Mesoporous silica functionalized with 1-furoyl thiourea urea for Hg(II) adsorption from aqueous media

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ABSTRACT

New organic–inorganic hybrid materials were prepared by covalently anchoring 1-furoyl thiourea on mesoporous silica (SBA-15). By means of various characterization techniques (X-ray diffraction, nitrogen adsorption–desorption, thermogravimetric analysis, and FTIR spectroscopy) it has been established that the organic groups were successfully anchored on the SBA-15 surfaces and the ordering of the inorganic support was preserved during the chemical modifications. The hybrid sorbents exhibited good ability to remove Hg(II) from aqueous solution. Thus, at pH 6, the adsorption capacity of mercury ions reached 0.61 mmol g^{-1}.

1. Introduction

Hybrid materials obtained by anchoring organic moieties to the porous inorganic surfaces have recently revealed noticeable applications in fields such as catalysis, adsorption and sensing [1,2]. They were commonly prepared by covalent immobilization of the organic chains on the support, by using the surface hydroxyl groups of the support as anchor points [3,4]. Due to their tunable pore size and narrow pore size distribution, the ordered mesoporous silica likes MCM-41 [5] and SBA-15 [6] were widely used as supports. SBA-15 is a promising candidate because, in comparison with other mesostructured materials, it posses larger pores (5–30 nm) and thicker pore walls (between 3.1 and 6.4 nm) which provide high hydrothermal stability [7,8].

SBA-15 surface modifications with chelating agents for adsorption/removal of metal ions have been reported in recent years. Thus, functional groups, such as imidazole [9], amino [10–13], iminodiacetic [14], EDTA [15] and N-propylsalicylaldimino [16] were successfully incorporated into the inorganic SBA-15 matrix. These materials have demonstrated ability to remove various heavy metal ions such as Pt^{2+}, Pd^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+} [11,12,14,16–18].

Mercury and its derivatives are among the most harmful contaminants of the industrial wastewaters because they greatly threaten the health of humans and the environment. One of the effective methods to remove inorganic Hg(II) from wastewater is the use of adsorbents modified by incorporating sulphur-containing organic groups. Among them, functionalized MCM-41 [19–24], HMS [25] and SBA-15 [26–31] mesoporous silica showed remarkable selectivity for Hg(II) adsorption. Anchoring the Hg chelating agents to the mesostructure can be accomplished either by grafting a thiol-functionalized silane reagent to the silica surface (via covalent bonds) [32,33] or by direct incorporation of the organosilyl group in the mixture during the mesoporous material synthesis (co-condensation) [34,35].

Keeping in view the interesting properties of the SBA-15 mesoporous materials modified with sulphur-containing chelating agents, the present study had two aims. First, we have synthesized, by grafting and co-condensation approaches, new hybrid materials, i.e., SBA-15 mesoporous silica modified with 1-furoyl thiourea (FTU). Secondly, we have studied the applicability of these hybrid materials for removal of Hg(II) from aqueous solutions. As already reported, due to the presence of three heteroatoms (S, O, N) and accordingly several functional groups, thiourea derivatives (unsupported or grafted on silica) are able to complex Hg(II) or other metallic ions [24,36–40], as well as to catalyse organic reactions [41,42].

