	0.70	5263.5	0.9979	35843	2.24	0.8395

it seems that the concentration of Hg(II) ions used in this study was not sufficient to reach the saturation level of the binding sites on the adsorbent and the concentration is still in the monolayer regime. Therefore, metal adsorption can be described by both Langmuir and Freundlich isotherms. However, higher concentration of Hg(II) ions could not be employed because of the precipitation of Hg(OH)₂. The maximum adsorption capacity observed for SG-NH-L was 0.79 mmol g⁻¹. The results show a contradiction between the adsorption capacity and the surface area of these adsorbents. The modified silica gel seems to have more active sites or capacity for Hg(II) binding than the modified MCM-41, while the modified MCM-41 has a higher surface area. It is believed that there was some residual surfactant from the synthesis of MCM-41 left in the pores of the adsorbent as shown by the ¹³C NMR spectra of the unmodified MCM-41. Therefore, only a limited amount of 3-aminopropyltriethoxysilane, initially added to MCM-41 to commence the modification, was functionalized onto the surface due to a limited number of available sites remaining. This resulted in lower ligand loading on the adsorbents. In an attempt to improve the adsorption capacity of MCM-41, the residual surfactant was removed by calcination at 500 °C (3 h). The template free MCM-41 (cal-MCM-41) was further used as the starting material for the modification with the same ligand. Surprisingly, the adsorption capacity of the latest material (cal-MCM-41-NH-L) was 21 mg g⁻¹ which is less than that of MCM-41-NH-L (44 mg g⁻¹). The XRD patterns of cal-MCM-41-NH-L showed less intense characteristic peaks, indicating a change in its original structure after the modification. This may result in a decrease in adsorption efficiency. Moreover, it is also possible that the calcination leads to the loss of silanol group on surface [37]. As a result, the number of the available site for the modification is decreased. Therefore, the surfactant should be removed by other alternative method, i.e. solvent extraction.

It should be also noted that the adsorption isotherms used to determine the adsorption capacity in this study were obtained at pH 3, which is not the optimum pH for extraction. The adsorption capacity of SG-NH-L and MCM-41-NH-L are expected to be higher than 0.79 and 0.70 mmol g⁻¹, respectively.

Furthermore, the behavior of these adsorbents, which are different in structure could be differentiated by the b (Eq. (1)) values observed. MCM-41-NH-L showed a much larger b value than SG-NH-L. This indicates that MCM-41-NH-L has the ability to adsorb Hg(II) ions from solution better than SG-NH-L. This is probably due to the access of Hg(II) ions through uniform mesopore channels of MCM-41 which is more favorable

Table 7
The maximum adsorption capacity for Hg(II) ions of modified adsorbents from the literature

Material	Ligand (method of modification)	N_p^a (mmol g ⁻¹)	Reference
Hexagonal mesoporous silica	2-Mercaptothiazoline (co-condensation method)	2.34	[25]
Silica gel	2-Mercaptobenzimidazole		[38]
	Heterogeneous method	1.35	
	Homogeneous method	1.43	
Sol-gel silica	1,5-Diphenylcarbazine (doping method)	0.029	[39]
Silica gel	Dithizone (grafting method)	0.32	[40]
MCM-41	2-Mercaptopyridine		[19]
	Heterogeneous method	0.09	
	Homogeneous method	0.12	
MCM-41	2-Mercaptothiazoline		[20]
	Heterogeneous method	0.25	
	Homogeneous method	0.70	
MCM-41	2-(3-(2-Aminoethylthio)propylthio)ethanamine (grafting method or heterogeneous method)	0.70 ^b	This work
Silica gel		0.79 ^b	

^a Results from adsorption isotherms at pH 6.

^b Results from adsorption isotherms at pH 3.

than the non-uniform pore channels of the amorphous silica gel. Therefore, MCM-41-NH-L showed a more promising ability for Hg(II) adsorption compared to SG-NH-L. Nevertheless, the preparation method for MCM-41 still requires improvements in order to achieve better adsorption capacities.

