

2-Mercaptothiazoline modified mesoporous silica for mercury removal from aqueous media

Damián Pérez-Quintanilla, Isabel del Hierro, Mariano Fajardo, Isabel Sierra*

*Departamento de Tecnología Química y Ambiental, E.S.C.E.T., Universidad Rey Juan Carlos, C/Tulipán s/n,
28933 Móstoles, Madrid, Spain*

Received 7 September 2005; received in revised form 25 October 2005; accepted 2 November 2005
Available online 1 December 2005

Abstract

Mesoporous silicas (SBA-15 and MCM-41) have been functionalized by two different methods. Using the heterogeneous route the silylating agent, 3-chloropropyltriethoxysilane, was initially immobilized onto the mesoporous silica surface to give the chlorinated mesoporous silica Cl-SBA-15 or Cl-MCM-41. In a second step a multifunctionalized N, S donor compound (2-mercaptothiazoline, MTZ) was incorporated to obtain the functionalized silicas denoted as MTZ-SBA-15-Het or MTZ-MCM-41-Het. Using the homogeneous route, the functionalization was achieved via the one step reaction of the mesoporous silica with an organic ligand containing the chelating functions, to give the modified mesoporous silicas denoted as MTZ-SBA-15-Hom or MTZ-MCM-41-Hom. The functionalized mesoporous silicas were employed as adsorbents for the regeneration of aqueous solutions contaminated with Hg (II) at room temperature. SBA-15 and MCM-41 functionalized with MTZ by the homogeneous method present good mercury adsorption values (1.10 and 0.7 mmol Hg (II)/g of silica, respectively). This fact suggests a better applicability of such mesoporous silica supports to extract Hg (II) from aqueous solutions. In addition, it was observed the existence of a correlation between mercury adsorption with pore size and volume since, SBA-15 with lower areas and higher pore sizes functionalized with sterically demanding ligands, show better adsorption capacities than functionalized MCM-41.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Functionalized mesoporous silica; Mercury adsorption; 2-Mercaptothiazoline

1. Introduction

Heavy metal ion removal from waters has been the subject of extensive technological research, and recovering processes can often result in considerable cost saving [1]. The synthesis of adsorbents for the removal of toxic heavy metal ions from waste-water is a continuing research objective of environmental pollution control processes. Several different types of materials, among them resins, active carbons and clays, have been studied and proposed for adsorption of heavy metal ions. Nevertheless, these materials have shown several problems like low mechanical and thermal stability and a weak chemical union with the metals. These factors have led to the scientific community to develop new techniques to remove heavy metals from the environment.

Porous silica is a class of materials that fulfils all the requirements. Silica is chemically inert but allows irreversible surface modification by reaction of the surface silanol groups. This methodology has been employed in the functionalization of amorphous silica support, and with the advent of mesoporous silica, it has been utilized extensively in the development of the surface chemistry of these materials. Mesoporous silica materials were first synthesized in 1992 [2]. The so-called M41S materials are prepared with micelles of quaternary ammonium detergents as the template. Depending on the amount of template different hexagonal, cubic and lamellar organic-inorganic mesophases can be formed. The hexagonal phase is referred to as MCM-41, the cubic phase as MCM-48 and the lamellar phase as MCM-50. Alternatively, the length of the hydrophobic tail of the detergent molecules can be varied to adjust the pore diameter to a certain value. The use of alkyl-trimethylammonium detergent molecules with C8–C18 hydrocarbon chains enables the synthesis of hexagonally ordered MCM-41 materials with pore diameters between 15 and 40 Å.

* Corresponding author. Tel.: +34 916647018; fax: +34 914888143.

E-mail addresses: damian.perez@urjc.es (D. Pérez-Quintanilla), isabel.sierra@urjc.es (I. Sierra).

Another type of mesoporous silica material is SBA-15 [3]. This material is prepared with non-ionic amphiphilic triblock copolymer micelles as the template under acidic reaction conditions. The material has a well-defined hexagonal symmetry and its specific surface area is somewhat smaller than that of M41S materials. Therefore the mechanical and hydrothermal stability of this material is also better. The pore diameters can be varied between 50 and 200 Å, by varying the synthesis temperature (between 30 and 90 °C) and the template.

Recently, a class of hybrid mesoporous materials has been developed based on organized monolayers of functional molecules covalently bound to the mesoporous support. The preparation of these new surfaces with coordinative ligands containing in his molecule nitrogen or sulphide atoms are clearly one of the most promising methods to remove mercury and other heavy metals from contaminated aqueous media. Despite of this fact, very few ligands have been used at the moment to functionalize the mesoporous supports (principally commercially available alkylthiols and alkylamines) [4–10], so new studies are required in order to found other commercially unavailable ligands with better adsorption capacity. There are two principal methods in order modify mesoporous silica with these organic ligands (homogeneous and heterogeneous). The first stage in the preparation of functionalized mesoporous silicas by the homogeneous method is the synthesis of the silylating agent, by reaction of a 3-chloropropylsilane with the molecule containing the donor atom. The resulting compound is then allowed to react with the silanol groups of activated silica, liberating the corresponding alcohol, to get the final functionalized support. The second methodology used, the heterogeneous method, involves a two step reaction of the solid support. Initially, the reaction of the activated mesoporous silica with a 3-chloropropylsilane ligand to obtain the chlorinated silica followed by the reaction of the chlorinated silica with the appropriate amount of the molecule containing the donor atom to yield the final product. Nowadays, the heterogeneous method has been used preferably to modify mesoporous silicas with commercially unavailable ligands [11]. However, studies carry out in our group demonstrate that silica presents better heavy metal adsorption values when it is modified by the homogeneous method.

This paper reports the use of two mesoporous silicas (SBA-15 and MCM-41) in the preparation of solid phases modified with a new ligand (2-mercaptothiazoline) by two different approaches (the homogenous and heterogeneous routes) and their application for the adsorption of mercury from aqueous media by the batch method.

2. Experimental

2.1. Reagents and materials

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($M_{av} = 5800$; $d = 1.019 \times 10^{-3}$ g/mL) and tetraethoxysilane (TEOS) 99% ($M = 208.33$, $d = 0.933 \times 10^{-3}$ g/mL) were purchased from Fluka (Spain). Sodium silicate $\text{SiO}_2 \cdot \text{NaOH}$ ($M = 242.23$, $d = 1.390 \times 10^{-3}$ g/mL) and cetyltrimethylammonium bromide (CTAB) ($M = 364.46$) were

purchased from Sigma–Aldrich (Germany). Sulphuric acid 96% ($M = 98.08$, $d = 1.840 \times 10^{-3}$ g/mL) was purchased from Panreac (Spain). 3-Chloropropyltriethoxysilane 95% (CPTS) ($M = 240.81$, $d = 1.007$ g/mL), triethylamine ($M = 101.19$, $d = 0.726$ g/mL) and 2-mercaptothiazoline 98% (MTZ) ($M = 119.21$), from Sigma–Aldrich, were used as supplied. Organic solvents (toluene, dimethylformamide, diethyl ether, ethanol, hexane and triethylamine) were purchased from SDS (France). These solvents were distilled and dried before use according to conventional literature methods [12]. Buffer solution of pH 6 was prepared by using sodium acetate and hydrochloric acid (Scharlau, Spain). Standard stock solution of Hg (II) was prepared by dissolving mercury (II) nitrate monohydrate 98% (Sigma–Aldrich) in dilute HNO_3 . Water (resistance $18 \text{ M}\Omega \text{ cm}^{-1}$) used in the preparation of standard solutions was obtained from a Millipore Milli-Q-System (Waters, USA). Triton X-100 and 1,5-diphenylthiocarbazon (dithizone) were purchased from Sigma–Aldrich. Glassware was soaked in (1 + 1) HNO_3 overnight and cleaned with Milli-Q water before use. All other reagents used were at least of analytical grade.