2. Experimental

2.1. Reagents and materials

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, $M_{av} = 5800$) and

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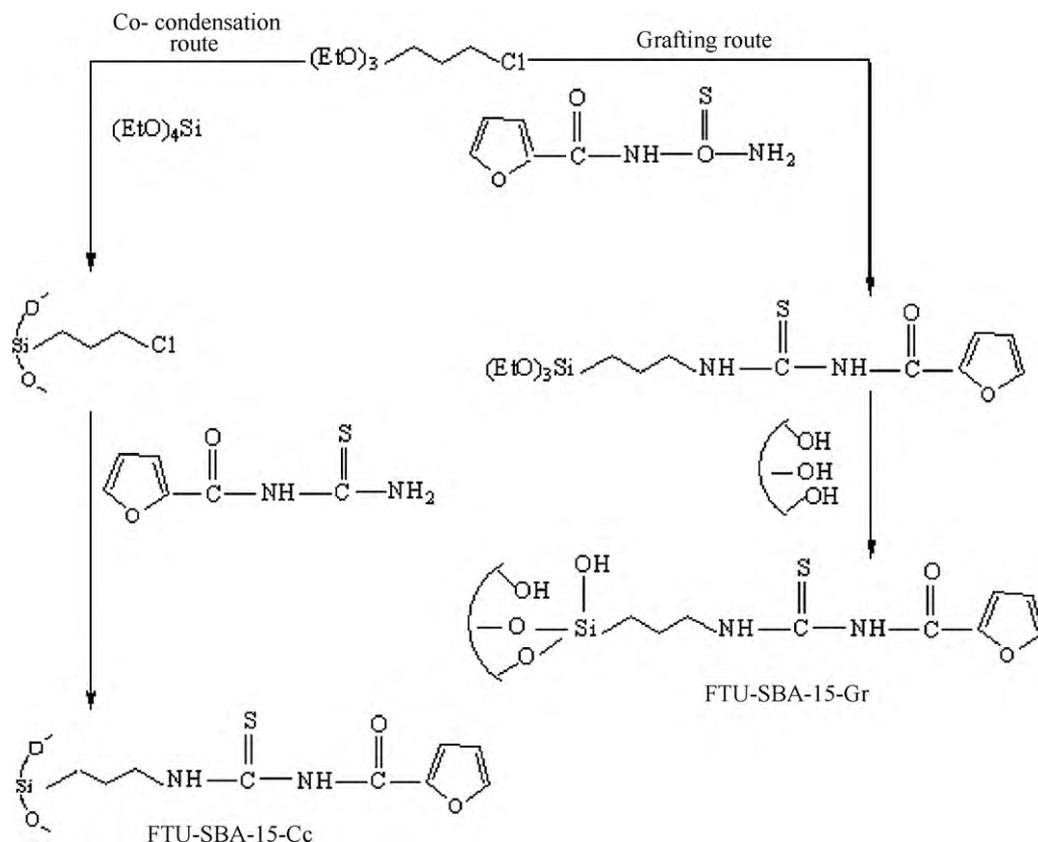
Scheme 1. Co-condensation and grafting routes for mesoporous silica functionalization.

tetraethylorthosilicate (TEOS) 99% were purchased from BASF and Aldrich, respectively. 3-Chloropropyltriethoxysilane 95% (CPTS) and triethylamine were from Aldrich. Organic solvents (toluene, dimethylformamide, diethyl ether, ethanol and hexane) were purchased from Fluka and Aldrich. These solvents were distilled and dried before use according to conventional literature methods [43]. Buffer solution of pH 6 was prepared by using sodium acetate and acetic acid (Fluka). Standard stock solution of Hg(II) was prepared by dissolving $Hg(NO_3)_2·H_2O$, 98% (Sigma–Aldrich) in dilute HNO_3. Water used in the preparation of standard solutions was obtained from Millipore Milli-Q System (Waters, USA). Triton X-100 and 1,5-diphenylthiocarbazone (dithizone) were from Aldrich.

2.2. Synthesis of 1-furoyl thiourea

1-Furoyl thiourea was prepared according to the procedure described in literature [44]. 6.5 g (0.05 mol) of furoyl chloride were added to a solution formed by 3.9 g (0.051 mol) of ammonium thiocyanate and 400 mL of dry acetone. The resulting slurry was heated at reflux for 30 min and then 15 mL of concentrated ammonium hydroxide were added, at a rate that allow to maintain the reflux. The mixture was heated at reflux for 30 min and then cooled to room temperature. It was added to 200 mL water and the resulting precipitate was collected by filtration, washed with water, and dried for 24 h at room temperature. 3.86 g (η = 78%) of FTU were obtained. After recrystallization from ethanol a white solid with melting point 179–180 °C was obtained.