When comparing the adsorption capacity of our materials to those of silica-based adsorbents reported by other authors (Table 7), the adsorbents prepared in this work have fairly good capacities for Hg(II) ions. Furthermore, the adsorption capacity of the materials is comparable to those of activated carbon (0.01–0.77 mmol g⁻¹) [1,3,5,6] and close to some of chelating resins (1–3.36 mmol g⁻¹) [8,9,12].

Furthermore, the practical application of the materials is also considered in term of metal release. In this case, the release of mercury from the used materials seems to be less likely when using the material to treat natural water (pH 4–8), due to the strong interaction between Hg and the ligand. The previous results also show that the materials can extract Hg in acidic solutions. On the other hand, in the extreme condition, i.e. strong acidic solution, a release of trace amount of Hg could be observed. Only in the presence of complexing agents, e.g. thiourea, Hg can be mostly released from the materials. This also reveals the possibility of regeneration of the used materials.

4. Conclusions

MCM-41 and amorphous silica gel functionalized with 2-(3-(2-aminoethylthio)propylthio)ethanamine were successfully prepared. The adsorbents showed a high selectivity toward Hg(II) ions over other metal ions. By the methods used to prepared the adsorbents in this study, the functionalized amorphous silica gel and functionalized MCM-41 showed similar

adsorption capacities at pH 3, while the functionalized MCM-41 showed larger binding ability for toxic Hg(II) ions from aqueous solutions compared to that of the functionalized amorphous silica gel due to its uniform structure. The extraction of Hg(II) ions occurred rapidly for modified MCM-41 and the optimal pH range for the extraction of Hg(II) ions was pH 4–7. Foreign ions, especially Cl⁻, affected the extraction efficiency of the adsorbents due to the difference in the structure of the adsorbents. A hypothesis of Hg extraction was proposed where it is believed that Hg(II) could be reduced to Hg(I) by the ligand on the adsorbents and the extraction occurred via complexation of these Hg species. The results show that the modified MCM-41 and amorphous silica gel have good potential to be used as selective adsorbents for Hg(II) ions.

Acknowledgement

This work was supported by a grant for graduate students from Department of Chemistry, Chulalongkorn University.

References

- [1] C. Namasivayam, K. Kadirvelu, Uptake of mercury(II) from wastewater by activated carbon from an unwanted agricultural solid by-product: coirpith, *Carbon* 37 (1999) 79–84.
- [2] E. Ekinci, T. Budinova, F. Yardim, N. Petrov, M. Razvigorova, V. Minkova, Removal of mercury ion from aqueous solution by activated carbons obtained from biomass and coals, *Fuel Process. Technol.* 77/78 (2002) 437–443.
- [3] K. Ranganathan, Adsorption of Hg(II) ions from aqueous chloride solutions using powdered activated carbons, *Carbon* 41 (2003) 1087–1092.
- [4] M.F. Yardim, T. Budinova, E. Ekinci, N. Petrov, M. Razvigorova, V. Minkova, Removal of mercury(II) from aqueous solution by activated carbon obtained from furfural, *Chemosphere* 52 (2003) 835–841.
- [5] K. Kadirvelu, M. Kavipriya, C. Karthika, N. Vennilamani, S. Pattabhi, Mercury(II) adsorption by activated carbon made from sago waste, *Carbon* 42 (2004) 745–752.
- [6] A.M. Starvin, T.P. Rao, Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant, *J. Hazard. Mater.* 113 (2004) 75–79.
- [7] F.-S. Zhang, J.O. Nriagu, H. Itoh, Mercury removal from water using activated carbons derived from organic sewage sludge, *Water Res.* 39 (2005) 389–395.
- [8] E. Yavuz, B.F. Senkal, N. Bicak, Poly(acrylamide) grafts on spherical polyvinyl pyridine resin for removal of mercury from aqueous solutions, *React. Funct. Polym.* 65 (2005) 121–125.
- [9] A.A. Atia, A.M. Donia, K.Z. Elwakeel, Selective separation of mercury(II) using a synthetic resin containing amine and mercaptan as chelating groups, *React. Funct. Polym.* 65 (2005) 267–275.
- [10] C. Sun, R. Qu, C. Ji, Q. Wang, C. Wang, Y. Sun, G. Cheng, A chelating resin containing S, N and O atoms: synthesis and adsorption properties for Hg(II), *Eur. Polym. J.* 42 (2006) 188–194.
- [11] S. Pramanik, P.K. Dhara, P. Chattopadhyay, A chelating resin containing bis(2-benzimidazolylmethyl)amine: synthesis and metal-ion uptake properties suitable for analytical application, *Talanta* 63 (2004) 485–490.
- [12] S. Chiarle, M. Ratto, M. Rovatti, Mercury removal from water by ion exchange resins adsorption, *Water Res.* 34 (2000) 2971–2978.
- [13] I.K. Tonle, E. Ngameni, D. Njopwouo, C. Carteret, A. Walcarius, Functionalization of natural smectite-type clays by grafting with organosilanes: physico-chemical characterization and application to mercury(II) uptake, *Phys. Chem. Chem. Phys.* 5 (2003) 4951–4961.
- [14] D.M. Manohar, K. Anoop Krishnan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry wastewater using 2-mercaptobenzimidazole-clay, *Water Res.* 36 (2002) 1609–1619.