2.2. Synthesis of SBA-15 mesoporous silica

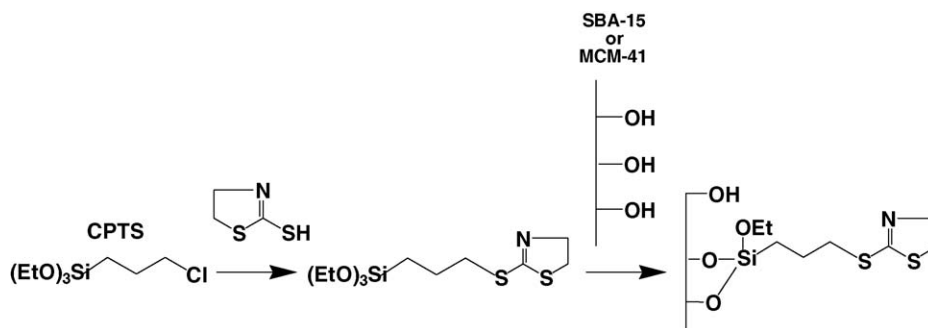
A hexagonal (plane group $p6mm$) material (SBA-15) was prepared by using a poly(alkaline oxide) triblock copolymer surfactant in acidic media according to the method of Zhao et al. [3]. Four grams of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) was dissolved in 30.00 g of water and 80.00 g of 2 M HCl solution with stirring at 35 °C. Then 8.80 g of TEOS was added to that homogeneous solution with stirring at room temperature for 20 h. The solid product was recovered, washed, and air-dried at room temperature. Then it was calcinated in air atmosphere from room temperature to 500 °C in 8 h and heated for 6 h.

2.3. Synthesis of MCM-41 mesoporous silica

A hexagonal (plane group $p6mm$) material (MCM-41) was prepared according to the method of Landau [13] using a hydrothermal crystallization. A sodium silicate solution (65.45 g, 14% NaOH; 27% SiO_2) was mixed with 4.20 g of 98% sulphuric acid and 140 mL of water. The mixture was stirred for 30 min at room temperature. CTAB (58.66 g) dissolved in 176 mL of water was added. The resulting gel was mixed with 70 mL of water (stirred at room temperature for 30 min). The gel was transferred to a Teflon-coated autoclave and heated at 121 °C for 144 h. A solid was produced, separated by suction filtration and dried at 100 °C for 8 h. The surfactant was removed by calcination in air at 530 °C for 6 h.

2.4. Preparation of functionalized mesoporous silicas

MTZ was covalently bonded to SBA-15 or MCM-41 giving mercaptothiazoline modified mesoporous silicas. The immobilization of these molecules on the silica support was carried out by two distinct methods (homogeneous and heterogeneous). The first stage in the preparation of functionalized mesoporous silicas



Scheme 1. Homogeneous route for mesoporous silica functionalization.

by the homogeneous method was the synthesis of the silylating agent, by reaction of CPTS with MTZ. The resulting compound was allowed to react with the silanol groups of activated silica, liberating the corresponding alcohol, to get the final functionalized support (Scheme 1). The second methodology used, the heterogeneous method, involves a two step reaction of the solid support: the reaction of activated mesoporous silica with CPTS to obtain the chlorinated silica followed by a second reaction with the appropriate amount of MTZ to yield the final product (Scheme 2).

2.4.1. Homogeneous method

Five grams (41.10 mmol) of MTZ was immersed in 50 mL of dimethylformamide (DMF). CPTS and triethylamine (TEA) were then added in a 1:2:1 stoichiometry (MTZ:CPTS:TEA). The mixture was heated for 48 h at 110 °C with magnetic stirring under a nitrogen atmosphere by using standard Schlenk-tube techniques. After cooling, the solvent was evaporated and the resulting product was extracted with hexane (2 × 30 mL). After hexane evaporation, the excess of CPTS was distilled under vacuum (150 °C and 0.75 mmHg).

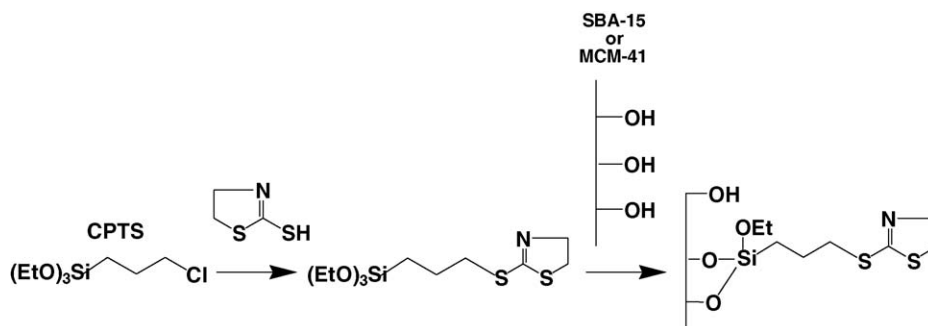
The resulting compound, having the consistency of viscous oil (orange color), was characterized by ¹H NMR, ¹³C NMR, IR and mass spectrometry. The ¹H NMR spectra of the MTZ derivative (see supplementary data) shows signals corresponding to methylene 5 (a triplet centred at 3.09 ppm) and methylenes 3 and 4 (multiplets at 0.73 and 1.80 ppm, respectively). The signals due to the ethoxy groups are located at 1.20 and 3.76 ppm. The sets of peaks found for protons of the MTZ group appear as triplets at 3.33 and 4.16 ppm, which can be attributed to the pendant alkyl chain, the ethoxy groups and the heterocycle. The ¹³C

NMR spectra of the MTZ derivative (see supplementary data) show signals at 10.0, 23.2 and 36.4 ppm assigned to the methylene groups 3, 4 and 5, respectively. The signal due to methylene 2 of the ethoxy group appears at 58.3 ppm and the signal of the methyl group at 20.0 ppm. Carbon atoms of the heterocycle resonate at lower field 58.3, 64.1 and 160.0 ppm. Infrared spectra (see supplementary data) show bands at ca. 2850 cm⁻¹, assigned to ν(C–H) stretching vibrations, and bands at ca. 1475 and 1600 cm⁻¹ which correspond, respectively, to ν(C=C) and ν(C=N) in the heterocycle. Finally, the mass spectrum of this compound displays the molecular peak at *m/z* = 323. The base peak in this compound is due to loss of an ethoxy group bonded to silicon atom. In addition, the spectrum displays an assortment of minor peaks consistent with the successive loss of ethoxy groups and the hydrocarbon chain bonded to the heterocycle.

Five grams of the MTZ derivative was reacted with 5.00 g of activated SBA-15 or MCM-41 (5 h at 160 °C under high vacuum) in 50 mL of dry toluene with mechanical stirring (48 h under reflux conditions under a nitrogen atmosphere). The resulting modified mesoporous silica (L-Sil-Hom: MTZ-SBA-15-Hom or MTZ-MCM-41-Hom) was filtered off and washed with toluene (2 × 30 mL), ethanol (2 × 30 mL) and diethyl ether (2 × 30 mL). Finally, the product was heated for 4 h at 110 °C under vacuum.

2.4.2. Heterogeneous method

Five grams of SBA-15 or MCM-41 were activated at 160 °C under vacuum for 5 h. The activated mesoporous silica was suspended in 50 mL of dry toluene and 5 mL (20.76 mmol) of CPTS were added. The mixture was stirred for 48 h under reflux conditions in a nitrogen atmosphere. The resulting product (Cl-SBA-15 or Cl-MCM-41) was filtered off and washed with toluene



Scheme 2. Heterogeneous route for mesoporous silica functionalization.

(2 × 30 mL), ethanol (2 × 30 mL) and diethyl ether (2 × 30 mL). The product was heated for 4 h at 110 °C under vacuum, and then immersed in 50 mL of toluene and 5.00 g (41.10 mmol) of MTZ was added. The mixture was stirred for 48 h under reflux conditions under a nitrogen atmosphere. The resulting modified silica (L-Sil-Het: MTZ-SBA-15-Het or MTZ-MCM-41-Het) was filtered off and washed with toluene (2 × 30 mL), ethanol (2 × 30 mL) and diethyl ether (2 × 30 mL). Finally, the resulting product was heated for 4 h at 110 °C under vacuum.

2.5. Characterization

¹H NMR and ¹³C NMR spectra were recorded using a Varian-Mercury Plus (400 MHz) spectrometer using CDCl₃ as solvent and reference. Mass spectra were recorded on a VG Autospec Spectrometer in the Aragon Materials Institute (Zaragoza, Spain). X-ray diffraction (XRD) pattern of the silicas were obtained on a Phillips Diffractometer model PW3040/00 X'Pert MPD/MRD at 45 kV and 40 mA, using a wavelength Cu Kα (λ = 1.5418 Å). Nitrogen gas adsorption–desorption isotherms were performed using a Micromeritics TriStar 3000 analyzer. Infrared spectra were recorded on a Nicolet-550 FT-IR spectrophotometer or on a Mattson Infinity FT-IR spectrophotometer in the region 4000–400 cm⁻¹ by using spectra quality KBr powder or CsI plates. Proton-decoupled ²⁹Si MAS-NMR spectra were recorded on a Varian-Infinity Plus Spectrometer at 400 MHz. Elemental analysis (%C and %N) was performed in the Investigation Service of the Universidad Autónoma de Madrid (Spain). The thermal stability of the modified mesoporous silicas was studied by using a Setsys 18 A (Setaram) thermogravimetric analyzer.