^{1}H NMR (400.13 MHz, methanol-d_4) δ (ppm): 6.69 (dd, J_{H2-H3} = 3.6, J_{H2-H1} = 1.7, H_2); 7.44 (dd, J_{H3-H2} = 3.6, J_{H3-H1} = 0.5, H_3); 7.82 (dd, J_{H1-H2} = 1.7, J_{H1-H3} = 0.5, H_1).

MS: (ESI$^+$/MeOH) m/z: 171 [M + H]$^+$; (ESI$^-$/MeOH) m/z: 169 [M + Cl]$^-$, 205 [M + Cl]$^-$.

2.3. Synthesis of SBA-15 mesoporous silica

SBA-15 material was synthesized as described in the literature [7]. Thus, 1.5 g of amphiphilic triblock copolymer Pluronic P123 was dispersed in 15 g of H_2O and 45 g of HCl 2 M with stirring at 40 °C for 4 h. Thereafter, 3.15 g of TEOS were added and the obtained homogeneous solution was stirred at 40 °C for 24 h. The resulting gel was then hydrothermally treated in a Teflon-lined autoclave at 100 °C for 2 days. The solid was centrifuged, filtered, washed with deionized water, and dried in air at room temperature. The as-synthesized SBA-15 was calcined at 550 °C during 8 h under air flow.

2.4. Preparation of functionalized mesoporous silica

SBA-15 silicas functionalized with FTU-chelating ligand were prepared by two methods, based on co-condensation and grafting approaches (Scheme 1). The co-condensation method involves two steps: initial co-condensation between TEOS and CPTS, followed by the reaction of the chlorinated silica with FTU. In the grafting method 3-chloropropylsilane initially reacts with the chelating species and the resulting compound will react thereafter with the silanol groups of the pre-fabricated SBA-15 support.

Co-condensation method. SBA-15 silica functionalized with CPTS by direct synthesis was obtained by the same procedure as that described above for the SBA-15 synthesis, with the difference that (i) CPTS (5%, w/w, in the mixture of silica source) was added 2 h after TEOS and (ii) the final product was not calcined. In order to remove the templating agent a Soxhlet extraction with EtOH/H_2SO_4 (100/1, v/v) was run for 24 h. The obtained solid was dried at 60 °C. The product was then immersed in 50 mL of toluene and 1 g (5.9 mmol) of FTU was added. The mixture was stirred for 48 h at reflux under a nitrogen atmosphere. The resulting modified

mesoporous silica (referred as FTU-SBA-15-Cc) 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.

Grafting method. 1.0 g (5.9 mmol) of FTU was immersed in 50 mL dimethylformamide. CPTS and triethylamine (TEA) were then added in a 1:2:1 stoichiometry (FTU:CPTS:TEA). The mixture was heated for 48 h at 110 °C with magnetic stirring under a nitrogen atmosphere. After cooling, the solvent was evaporated and the resulting product EtO-FTU was extracted with hexane (2×30 mL). After hexane evaporation, the excess of CPTS was distilled under vacuum (150 °C and 0.75 mm Hg). 1.0 g of EtO-FTU was reacted with 1.0 g of activated SBA-15 (3 h at 120 °C under high vacuum) in 50 mL of dry toluene with magnetic stirring, 48 h at reflux under a nitrogen atmosphere. The resulting modified mesoporous silica (referred as FTU-SBA-15-Gr) 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.

2.5. Characterization

^{1}H NMR spectra were recorded in methanol-d_4 at 20 °C using a Bruker DRX-400 spectrometer. Small-angle XRD data were acquired on a Bruker diffractometer using Cu Kα radiation. N_2 adsorption–desorption isotherms were measured at −196 °C with a Micromeritics ASAP 2010 instrument. The sample was previously degassed under vacuum at 50 °C for 12 h. Specific surface area was calculated by the BET method and the mesopore volume was determined from the isotherm at the end of capillary condensation. The pores size distribution was obtained from the desorption branch using the BJH method and the Harkins-Jura standard isotherm. FTIR spectra of all samples were performed in KBr pellets using a Bruker Alpha spectrometer. C, H, and N contents were evaluated by combustion on a Fisons EA1108 elemental analysis apparatus. Thermogravimetric analysis was carried out in a Netzsch TG 209C thermobalance.