- [15] M.E. Mahmoud, G.A. Gohar, Silica gel-immobilized-dithioacetal derivatives as potential solid phase extractors for mercury(II), *Talanta* 51 (2000) 77–87.
- [16] E.M. Soliman, M.B. Saleh, S.A. Ahmed, New solid phase extractors for selective separation and preconcentration of mercury(II) based on silica gel immobilized aliphatic amines 2-thiophenecarboxaldehyde Schiff's bases, *Anal. Chim. Acta* 523 (2004) 133–140.
- [17] V. Antochshuk, O. Olkhovik, M. Jaroniec, I.S. Park, R. Ryoo, Benzoylthiourea-modified mesoporous silica for mercury(II) removal, *Langmuir* 19 (2003) 3031–3034.
- [18] A. Bibby, L. Mercier, Mercury(II) ion adsorption behavior in thiol-functionalized mesoporous silica microspheres, *Chem. Mater.* 14 (2002) 1591–1597.
- [19] D. Perez-Quintanilla, I. del Hierro, M. Fajardo, I. Sierra, Mesoporous silica functionalized with 2-mercaptopyridine: synthesis, characterization and employment for Hg(II) adsorption, *Micropor. Mesopor. Mater.* 89 (2006) 58–68.
- [20] D. Perez-Quintanilla, I. del Hierro, M. Fajardo, I. Sierra, 2-mercaptothiazoline modified mesoporous silica for mercury removal from aqueous media, *J. Hazard. Mater.* 134 (2006) 245–256.
- [21] D. Perez-Quintanilla, I. del Hierro, M. Fajardo, I. Sierra, Preparation of 2-mercaptobenzothiazole-derivatized mesoporous silica and removal of Hg(II) from aqueous solution, *J. Environ. Monit.* 8 (2006) 214–222.
- [22] S.B. Choudhury, D. Ray, A. Chakravorty, Sulfur-ligated nickel oxidation states. Chemistry of a family of $Ni_2S_2N_4$ ($z = +2, +3, +4$) complexes incorporating hexadentate thioether-imine-oxime binding, *Inorg. Chem.* 30 (1991) 4354–4360.
- [23] H. Chen, Y. Wang, Preparation of MCM-41 with high thermal stability and complementary textural porosity, *Ceram. Int.* 28 (2002) 541–547.
- [24] B. Lee, Y. Kim, H. Lee, J. Yi, Synthesis of functionalized porous silicas via templating method as heavy metal ion adsorbents: the introduction of surface hydrophilicity onto the surface of adsorbents, *Micropor. Mesopor. Mater.* 50 (2001) 77–90.
- [25] S.M. Evangelista, E. DeOliveira, G.R. Castro, L.F. Zara, A.G.S. Prado, Hexagonal mesoporous silica modified with 2-mercaptothiazoline for removing mercury from water solution, *Surf. Sci.* 601 (2007) 2194–2202.
- [26] S.A. Alekseev, V.N. Zaitsev, Organosilicas with covalently bonded groups under thermochemical treatment, *Chem. Mater.* 18 (2006) 1981–1987.