2.6. Chemical stability of the functionalized mesoporous silicas

To determine the chemical stability of the materials, acidic and basic solutions were prepared (1, 3 and 6 M HCl or NaOH). The functionalized mesoporous silicas were shaken in these solutions for 24 h, filtered off through Whatman No. 44 filter paper, washed with Milli-Q water and finally dried at 110 °C. After this treatment, the amount of attached molecules on the mesoporous silica surface was determined by elemental analysis.

2.7. Hg (II) adsorption on the functionalized mesoporous silicas

A batchwise process was employed to study the adsorption of Hg (II) from aqueous solutions of pH 6 onto the modified mesoporous silicas at 25 °C. Adsorption experiments were repeated three times.

2.7.1. Effect of the stirring time

The adsorption equilibrium time was investigated by carrying out kinetics experiments. A sample of modified mesoporous silica (0.2 g) was suspended in acetate buffer solution (pH 6) (30 mL). A 0.1 M Hg (II) solution (5 mL) was added and the

mixture was stirred mechanically (300 rpm) for time periods of 2, 4 and 24 h at 25 °C. After this time, the mixture was filtered through Whatman No. 44 filter paper and the solid was washed with Milli-Q water. Finally, the total volume of the filtrate was made up to 100 mL with Milli-Q water. An aliquot of this solution (1 mL) was diluted to a final volume of 50 mL with Milli-Q water and the unbound Hg (II) ions present in this solution were subjected to colorimetric analysis as indicated in Section 2.8.

2.7.2. Effect of the initial metal concentration

A sample of modified mesoporous silica (0.2 g) was suspended in acetate buffer solution (pH 6) (30 mL). Different aliquots of 0.1 M Hg (II) solution were added to give final concentrations in the range 1.7–2870 ppm. The mixture was stirred mechanically (300 rpm) during 4 h at 25 °C to attain equilibrium. After equilibration, the mixture was filtered through Whatman No. 44 filter paper and the solid was washed with Milli-Q water. Finally, the total volume of the filtrate was made up to 100 mL with Milli-Q water using a volumetric flask. Aliquots of different volumes were diluted to a final volume of 50 mL with Milli-Q water and the unbound Hg (II) ions present in these solutions were subjected to colorimetric analysis as indicated in Section 2.8.

2.8. Determination of Hg (II)

Hg (II) was determined by colorimetry by using a Varian Cary 50 UV–vis spectrophotometer [14]. In order to prepare the calibration curves, 5 mL of Hg (II) 0.1 M solution were added to 30 mL of aqueous solution of pH 6. The mixture was maintained under mechanical stirring for 4 h at 25 °C and was then filtered through Whatman No. 44 paper, which was washed with abundant Milli-Q water. Finally, the total volume of the filtrate was completed to 100 mL with Milli-Q water by using a volumetric flask. Different aliquots of this solution were diluted to a final volume of 50 mL with Milli-Q water to achieve standard solutions with an Hg (II) concentration between 0.025 and 0.150 mM.

One millilitre of each standard solution or 1 mL of the sample solution (see Section 2.7) was added to small beakers and their pH was adjusted to an optimum value (pH 2) for the formation of the mercury–dithizone complex by using 5 mL of 1 M HCl. A saturated solution of dithizone in Triton X-100 (7 mL) was then added, and the solutions were allowed to equilibrate for a few min before recording the absorbance at 492 nm. Metal dithizonates formed under these conditions were stable for at least 45 min.

3. Results and discussion

3.1. X-ray diffraction

Figs. 1 and 2 show the XRD pattern for mesoporous silicas. The SBA-15 displayed a well-resolved pattern at low 2θ with a very sharp (1 0 0) diffraction peak at 0.96° and two weak peaks (1 1 0 and 2 0 0) at 1.60° and 1.85°, respectively, that can be indexed as a hexagonal lattice with *d*-spacing values of 92.03,

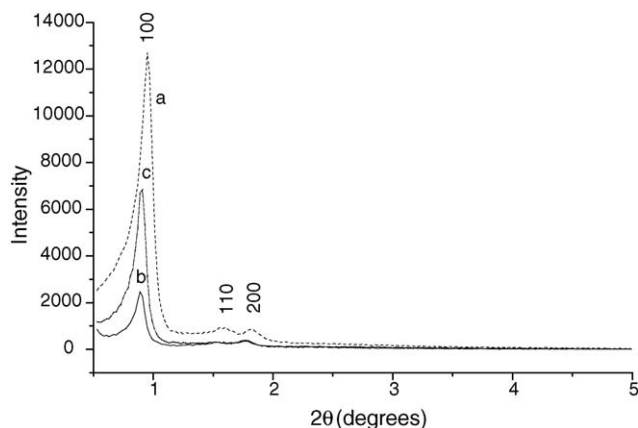


Fig. 1. XRD patterns of (a) SBA-15, (b) MTZ-SBA-15-Het and (c) MTZ-SBA-15-Hom.

55.68 and 48.60 Å, respectively. A unit cell parameter, a_0 , of 106.27 Å was obtained using the following equation [3]:

$$a_0 = \frac{2d_{100}}{\sqrt{3}}$$

In the case of MCM-41, we can also see a very sharp (100) diffraction peak at 2.43° and three additional high order peaks (110, 200 and 210) with lower intensities at 4.17°, 4.75° and 6.28°, respectively. d -Spacing values for these XRD peaks were 36.32, 21.15, 18.60 and 14.07 Å, respectively. a_0 was equal to 41.94 Å.

For functionalized silicas, MTZ-SBA-15-Het, MTZ-SBA-15-Hom, MTZ-MCM-41-Het and MTZ-MCM-41-Hom, a considerable decrease in the XRD peaks intensity was observed. It should be noted that the intensity decrease in the (100) peak for functionalized silicas providing further evidence of functionalization occurring mainly inside the mesopore channels. Collectively, the XRD pattern of the functionalized silicas also suggest not only a significant degree of short range ordering of the structure and well-formed hexagonal pore arrays of the samples, but also the maintenance of the structural order of the synthesized materials after functionalization.

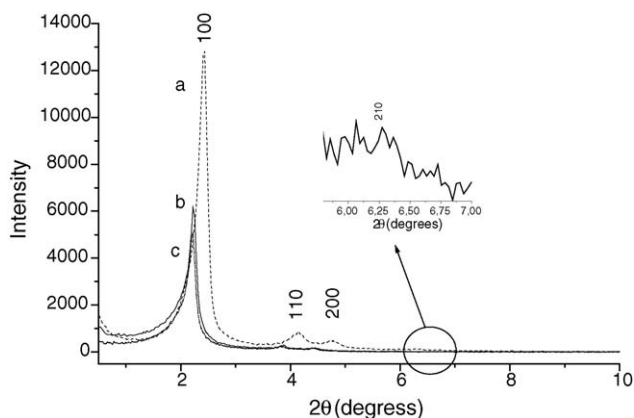


Fig. 2. XRD patterns of (a) MCM-41, (b) MTZ-MCM-41-Het and (c) MTZ-MCM-41-Hom.

3.2. Nitrogen adsorption–desorption isotherms

Figs. 3 and 4 show the nitrogen adsorption–desorption isotherms for mesoporous silicas. For bare SBA-15, MTZ-SBA-15-Hom and MTZ-SBA-15-Het (Fig. 3) isotherms are type IV according to the I.U.P.A.C. classification and have a H1 hysteresis loop that is representative of mesopores. The volume adsorbed for all isotherms sharply increased at a relative pressure (P/P_0) of approximately 0.6, representing capillary condensation of nitrogen within the uniform mesopore structure. The inflection position shifted slightly toward lower relative pressures and the volume of nitrogen adsorbed decrease with functionalization. On the other hand, the hysteresis loop of the isotherm of MCM-41 is smoother than that of SBA-15 and different to that of the functionalized MCM-41, because in the MTZ-MCM-41-Hom and MTZ-MCM-41-Het the hysteresis cycle disappears. These differences can be attributed to a decrease in the pore volume after functionalization. We are also able to observe that the inflection position shifted slightly toward lower relative pressures and the volume of nitrogen adsorbed decreases with functionalization.