2.6. Hg(II) adsorption on mesoporous adsorbents

A batch method was employed to study the adsorption of Hg(II) from aqueous solutions onto the unmodified and modified mesoporous silica. The adsorbent (0.2 g) was suspended in 30 mL of aqueous solution at pH 6. Then 5 mL of $Hg(NO_3)_2 \cdot H_2O$ solution were added and the mixture was stirred for 4 h at room temperature. The initial concentration of mercury in the adsorption batch was 4 mM. The solid was separated by filtration through Whatman No. 44 filter paper and washed with abundant Milli-Q water. The concentration of unbound Hg(II) ions from the supernatant and the washing waters was spectrofotometrically determined as mercury-dithizone complex by using a Thermo Evolution 600 UV–vis spectrophotometer [45].

3. Results and discussion

3.1. Material characterization

3.1.1. X-ray diffraction

The XRD measurements confirmed the SBA-15 structure for both unmodified and grafted samples (Fig. 1). The SBA-15 material exhibited a strong (1 0 0) reflection peak (at $2\theta = 0.7°$) and smaller (1 1 0), (2 0 0), (2 1 0) diffraction peaks, which are characteristic of a well ordered SBA-15 type materials [7]. No significant changes upon SBA-15 silica functionalization with 1-furoyl thiourea by two methods were observed. However, as already reported for other hybrid materials [16,17], the XRD peak intensity decreased in the
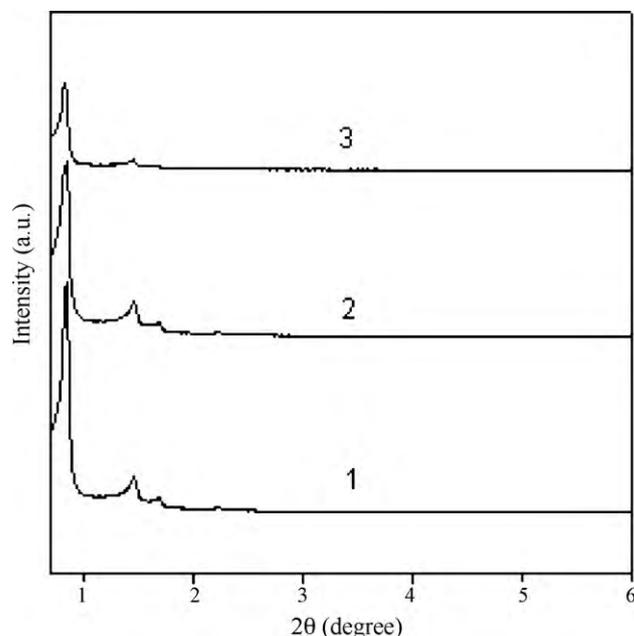
Fig. 1. X-ray diffraction patterns of SBA-15 (1), FTU-SBA-15-Cc (2) and FTU-SBA-15-Gr (3) samples.

case of the FTU-grafted samples compared to the pure SBA-15 silica. These results prove the evidence that functionalization occurred mainly inside the mesopore channels.