- [27] L.N.H. Arakaki, J.G.P. Espinola, M.G. da Fonseca, S.F. de Oliveira, A.N. de Sousa, T. Arakaki, C. Airolidi, Thioglycolic acid grafted onto silica gel and its properties in relation to extracting cations from ethanolic solution determined by calorimetric technique, *J. Colloid Interf. Sci.* 273 (2004) 211–217.
- [28] A. Walcarius, C. Delacote, Mercury(II) binding to thiol-functionalized mesoporous silicas: critical effect of pH and sorbent properties on capacity and selectivity, *Anal. Chim. Acta* 547 (2005) 3–13.
- [29] A. Walcarius, M. Etienne, B. Lebeau, Rate of access to the binding sites in organically modified silicates. 2. Ordered mesoporous silicas grafted with amine or thiol groups, *Chem. Mater.* 15 (2003) 2161–2173.
- [30] A. Walcarius, M. Etienne, J. Bessiere, Rate of access to the binding sites in organically modified silicates. 1. Amorphous silica gels grafted with amine or thiol groups, *Chem. Mater.* 14 (2002) 2757–2766.
- [31] A. Walcarius, C. Delacote, Rate of access to the binding sites in organically modified silicates. 3. Effect of structure and density of functional groups in mesoporous solids obtained by the co-condensation route, *Chem. Mater.* 15 (2003) 4181–4192.
- [32] A. Beerbower, W.B. Jensen, The HSAB principle and extended solubility theory, *Inorg. Chim. Acta.* 75 (1983) 193–197.
- [33] J.A. Dean, *Lange's Handbook of Chemistry*, thirteenth ed., McGraw-Hill Book Co., Singapore, 1987.
- [34] P. Patnaik, *Dean's Analytical Chemistry Handbook*, second ed., The McGraw-Hill Companies, Inc., New York, USA, 1995.
- [35] A. Suna Erses, M.A. Fazal, T.T. Onay, W.H. Craig, Determination of solid waste sorption capacity for selected heavy metals in landfills, *J. Hazard. Mater.* 121 (2005) 223–232.
- [36] D. Sarkar, M.E. Essington, K.C. Misra, Adsorption of mercury(II) by kaolinite, *Soil Sci. Soc. Am. J.* 64 (2000) 1968–1975.
- [37] C. Zhang, W. Zhou, S. Liu, Synthesis and characterization of organofunctionalized MCM-41 by the original stepped templated sol–gel technology, *J. Phys. Chem. B* 109 (2005) 24319–24325.
- [38] E.F.C. Alcantara, E.A. Faria, D.V. Rodrigues, S.M. Evangelista, E. DeOliveira, L.F. Zara, D. Rabelo, A.G.S. Prado, Modification of silica gel by attachment of 2-mercaptobenzimidazole for use in removing Hg(II) from aqueous media: a thermodynamic approach, *J. Colloid Interf. Sci.* 311 (2007) 1–7.
- [39] A. Khan, F. Mahmood, M.Y. Khokhar, S. Ahmed, Functionalized sol–gel material for extraction of mercury(II), *React. Funct. Polym.* 66 (2006) 1014–1020.
- [40] A.R. Cestari, E.F.S. Vieira, E.C.N. Lopes, R.G. da Silva, Kinetics and equilibrium parameters of Hg(II) adsorption on silica-dithizone, *J. Colloid Interf. Sci.* 272 (2004) 271–276.