Table 1 shows the physical parameters of nitrogen isotherms, such the BET surface area (S_{BET}) and Barret–Joyner–Halenda (BJH) average pore diameter for mesoporous silicas. As expected, the S_{BET} for the SBA-15 is lower (740 m²/g) than for the MCM-41 (1172 m²/g), whereas the BJH average pore diameter is higher (71.9 and 34.0 Å, respectively). The wall thickness

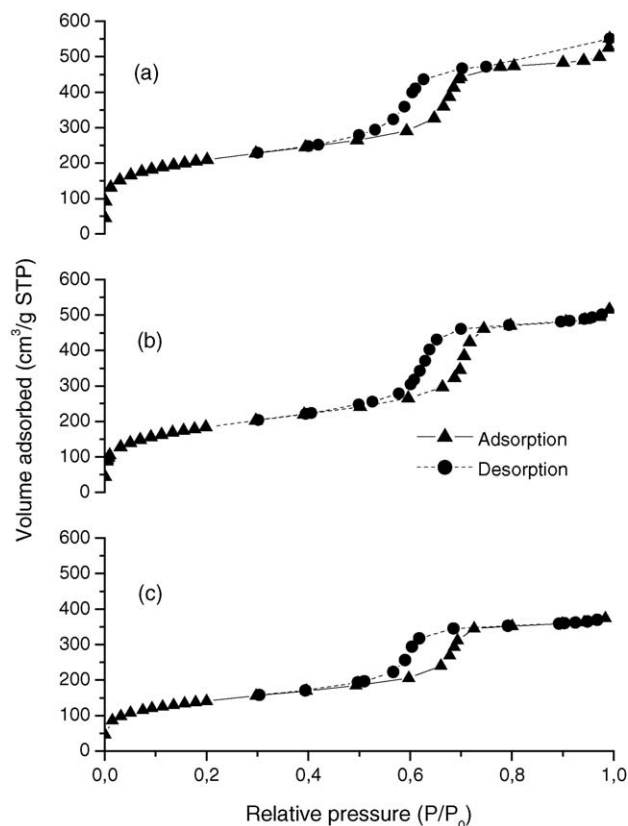


Fig. 3. Nitrogen adsorption–desorption isotherms of (a) SBA-15, (b) MTZ-SBA-15-Het and (c) MTZ-SBA-15-Hom.

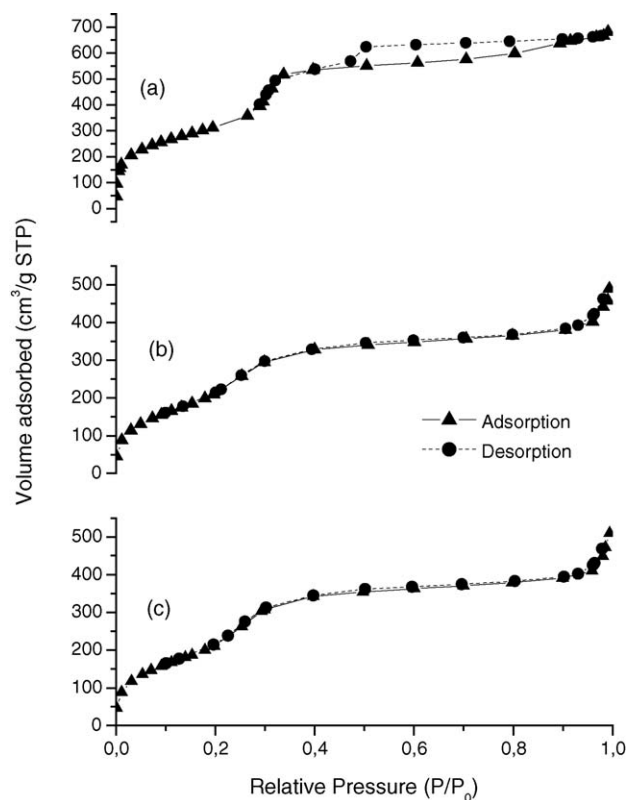


Fig. 4. Nitrogen adsorption–desorption isotherms of (a) MCM-41, (b) MTZ-MCM-41-Het and (c) MTZ-MCM-41-Hom.

for SBA-15 and MCM-41 (34.37 and 7.94 Å, respectively) was calculated using the following equation [3]:

$$\text{wall thickness} = \frac{2d_{100}}{\sqrt{3}} - \text{BJH average pore diameter}$$

After functionalization, a decrease in the S_{BET} and BJH average pore diameter was observed (Table 1) that can be easily interpreted due to the fact that the presence of pendant group on the surface that partially blocks the adsorption of nitrogen molecules.

3.3. FT-IR spectroscopy analysis

Figs. 5 and 6 show the IR patterns of mesoporous silicas between 4000 and 400 cm^{-1} . The main features of the SBA-15 and MCM-41 spectra are a large broad band between 3400 and 3200 cm^{-1} which is attributed to O–H bond stretching of the

Table 1
Physical parameters of mesoporous silicas measured by N_2 adsorption–desorption isotherms

Sample	BET surface area (m^2/g)	Pore diameter (BJH) (Å)
SBA-15	740	71.9
MTZ-SBA-15-Het	662	71.4
MTZ-SBA-15-Hom	507	69.0
MCM-41	1172	34.0
MTZ-MCM-41-Het	805	21.8
MTZ-MCM-41-Hom	804	21.7

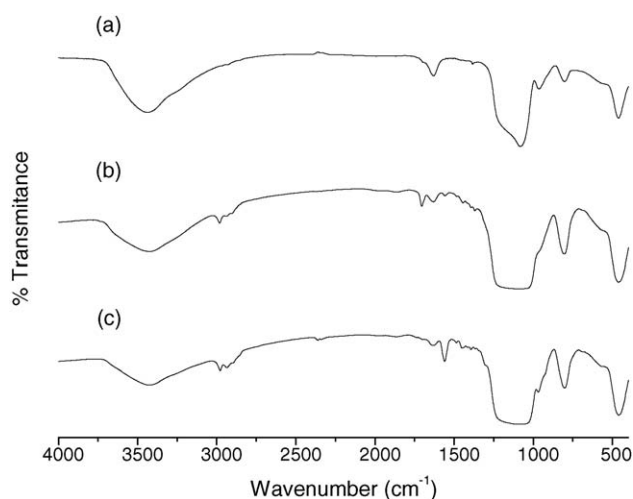


Fig. 5. FT-IR spectra of (a) SBA-15, (b) MTZ-SBA-15-Het and (c) MTZ-SBA-15-Hom.

surface silanols groups, and to the remaining adsorbed water molecules. The siloxane, $-(\text{Si}-\text{O})_n-$, peak appears as a broad and strong peak centred at 1100 cm^{-1} . Si–O bond stretching of silanol groups was detected at 900 cm^{-1} . The adsorption band at 1630 cm^{-1} is caused by deformational vibrations of adsorbed water molecules [15,16]. On the other hand, functionalized mesoporous silicas presented characteristic bands for aliphatic C–H stretching vibrations for pendant alkyl chains around 3000–2800 cm^{-1} and bands at ca. 1600 and 1475 cm^{-1} due to C=N and C=C stretching vibrations of the attached MTZ group.

3.4. ^{29}Si MAS-NMR spectra

Figs. 7 and 8 show the ^{29}Si MAS-NMR spectra of mesoporous silicas. Bare silica (SBA-15 and MCM-41) shows mainly two peaks at -105 and -95 ppm which are assigned to Q^4 framework silica sites ($(\text{SiO})_4\text{Si}$) and Q^3 silanol sites ($(\text{SiO})_3\text{SiOH}$), respectively [3,12]. Clearly, Q^4 is the dominant peak in both

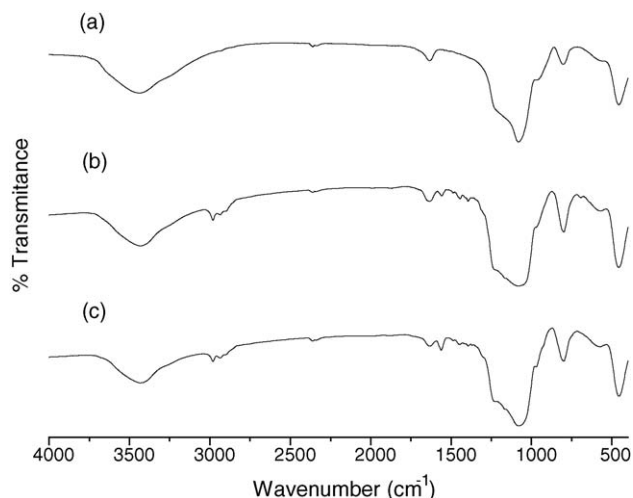


Fig. 6. FT-IR spectra of (a) MCM-41, (b) MTZ-MCM-41-Het and (c) MTZ-MCM-41-Hom.