3.1.2. Nitrogen adsorption–desorption isotherms

Both FTU-SBA-15-Cc and FTU-SBA-15-Gr materials displayed an irreversible nitrogen adsorption–desorption isotherm of type IV, similar to that obtained from pure SBA-15 (Fig. 2). The H1 hysteresis loop, with a sharp desorption step at about $0.65 p/p_0$ is characteristic of well structured mesoporous materials with 0.7–0.8 nm pore diameter. The BET surface area and the mesopore volume of the SBA-15 sample were 522 $m^2 g^{-1}$ and 1.19 mL g^{-1}, respectively. These values (standardized versus pure silica weights) strongly decreased after grafting with FTU ligands. Thus, the surface area and the mesopore volume for FTU-SBA-15-Gr were 316 $m^2 g^{-1}$ and 0.62 mL g^{-1}, respectively. The textural parameters of the FTU-SBA-15-Cc were also lower comparatively to the SBA-15 support (378 $m^2 g^{-1}$ BET surface area and 0.77 mL g^{-1} mesopore volume, respectively). All these results suggest that the grafted species are located inside the mesopores and not only on the outer surface.
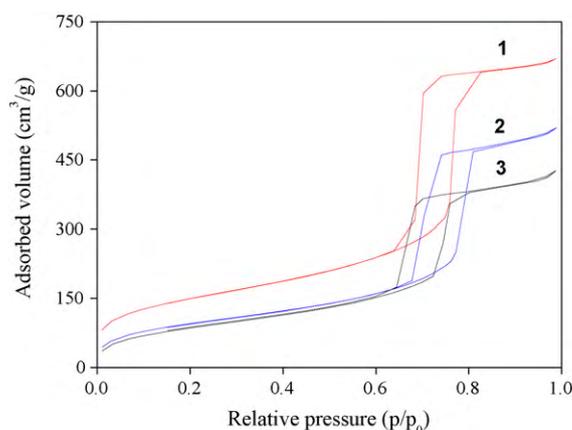
Fig. 2. N_2 adsorption–desorption isotherms of SBA-15 (1), FTU-SBA-15-Cc (2) and FTU-SBA-15-Gr (3) samples.
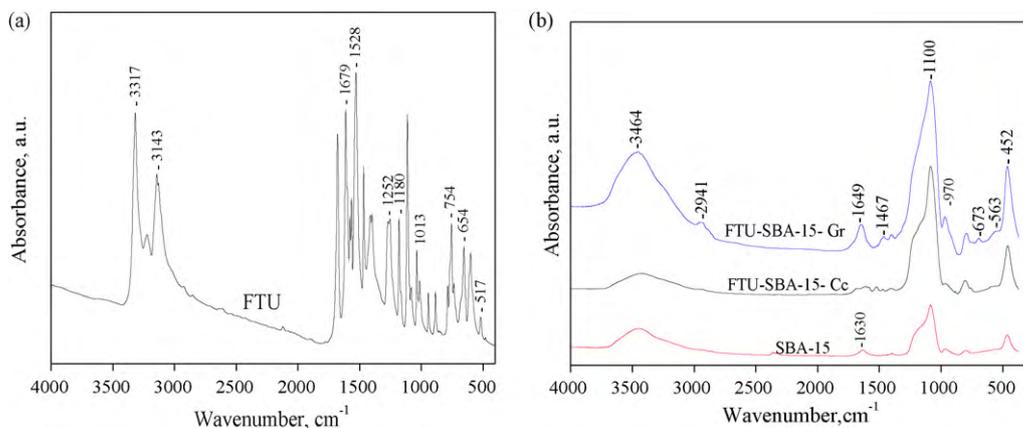
Fig. 3. FT-IR spectra of FTU (a) and functionalized mesoporous materials (b).

3.1.3. FT-IR spectroscopy analysis

FTIR spectrum of 1-furoyl thiourea illustrated in Fig. 3a was recorded in the range of 4000–400 cm^{-1}. The characteristic bands and their assignments are: υ(N–H) bands at 3317 cm^{-1} and 3143 cm^{-1} for free NH and associated NH (as–NH$\cdots$O=C–, which is a strong intramolecular hydrogen bridge [46]); υ(C=O) band at 1679 cm^{-1}; υ(C–O$_{furan}$–C) band at 1013 cm^{-1}; the four thioureido bands, υ(C–N) + δ(NH) (I), υ(C–N) + υ(C=S) (II and III), υ(C=S) (IV), are presented at 1528, 1252, 1180 and 754 cm^{-1} [46,47]. The other peaks which appear below 700 cm^{-1}, correspond to π(C=S) and δ(C=S).