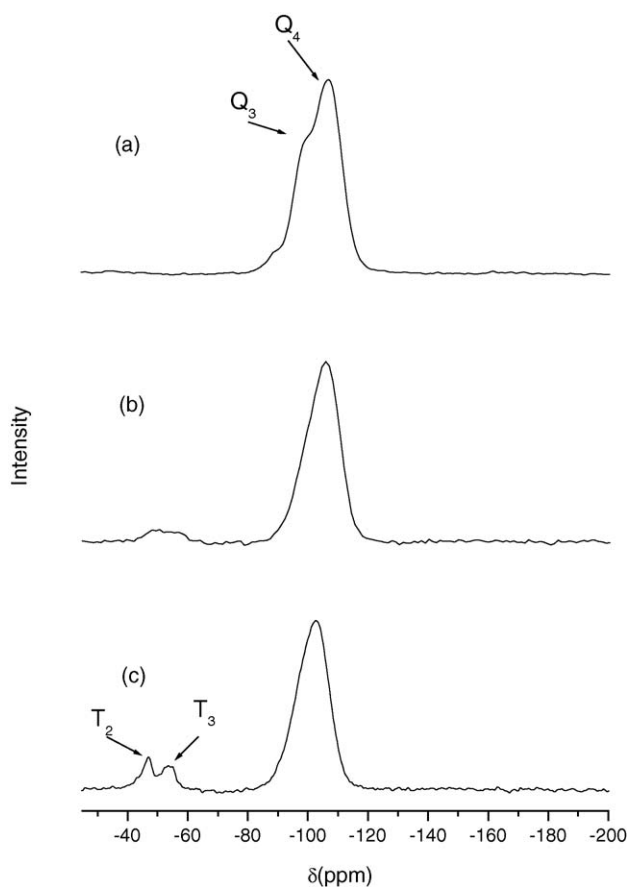


Fig. 7. ^{29}Si NMR spectra of (a) SBA-15, (b) MTZ-SBA-15-Het and (c) MTZ-SBA-15-Hom.

spectra because it is the most abundant site. Functionalized silicas present a large decrease in the intensity of the Q^3 signal, which verified the anchoring of the functional groups to $\text{Si}-\text{OH}$. In addition, two new peaks appeared at -45 and -60 ppm which are assigned to T^2 ($(\text{SiO})_2\text{SiOH-R}$) and T^3 ($(\text{SiO})_3\text{Si-R}$) sites, respectively.

3.5. Elemental analysis

It is possible to calculate the amount of attached molecules onto the mesoporous silica surface (L_0) from the percentage of nitrogen in the functionalized mesoporous silicas, calculated by elemental analysis, using the following expression:

$$L_0 = \frac{\%N}{\text{nitrogen atomic weight}} \times 10$$

Comparing the amount of attached molecules on the silica surface (Table 2), it can be concluded that the degree of functionalization obtained with SBA-15 and MCM-41 was similar. However, as it can be observed, the quantity of anchored molecules is always superior via the homogeneous functionalization method.

The presence of three alkoxy groups in the CPTS and silylating agent means that they can react with the silica surface via one, two or all alkoxy groups. The C/N molar ratio obtained in homogeneous route indicates a 1:2 stoichiometry, between the silanol

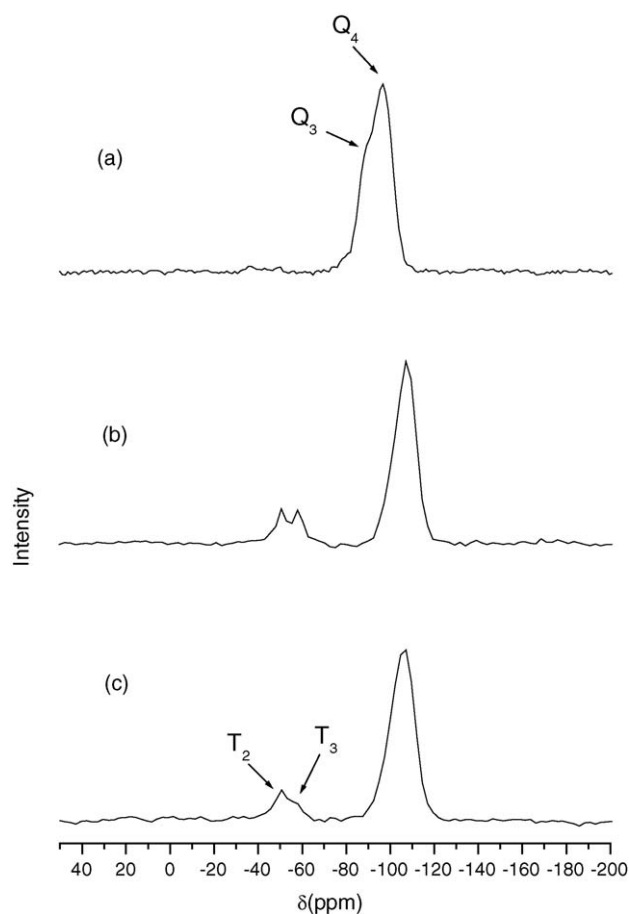


Fig. 8. ^{29}Si NMR spectra of (a) MCM-41 (b) MTZ-MCM-41-Het and (c) MTZ-MCM-41-Hom.

groups on the silica surface and the silylating agent. However, via heterogeneous route, the C/N ratio is higher than expected, due to the presence of remaining unreacted chloropropyl groups on the silica surface. In this case, the reaction of the chlorinated silica with MTZ is not completed, even when working in excess of chelating ligand. The steric hindrance imposed by pendant chloropropyl chains covalently bond to the mesoporous silica surface may explain the lower degree of functionalization observed in silicas prepared by the heterogeneous method (MTZ-SBA-15-Het and MTZ-MCM-41-Het).

Taking into account L_0 and S_{BET} of the mesoporous silicas, the average surface density, d , of the attached molecules and the average intermolecular distance, l , can be calculated by applying the following equations [17]:

$$d = N \frac{L_0}{S_{\text{BET}}}$$

$$l = \left(\frac{1}{d}\right)^{1/2}$$

where N is Avogadro's number. As expected (Table 3) in mesoporous silicas functionalized by the homogeneous method d is higher and l is lower than in mesoporous silicas functionalized by the heterogeneous method, due to the better degree of functionalization obtained with the homogeneous method. Also we

Table 2
Functionalization degree of mesoporous silicas prepared by heterogeneous and homogenous methods

	Nitrogen (wt.%) ^a	Nitrogen (mmol/g)	Carbon (wt.%) ^a	Carbon (mmol/g)	L _o (mmol/g) ^b	C/N ^c
MTZ-SBA-15-Het	0.53 ± 0.07	0.38	5.73 ± 0.01	4.78	0.38	12.6
MTZ-SBA-15-Hom	1.47 ± 0.09	1.22	11.38 ± 0.03	9.48	1.22	7.8
MTZ-MCM-41-Het	0.55 ± 0.04	0.39	12.01 ± 0.04	10.01	0.39	25.5
MTZ-MCM-41-Hom	1.54 ± 0.01	1.28	12.40 ± 0.07	10.33	1.28	8.1

^a Average of two determinations ± S.D.

^b L_o = millimoles of ligand per gram of functionalized silica = (% nitrogen × 10)/N atomic weight.

^c C/N = mmol g⁻¹ C/mmol g⁻¹ N.

observed that values of *d* and *l* for the functionalized SBA-15 are higher and lower, respectively, than values observed for the functionalized MCM-41. These results confirm a higher efficiency in the functionalization of the SBA-15, probably due to its higher pore diameter.

3.6. Thermal stability

Thermal stability of the modified mesoporous silicas has been established by thermogravimetric analysis. The TGA profiles indicate a comparable stability of the new materials, independently of the synthetic method employed. As can be seen in Figs. 9 and 10, bare silica presents a small loss of mass (7 and 3% for SBA-15 and MCM-41, respectively) between room temperature and 120 °C due to physically adsorbed water (endothermic process). A second loss of mass of 0.5% (between 600 and 800 °C) is attributed to the increase of siloxane bridges (Si–O–Si) because of isolated silanol condensation (exothermic process). The TGA curves of the different modified materials prepared (MTZ-SBA-15-Het, MTZ-MCM-41-Het, MTZ-SBA-15-Hom and MTZ-SBA-15-Hom) are essentially identical. They show that degradation process occurs between 275 and 600 °C and the weight loss is about 16–20%, due to the breakage of pendant groups anchored on the silica surface (exothermic process). The mass loss observed for modified silicas via the homogeneous method (MTZ-SBA-15-Hom and MTZ-MCM-41-Hom) is in agreement with the amount of ligand covalently bound to the support (Table 2), calculated by elemental analysis. However, for samples prepared by the heterogeneous route (MTZ-SBA-15-Het and MTZ-MCM-41-Het), a higher weight loss than the expected value is observed. An explanation for this is the presence on the silica surface of unreacted chloropropyl pendant chains. The thermal stability of these samples is in agreement

Table 3
Surface molecular density and intermolecular distance for mesoporous silicas functionalized by heterogeneous and homogenous methods

	<i>d</i> ^a	<i>l</i> ^b
MTZ-SBA-15-Het	0.3	1.8
MTZ-SBA-15-Hom	0.8	1.1
MTZ-MCM-41-Het	0.2	2.2
MTZ-MCM-41-Hom	0.7	1.2

^a Molecular density (molecules/nm²).

^b Intermolecular distance (nm).

with previous results given in the literature for other functionalized mesoporous silicas [1,18,19].

3.7. Chemical stability

The chemical stability of the functionalized mesoporous silicas was examined in acid and basic solutions. Each sample was mixed with 1, 3 and 6 M HCl or NaOH solutions and stirred at room temperature during 24 h. The change in the degree of functionalization was calculated by elemental analysis of the samples before and after the chemical treatment. As is shown in Table 4, after acid treatment (6 M HCl) the percentage of nitrogen in the functionalized mesoporous silicas was not modified, except in the MTZ-SBA-15-Het where an important decrease was observed. The high stability exhibited by the attached organofunctional group presumably is due to the –(CH₂)₃– group which binds the MTZ to the mesoporous silica

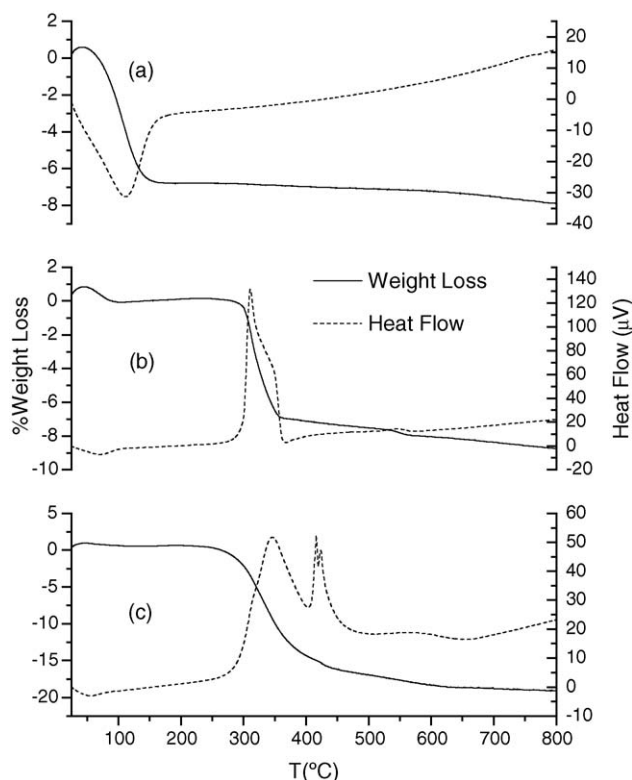


Fig. 9. Thermogravimetric curves and heat flow of (a) SBA-15, (b) MTZ-SBA-15-Het and (c) MTZ-SBA-15-Hom.

Table 4

Functionalization degree of mesoporous silicas prepared by heterogeneous and homogenous methods after its treatment with acid (6 M HCl)

	Nitrogen (% weight) ^a	Nitrogen (mmol/g)	Carbon (% weight) ^a	Carbon (mmol/g)	L _o (mmol/g) ^b	C/N ^c
MTZ-SBA-15-Het	0.19 ± 0.02	0.13	4.46 ± 0.06	3.71	0.13	28.1
MTZ-SBA-15-Hom	1.48 ± 0.01	1.23	10.86 ± 0.05	9.05	1.23	7.3
MTZ-MCM-41-Het	0.47 ± 0.01	0.34	7.89 ± 0.01	6.57	0.34	19.5
MTZ-MCM-41-Hom	1.52 ± 0.01	1.08	8.64 ± 0.01	7.20	1.08	6.6

^a Average of two determinations ± S.D.^b L_o = millimoles of ligand per gram of functionalized mesoporous silica = (% nitrogen × 10)/M atomic nitrogen.^c C/N = mmol g⁻¹ C/mmol g⁻¹ N.

surface. It has been shown that when the length of the hydrocarbon bridge was more than two methylene groups, the rupture of Si–C bond did not occur in mineral acid medium [20,21]. On the other hand, functionalized mesoporous silicas were not stable in alkali solutions due to the breaking of the Si–O–Si bonds by hydroxide ions attack [13].

3.8. Adsorption of Hg (II) from aqueous solution

Adsorption studies of Hg (II) were carried out in buffer a pH 6 because preliminary studies carried out in our group with amorphous silica functionalized with the same ligand demonstrated that at this pH the adsorption is maximum (unpublished data). At pH greater than 6, metal hydrolysis and breakage of the covalent bond between surface hydroxyls groups and the silylating agent may occur, also free silanol groups become active at higher pH and can contribute also in the metal adsorption process.

The amount of mercury taken up by the previously synthesized materials from aqueous solution was determined using the equation:

$$N_f = \frac{n_i - n_e}{m}$$

where n_i is the initial number of moles of mercury added to the system, n_e the amount remaining after the equilibrium and m is the mass in grams of the adsorbent.

One important characteristic of the prepared material is the velocity with which the solid phase adsorbs Hg (II) from the aqueous solution and attains the equilibrium conditions. Plots of N_f versus stirring time indicate that the time required to establish sorption equilibrium was no greater than 4 h. The reasonably fast kinetics of the matrix–metal ion interaction reflect the good accessibility of the chelating sites of the modified matrix.

Other important characteristic of a heavy metal adsorbent is its capacity with respect to the particular ion under investigation. In order to determine this capacity, the amount of mercury loaded by the synthesized material (N_f) was calculated as a function of the initial concentration of the metal in the solution (1.7, 6.5, 33, 286, 647 and 2870 ppm). The resulting isotherms provided the maximum adsorption value with an initial Hg (II) concentration of 647 ppm, and this value was between 0.12 ± 0.01 and 1.10 ± 0.02 mmol Hg (II)/g (Table 5). On the other hand, the maximum adsorption capacity of the unmodified mesoporous silica was found to be only 0.005 ± 0.002 mmol Hg (II)/g of SBA-15 and 0.06 ± 0.02 mmol Hg (II)/g of MCM-41, which is much lower than values given for modified silicas. As can be seen in Table 5, in both cases, mercury adsorption was higher in the mesoporous silicas prepared by the homogeneous method (MTZ-SBA-15-Hom and MTZ-MCM-41-Hom). The higher amount of molecules with basic properties anchored by the homogenous route justified the better values obtained

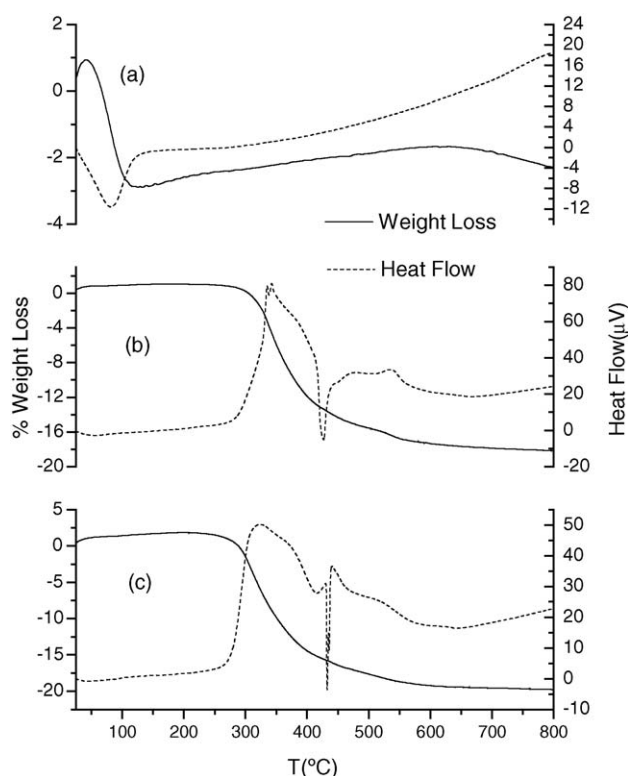


Fig. 10. Thermogravimetric curves and heat flow of (a) MCM-41, (b) MTZ-MCM-41-Het and (c) MTZ-SBA-15-Hom.