In the FTIR spectrum of SBA-15 silica (Fig. 3b), the large broad band at 3400 cm^{-1} is attributed to O–H bond stretching of the surface silanols groups, and to the remaining adsorbed water molecules. The adsorption band at 1630 cm^{-1} is determined by deformational vibrations of adsorbed water molecules. The siloxane, –(Si–O)$_n$–, peak appears centered at 1100 cm^{-1} and Si–O bond stretching of silanol groups was detected at 970 cm^{-1}.

Characteristic bands are presented in the FTIR spectra of the FTU-SBA-15 materials (Fig. 3b). The band at 2941 cm^{-1} which corresponds to υ(O$\cdots$H) intramolecular hydrogen bridge between carbonyl and amino groups [48], and probably overlaps the symmetric and asymmetric stretching of υ(C–H) from the chloropropyl of the sililating agent. The band which appear at 1467 cm^{-1} corresponds to δ(C–H) of the same coupling agent. The band at 1649 cm^{-1} was assigned to υ(C=O) stretching vibrations which is a principal band for the FTU ligand. Furthermore, this band was observed at lower frequencies than in the free ligand, due to the intramolecular hydrogen bridge, too. Another characteristic bands in the 800–500 cm^{-1} spectral region correspond to the
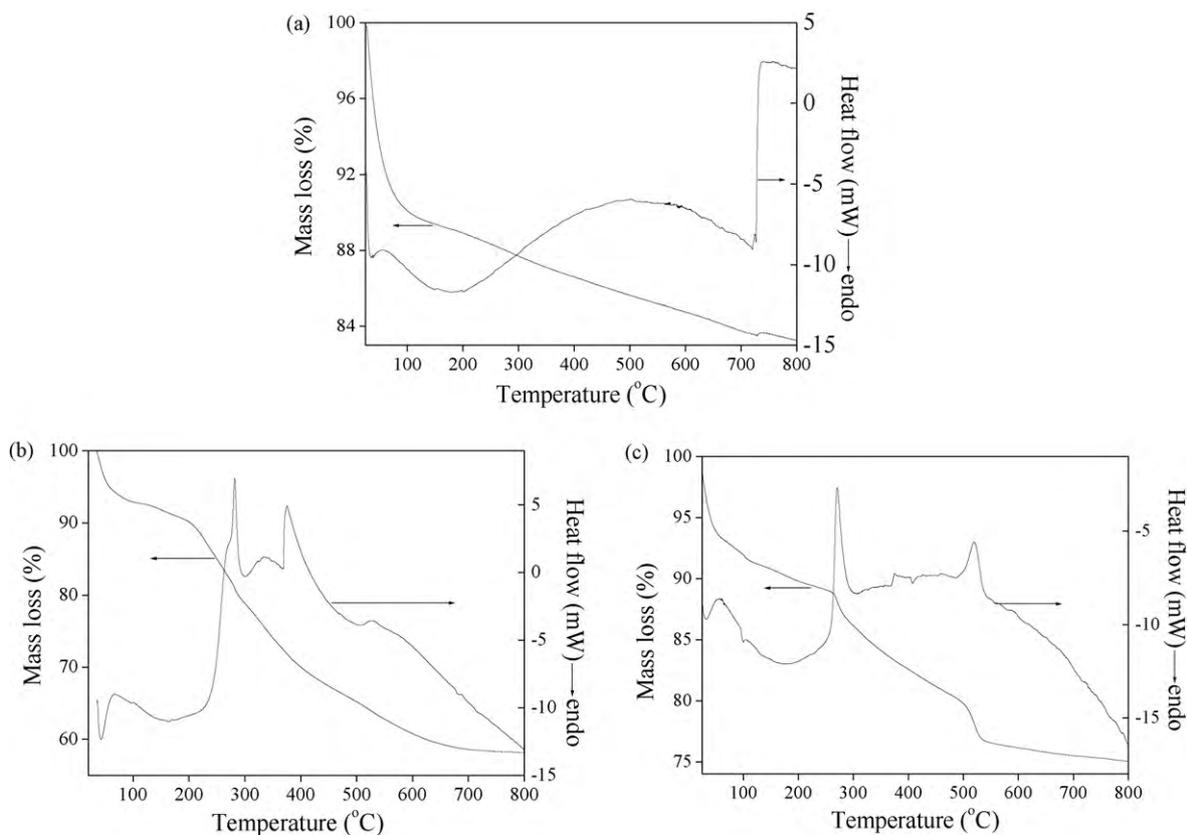
Fig. 4. TG-DTA curves for (a) SBA-15, (b) FTU-SBA-15-gr, and (c) FTU-SBA-15-Cc.

Table 1
TGA and elemental analysis results.

Sample	Organic group amount[a] (g/g solid)	Elemental analysis					
		Nitrogen (mmol/g)	Organic group amount[b]		Carbon (mmol/g)	C/N, atom ratio	
			g/g solid	mmol/g solid			
FTU-SBA-15-Gr	0.29	2.24	0.26	1.12	10.08	4.50	
FTU-SBA-15-Cc	0.13	0.96	0.11	0.55	4.83	5.03	

[a] Calculated from TG analysis.
[b] Based on nitrogen content and chemical structure from Scheme 1.

fourth thioureido band υ(C=S) at 673 cm^{-1}, with a dominant contribution from π(C=S), δ(C=S) of the attached FTU ligand at 563 and 452 cm^{-1}, respectively. It is important to note that the characteristic bands of the ligands are present in the spectra of both FTU-SBA-15-Gr and FTU-SBA-15-Cc samples, but their intensities are different. The bands in FTU-SBA-15-Gr spectrum are more intense, suggesting that the amount of the organic functions of the grafted sample is higher than that of the material prepared via co-condensation method.

3.1.4. Elemental and thermal analysis

The amount of the functional groups grafted on the SBA-15 surface was determined by both thermogravimetric and elemental analysis. The TGA profiles of SBA-15, FTU-SBA-15-Gr and FTU-SBA-15-Cc are plotted in Fig. 4. As expected, SBA-15 exhibits a first mass loss (about 10 wt.%) between 20 and 150 °C, which is due to the physically adsorbed water (Fig. 4a). The second weight loss (6 wt.%) observed between 150 and 800 °C can be ascribed to the condensation of the surface silanol groups. In the case of modified silicas (Fig. 4b and c), the loss of physisorbed water (below 150 °C) was about 8 wt.%. Based on the TGA profiles, we can consider that the degradation process of the anchored organic groups occurs between 200 and 600 °C. The mass losses in this range were 29.2 and 12.7 wt.% for FTU-SBA-15-Gr and FTU-SBA-15-Cc, respectively. These results indicate that the amount of chelating molecules immobilized onto SBA-15 silica via the grafting method was higher than that obtained using the co-condensation route. The elemental analysis summarized in Table 1 confirms this assertion. Indeed, taking into account the nitrogen content and the molecular weight of the organic ligand in the FTU-SBA-15 samples (Scheme 1), the amount of the organic groups into FTU-SBA-15-Gr and FTU-SBA-15-Cc was 0.26 and 0.11 g/g, respectively. On the other hand, the C/N atom ratio of the sample synthesized by grafting route was 4.5 (Table 1), which is in accord with the ligand composition (C/N = 9/2). In comparison with FTU-SBA-15-Gr, the hybrid material synthesized via co-condensation method exhibited a C/N ratio of 4.71. This higher amount of carbon, probably due to the presence of the unreacted chloropropyl moieties, indicates that the second grafting step was incomplete (Scheme 1). Based on this result we estimate at about 85% the yield of coupling between the grafted silylating agent and FTU.

Table 2
Adsorption capacity of Hg(II) in aqueous media (pH 6) by FTU functionalized SBA-15 silica.