Table 5

Adsorption capacity of Hg (II) in aqueous media (pH 6) by mesoporous silicas prepared by heterogeneous and homogeneous methods

Silica preparation	N_f^a
MTZ-SBA-15-Het	0.12 ± 0.01
MTZ-SBA-15-Hom	1.10 ± 0.02
MTZ-MCM-41-Het	0.25 ± 0.01
MTZ-MCM-41-Hom	0.70 ± 0.01

^a Adsorption capacity (mmol of Hg (II) adsorbed per gram of functionalized silica). Average of three determination ± S.D.

Table 6
Fraction of surface-attached ligand bonded to the Hg (II) for mesoporous silicas prepared by heterogeneous and homogenous methods in water solution

Silica preparation	φ^a
MTZ-SBA-15-Het	0.24
MTZ-SBA-15-Hom	0.90
MTZ-MCM-41-Het	0.64
MTZ-MCM-41-Hom	0.55

^a Fraction of surface attached ligand bonded to the Hg (II).

versus the heterogeneous route (Table 2). Assuming, that only the organofunctional groups are responsible for metal adsorption, the maximum value of N_f is determined by the number of molecules attached to the surface, the nature of the surface complexes and the stability of the complexes. Comparing results shown in Table 2 with the adsorption capacity observed for bare silica (0.005 ± 0.002 mmol Hg (II)/g of SBA-15 and 0.06 ± 0.02 mmol Hg (II)/g of MCM-41), it is clear that functionalization of mesoporous materials improves its heavy metal adsorption capacity.

As an indicator of mercury adsorption efficiency, the fraction of surface attached ligand bonded to metal ion (φ) is calculated by the equation [22,23]:

$$\varphi = \frac{N_f}{L_o}$$

The values of φ for each preparation in aqueous solutions at pH 6 are shown in Table 6. As can be observed, the modified mesoporous silica (MTZ-SBA-15-Hom) displays the best mer-

cury adsorption efficiency ($\varphi = 0.9$) that indicates a high access of mercury ions to every complexing sites in the uniform mesopore channels.

Reported Hg (II) adsorption data in aqueous media using functionalized mesoporous silica with several ligands are collected in Table 7. The names of the mesoporous silica materials contribute a problem because they cannot easily be used as a description of the structure. They were chosen by the institution which discovered the respective material. Thus codes MCM-41, MCM-48 and MCM-50, mentioned before, stand for Mobil Composition of Matter 41, 48 and 50. The numbers are just consecutive identifiers that were given to these materials. A problem is that, even though these three materials are structurally related (as their codes imply), the material MCM-22 for example has nothing in common with the other three materials. Even worse is that there are materials which are almost identical to MCM-41 but have completely different codes as HMS included in this comparative study. Therefore, the literature of the field is difficult to understand or even confusing if the reader is not up to date. BET surface area for mesoporous materials included in Table 7 ranges from 812 for the HMS-T00b with lower surface area to 1264 m²/g for the MCM-41. The porous diameter varied from 19 Å, within the lower limit defined for the IUPAC for mesoporous materials, to 200 Å. Focusing on the type of ligand, the most common ligands anchored onto mesoporous supports involve alkylthiols and alkylamines as functional groups. The functionalization of the supports is achieved by one step reaction of silanol groups with 3-mercaptopropyltrialkoxysilane and 3-aminopropyltrialkoxysilane, the so-called homogeneous method (entries 1–15). Alkoxysilanes are much less reactive than other chlorosilane and disilazane compounds used

Table 7
Bibliographic dates about functionalized mesoporous silica for the mercury adsorption in aqueous media

Entry	Silica	S_{BET} (m ² /g) ^a	Porous diameter (Å) ^b	Anchored ligand	Synthetic method	L_o ^c	N_f ^d	Ref.
1	HMS	854	–	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	1.5	1.5	Mercier et al. [24]
2	HMS-C12	854	36	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	1.5	1.5	Mercier et al. [25]
3	HMS-C18	1200	19	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	0.90	0.55	Mercier et al. [25]
4	HMS-T00a	825	20	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	1.30	0.66	Kim et al. [26]
5	HMS-T00b	812	28	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	1.77	0.87	Kim et al. [26]
6	HMS-T05	825	30	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	0.99	0.71	Kim et al. [26]
7	HMS-T10	839	31	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	1.55	0.64	Kim et al. [26]
8	HMS-T15	939	31	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	0.49	0.50	Kim et al. [26]
9	MCM-41	–	–	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	–	2.28	Liu et al. [27]
10	MCM-41	–	–	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	–	2.99	Liu et al. [28]
11	MCM-41	–	–	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	–	0.40	Liu et al. [27]
12	MCM-41	1000	200	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	–	3.06	Chen et al. [29]
13	MCM-41	900	50	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	1.95	–	Antochshuk et al. [11]
14	MCM-41	900	55	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	5.2	1.05	Feng et al. [30]
15	MCM-41	1264	25	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	0.57	0.59	Mercier et al. [25]
16	MCM-41	900	50	≡Si-(CH ₂) ₃ -NH-CS- NH-CH ₂ -CH=CH ₂	Heterogeneous	1.70	1.5	Antochshuk et al. [11]
17	SBA-15	814	76	≡Si-(CH ₂) ₃ SH ^e	Homogeneous	–	2.43	Liu et al. [27]
18	SBA-15	814	76	≡Si-(CH ₂) ₃ NH ₂ ^e	Homogeneous	–	0.38	Liu et al. [27]

(–) Date not calculated.

^a BET area of the functionalized mesoporous silica.

^b Porous diameter of functionalized mesoporous silica.

^c mmol of ligand per gram of functionalized silica.

^d mmol of Hg (II) adsorbed per gram of functionalized silica.

^e Available commercially ligand.

for this purpose, therefore small amounts of water improve the surface functionalization reaction obtaining higher loading of functional groups on the silica surfaces. On the other hand, when mesoporous silica has been modified using a new ligand, commercially unavailable, the heterogeneous method has been preferably used. The alkylamine, alkylchlorine or alkylthiol monolayer covalently bound to the support reacts with a chelating ligand in a two steps procedure (entry 16). As can be seen in Table 7, the range of data reported for L_0 and N_f is very wide. The surface coverage oscillates between the 0.49 mmol/g for HMS-T15 modified with 3-aminopropyltrimethoxysilane (entry 8) and 5.2 mmol/g for MCM-41 modified with 3-mercaptopropyltrimethoxysilane (entry 14). The loading capacity data published are again quite varied, with a maximum N_f reported of 3.06 mmol Hg/g of mesoporous silica obtained by Chen (entry 12) for MCM-41 coated with $\equiv\text{Si}-(\text{CH}_2)_3\text{SH}$ and a minimum of 0.38 mmol Hg/g of mesoporous silica obtained by Liu (entry 18) for SBA-15 coated with $\equiv\text{Si}-(\text{CH}_2)_3\text{NH}_2$. It is interesting to note no close correlation among published data, for example MCM-41 material (entries 9–16) based on mercaptopropylsilyl or aminopropylsilyl functionalization of a calcined form of MCM-41, with comparable surface area and pore size, presents different ligand concentration and mercury retention. Nevertheless, it is clear the influence of the ligand nature grafted onto the silica on metal uptake capacity (entries 9 and 12). Comparing the values shown in Table 7 with the values reported in the present work, we can observe that the functionalization degree of the mesoporous silicas obtained by the heterogeneous method is lower than the reported values. This result can be attributed to the major size of the employed ligand. Regarding the N_f values, it can be observed that SBA-15 and MCM-41 functionalized with MTZ by the homogeneous method present good N_f values (1.10 and 0.7 mmol Hg (II)/g of silica, respectively) comparable to those previously published. It can be concluded the existence of a correlation between mercury adsorption with pore size and framework pore volume, since SBA-15 with lower areas and higher pore sizes functionalized with sterically demanding ligands show better adsorption capacities than functionalized MCM-41.

4. Conclusions

- (1) The mercaptothiazoline ligand, with sulphur and nitrogen donor atoms, is a suitable reagent for the preparation of surface monolayers by functionalization of well ordered mesoporous materials (SBA-15 and MCM-41).
- (2) The synthetic methods used, homogeneous and heterogeneous methods, yield different types of materials with different Hg (II) adsorption capacity.
- (3) The surface coverage of covalently bonded donor ligands and the Hg (II) adsorption capacity show by the materials prepared via the homogeneous method is higher than those prepared via the heterogeneous one. This fact suggests a better applicability of such mesoporous silica supports to extract Hg (II) from aqueous solutions.
- (4) A correlation between mercury adsorption, pore size and framework pore volume is found since functionalized SBA-

15 show better adsorption capacity than functionalized MCM-41.

Acknowledgements

The authors acknowledge the Projects GCO-2003-20 and PPR-2004-48 from the Universidad Rey Juan Carlos and the CAM Projects 07N/011/2002 and GR/MAT/0929/2004 for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2005.11.004.

References

- [1] B. Lee, Y. Kim, H. Lee, J. Yi, Synthesis of functionalized porous 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.
- [2] J.S. Beck, J.C. Vartulli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, T.-W.C. Ch, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, A new family of mesoporous molecular sieves prepared with liquid crystal templates, *J. Am. Chem. Soc.* 114 (1992) 10834–10843.
- [3] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures, *J. Am. Chem. Soc.* 120 (24) (1998) 6024–6037.
- [4] B.J. Liu, X. Feng, G.E. Fryxell, L.-Q. Wang, A.Y. Kim, M. Gong, Hybrid mesoporous materials with functionalized monolayers, *Chem. Eng. Technol.* 21 (1) (1998) 97–100.
- [5] J. Brown, L. Mercier, T.J. Pinnavaia, Selective adsorption of Hg^{2+} by thiol-functionalized nanoporous silica, *Chem. Commun.* (1999) 69–70.
- [6] J. Brown, R. Richer, L. Mercier, One-step synthesis of high capacity mesoporous Hg^{2+} adsorbents by non-ionic surfactant assembly, *Micropor. Mesopor. Mater.* 37 (2000) 41–48.
- [7] P. Price, J. Clark, D. Macquarrie, Modified silicas for clean technology, *J. Chem. Soc., Dalton Trans.* (1999) 101–110.
- [8] R.I. Nooney, M. Kayanaraman, G. Kennedy, E.J. Maginn, Heavy metal remediation using functionalized mesoporous silicas with controlled macrostructure, *Langmuir* 17 (2001) 528–533.
- [9] A. Bibby, L. Mercier, Mercury(II) ion adsorption behavior in thiol-functionalized mesoporous silica microspheres, *Chem. Mater.* 14 (2002) 1591–1597.
- [10] H.-J. Im, C.E. Barnes, S. Dai, Z. Xue, Functionalized sol-gels for mercury(II) separation: a comparison of mesoporous materials prepared with and without surfactant templates, *Micropor. Mesopor. Mater.* 70 (2004) 57–62.
- [11] V. Antochshuk, M. Jaroniec, 1-Allyl-3-proylthiourea modified mesoporous silica for mercury removal, *Chem. Commun.* (2002) 258–259.
- [12] D.D. Perrin, W.L. Armaredo, D.R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, Oxford, 1980.
- [13] M.V. Landau, S.P. Varkey, M. Herskowitz, O. Regev, S. Pevzner, T. Sen, Z. Luz, Wetting stability of Si-MCM-41 mesoporous material in neutral, acidic and basic aqueous solutions, *Micropor. Mesopor. Mater.* 33 (1999) 149–163.
- [14] R.P. Paradkar, R.R. Williams, Micellar colorimetric determination of dithizone metal chelates, *Anal. Chem.* 66 (1994) 2752–2756.
- [15] E. Pretsch, T. Clero, J. Seibl, W. Simon, *Tablas para la Elucidación Estructural de Compuestos Orgánicos por métodos Espectroscópicos*, Alhambra, Madrid, 1991.
- [16] D. Pavia, G. Lampman, G. Kriz, *Introduction to Spectroscopy*, Harcourt College Publishers, USA, 2001.

- [17] N.L. Dias Filho, Adsorption of copper(II) and cobalt(II) complexes on a silica gel surface chemically modified with 3-amino-1,2,4-triazole, *Colloid. Surf. A: Physicochem. Eng. Asp.* 144 (1998) 219–227.
- [18] D.J. Macquarrie, D.B. Jackson, J.E.G. Mdoe, H.J. Clark, Organomodified hexagonal mesoporous silicates, *New J. Chem.* 23 (1999) 539–544.
- [19] L. Bois, A. Bonhommé, A. Ribes, B. Pais, G. Raffin, F. Tessier, Functionalized silica for heavy metal ions adsorption, *Colloid. Surf. A: Physicochem. Eng. Asp.* 221 (2003) 221–230.
- [20] P. Roumeliotis, A.A. Kurganov, V.A. Davankov, Effect of the hydrophobic spacer in bonded [Cu(L-hydroxypropyl)alkyl]⁺ silicas on retention and enantioselectivity of α -amino acid in high-performance liquid chromatography, *J. Chromatogr.* 266 (1983) 439–450.
- [21] G.V. Kudryavtsev, D.V. Milchenko, S.Z. Bernadyuk, T.E. Vertinskaya, G.V. Lisichkin, Synthesis and properties of phosphoric acid cation exchangers based on silica, *Theor. Exp. Chem. USSR* 23 (6) (1987) 711–716.
- [22] N.L. Dias Filho, Y. Gushikem, 2-Mercaptoimidazole covalently bonded to a silica gel surface for the selective separation of mercury(II) from non aqueous solution, *Sep. Sci. Technol.* 32 (15) (1997) 2535–2545.
- [23] P. Lessi, N.L. Filho, J.C. Moreira, J.T.S. Campos, Sorption and preconcentration of metal ions on silica gel modified with 2,5-dimercapto-1,3,4-thiadiazole, *Anal. Chim. Acta* 327 (1996) 183–190.
- [24] L. Mercier, T.J. Pinnavaia, Access in mesoporous materials: advantages of a uniform pore structure in the design of a heavy metal ion adsorbent for environmental remediation, *Adv. Mater.* 9 (1997) 500–503.
- [25] L. Mercier, T.J. Pinnavaia, Heavy metal ion adsorbents formed by the grafting of a thiol functionality to mesoporous silica molecular sieves: factors affecting Hg(II) uptake, *Environ. Sci. Technol.* 32 (1998) 2749–2754.
- [26] Y. Kim, B. Lee, J. Yi, Effect of framework and textural porosities of functionalized mesoporous silica on metal ion adsorption capacities, *Sep. Sci. Technol.* 39 (6) (2004) 1427–1442.
- [27] A.M. Liu, K. Hidajat, S. Kaki, D.Y. Zhao, A new class of hybrid mesoporous materials with functionalized organic monolayers for selective adsorption of heavy metal ions, *Chem. Commun.* (2000) 1145–1146.
- [28] B.J. Liu, X. Feng, G.E. Fryxell, G.L.-Q. Wan, A.Y. Kim, M. Gong, Hybrid mesoporous materials with functionalized monolayers, *Adv. Mater.* 10 (2) (1998) 161–164.
- [29] X. Chen, X. Feng, J. Liu, G.E. Fryxell, M. Gong, Mercury separation and immobilization using self-assembled monolayers on mesoporous supports (SAMMS), *Sep. Sci. Technol.* 34 (6&7) (1999) 1121–1132.
- [30] X. Feng, G.E. Fryxell, L.-Q. Wang, A.Y. Kim, J. Liu, K.M. Kemner, Functionalized monolayers on ordered mesoporous supports, *Science* 276 (1997) 923–926.