Sample	N_f[a]	Hg(II)/ligand (mol/mol)
FTU-SBA-15-Cc	0.28 (6)	0.52
FTU-SBA-15-Gr	0.61 (2)	0.54

[a] Adsorption capacity (mmol of Hg(II) adsorbed per gram of functionalized silica).

3.2. Adsorption of Hg(II) from aqueous solution

After the successful grafting of furoyl thiourea groups on the SBA-15 support, the novel hybrid materials were tested as adsorbents for mercury species. The adsorption capacity was investigated in batch mode, using aqueous solutions with an initial Hg(II) concentration of 200 mg L^{-1}, at pH 6. As already reported [49,50] below pH 5.5 the dominant specie is Hg^{2+}, while the Hg(OH)$_2$ is the main form above pH 5.5. The number of moles of divalent mercury species per gram of adsorbent (N_f) was determined using the following equation:

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

where n_i is the initial number of metal ion moles in solution, n_s is the number of moles at equilibrium after adsorption, and m is the mass (g) of adsorbent. Each value was the means of three determinations with an accepted relative standard deviation of ±3%.

In a preliminary test performed in the presence of parent SBA-15 as adsorbent, it was found that the unfunctionalized material exhibited an insignificant adsorption capacity for the Hg species (0.04 mmol g^{-1}). In contrast, interesting adsorption capacity was obtained with both FTU-SBA-15-Cc and FTU-SBA-15-Gr adsorbents (Table 2). This performance is indeed attributed to the complexation reaction between Hg and grafted FTU ligands. Data in Table 2 indicate that the Hg adsorption capacity shown by the mesoporous silica functionalized by grafting route exceeded by twice the value exhibited by the material prepared via co-condensation method. In fact, these results are in excellent agreement with the ligand loading values of both samples (see Table 1).

Based on composition data of the hybrid materials and N_f values, we calculated the moles of metal adsorbed per mole of sulphur (ligand): 0.52 for FTU-SBA-15-Cc and 0.54 for FTU-SBA-15-Gr. This result suggests that, for both adsorbents, two sulphur-containing grafted ligands are necessary to complex a mercury ion. In addition, the FTIR spectrum (not shown) of the Hg(II) complex showed υ(C–N) + υ(C=S) (II and III) and υ(C=S) (IV) thioureido bands appearing at lower frequencies than in the spectra of the free lig-

Table 3
Comparative values of Hg sorption capacities on different functionalized mesoporous materials.

Mesoporous support	Ligand	N_f (mmol Hg/g)	Reference
MCM-41	Propylthiol	0.59	[25]
SBA-15	Propylthiol	2.88	[27]
HMS	Propylthiol	1.51	[51]
HMS	Propylthiol	1.26	[52]
MSU	Propylthiol	0.59	[35]
HMS	Propylthiol	1.50	[53]
MCM-41	Dithiocarbamate	0.20	[24]
MCM-41	Mercaptobenzothiazole	0.21	[31]
SBA-15	Mercaptobenzothiazole	0.24	[31]
SBA-15	Mercaptothiazoline	1.10	[30]
MCM-41	Mercaptothiazoline	0.70	[30]
SBA-15	2-Mercaptopyridine	0.19	[29]
MCM-41	2-Mercaptopyridine	0.10	[29]

ands (Fig. 3b), that indicated that Hg(II) species are coordinated by the sulfur atoms of FTU.

By comparing the adsorption capacity of FTU modified SBA-15 materials with those of other sorption studies on mesoporous materials functionalized with S-containing ligands (Table 3) we can conclude that FTU is a promising chelating agent for Hg(II).

4. Conclusions

In this work, we demonstrated that new hybrid materials based on SBA-15 inorganic support and 1-furoyl thiourea organic ligands can be prepared by both co-condensation and grafting methods. The exploratory adsorption study indicates that these materials are potential adsorbents for the removal of Hg(II) from aqueous solutions. The ligand density on SBA-15 surface, as well as the Hg adsorption capacity, were higher for the adsorbent prepared by the post synthesis grafting procedure.

Acknowledgements

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