Phenylthiourea Modified Highly Ordered Nanoporous Silica for Heavy Metal Ion (Hg^{2+}) Trapping

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Abstract

The phenylthiourea-substituted triethoxysilane as a silane agent was synthesized and grafted on highly ordered nanoporous silica (LUS-1) with a textured morphology and hexagonal array. This material (Tu-LUS-1) contained 0.8 mmol/g of soft base phenylthiourea group and surface area 760 m^{2}g^{-1} and was able to adsorb 0.75 mmolHg/g of TU-LUS-1 in endothermic reaction.

1. Introduction

Environmental pollution as a consequence of rapid technological development is a serious concern for ecology. Heavy metal ions, especially mercury and lead, contamination represent a significant threat to the ecosystem and specially to people due to the severe toxicological effects on living organisms [1, 2]. The most important component of the ecosystem is water. The development of techniques for removal of heavy metal ions from waste stream is a very attractive area of research. Effective approaches to the removal of heavy metal ions from solution have involved the use of various solid adsorbents,

including activated carbon, organic ion exchange polymers, and organically modified inorganic supports [3-7]. Among these inorganic supports, nanoporous materials such as clays, zeolites and silicas have focused the attention.

Ordered nanoporous silica such as MCM-41 [8], LUS-1 [9, 10] and SBA-15 [11] with very high surface area, uniform structure and extremely narrow pore size distribution has great potential applications in catalysis [12], preconcentration of metals [13-15] and modified carbon paste electrodes [16]. These materials can be suitable supports for adsorbent design. For this potential application, hybrid organic-inorganic silicas have been developed by anchoring organic ligands to the mesoporous silica surface, allowing its use in specific adsorption [17]. There is an upsurge in the development of sulfur and amine functionalized mesoporous silica based materials that are specific for mercury ions removal with high metal loading capacity [18-24].

The hard soft acid base theory [25] shows that a strong interaction between mercury(II) ion (as a soft acid) and adsorbent can be achieved when a complementary ligand (as a soft base) is attached to the matrix surface. Therefore, the functional groups containing a "soft base" atom (such as sulfur) would be able to retain a "soft acid" atom (such as mercury(II) ion) without meddling of "hard acids" such as K^+, Na^+, Mg^{2+} and Ca^{2+} remediation processes. In comparison to mercaptopropyl ligand modified mesoporous silica, introduction of multifunctional ligands containing more binding sites (such as thiourea) towards mercury ions allows one to increase adsorption capacity and to regenerate such adsorbents under mild conditions [26-28].

In the current study, we have used the phenylthiourea-substituted triethoxysilane

$(EtO)_3Si(CH_2)_3NHC(=S)NHPh$ (*SilTu*), which was first reported by Ferrari et al. [29] for the modification of LUS-1 to evaluate the mercury sorption behavior from aqueous solution.

2. Experimental procedure

2.1. Chemicals

Surfactant Hexadecyltrimethylammonium-*p*-toluene-sulfonate (CTATos), 3-(Triethoxysilyl)-propylamine $(EtO)_3Si(CH_2)_3NH_2$, phenylisothiocyanate, toluene, mercury(II)nitrate and NaOH from Merck and Ludox HS-40 (40% SiO_2) from Aldrich were purchased. All reagents were used without further purification.

2.2. Synthesis of LUS-1

LUS-1 was prepared according to a synthetic procedure previously established [10]. Typically, Ludox (15.5g, 0.26 mol) was added to sodium hydroxide (2g, 5×10^{-2} mol) in distilled water (50ml), and then stirred at 313 K until clear (about 24 h). A second solution of CTATos (2.5g, 5.5×10^{-3} mol) in distilled water (90 ml) was stirred during 1 h at 333K. The first solution was added dropwiseto second one, then stirred at 333K during 2 h. The resulting sol-gel was heated in an autoclave at 403 K during 20h. After filtration and washing with distilled water, the as-made solid was dried at 353 K. The extraction of surfactant was performed with 0.1 N HCl / ethanol solution [30].

2.3. Synthesis of *SilTu*

The *SilTu*was prepared according to the already reported route [29] by reaction of 3-(Triethoxysilyl)-propylamine with phenylisothiocyanate in Toluene.
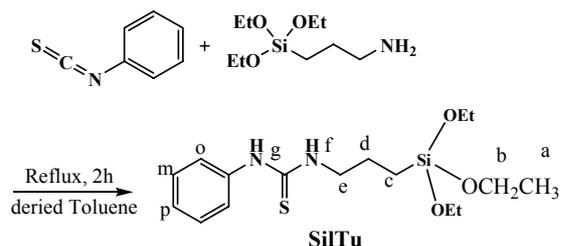
SilTu: δ_H (CDCl$_3$):8.05(s, 1H, NH$_g$), 7.51 (m, 2H, H$_m$), 7.38(m, 1H, H$_p$), 7.22(m, 2H, H$_o$), 6.29(s, 1H, NH$_f$), 3.81(q, 6H, H$_b$), 3.63(m, 2H, H$_e$), 1.73(m, 2H, H$_d$), 1.15(t, 9H, H$_a$), and 0.59(m, 2H, H$_c$).

2.4. Synthesis of TU-LUS-1

LUS-1 was dried at 353 K under vacuum for 3h. A mixture containing dry LUS-1 (3 g), dry toluene (100ml) and *SilTu* (2.43 g, 6.84×10^{-2} mol) was refluxed for 10 h. The mixture was filtered and washed, in sequence, with toluene, ethanol, and acetone and finally dried at room temperature under vacuum. The degree of functionalization of Tu-LUS-1 was determined by sulfur analysis.

2.5. Mercury (II) extraction studies with TU-LUS-1

Effect of pH: Sorption isotherm of mercury (II) ion as a function was obtained by equilibrating 0.05 g of TU-LUS-1 with 10 ml of solution containing 5×10^{-5} M Hg^{2+}, added in the form of mercury(II) chloride at room temperature. The initial pH of the stock solution, in the pH range 3-7, was adjusted by dilute HCl or NaOH. Distribution coefficient (K$_d$, ml/g) for mercury was calculated by:

$$K_d = [(C_i - C_e)/C_e] \times [V/m]$$

Where C_i and C_e are the initial and final (equilibrium) concentrations of the mercury ions in

solution (mg/ml), V is the solution volume (ml), and m is the mass of sorbent (g).

Kinetic studies: The kinetics of the sorption of mercury(II) ion was studied by equilibration of 0.05 of TU-LUS-1 with 10 ml of solution containing 0.1 M HCl and 4×10^{-5} Hg^{2+}, at room temperature. The equilibration was stopped at prefix time intervals. The solution phase activity was measured after filtering the solution. From the initial activity and the activity measured at various intervals of the time the percentage of mercury sorbed was calculated. Similar experiments were carried out with initial concentrations 5×10^{-4} and 5×10^{-3} M Hg^{2+}.

Effect of mercury concentration and temperature: Sorption isotherm as a function of mercury concentration was obtained at 25 °C by equilibrating 0.05 of TU-LUS-1 with 10ml of the solution containing 0.1M HCl and Hg^{2+} solution with different concentration from 4×10^{-5} to 1.5×10^{-3}. After an hour of equilibration the mixture was filtered and the activity of the supernatant was measured as described above. Similar experiments were also performed at temperatures of 32°C and 40 °C.

2.6. Instruments

^{1}H-NMR spectra were recorded on a Brucker Advance (500 MHz) spectrometer using CDCl$_3$ as a solvent and reference. XRD patterns of samples were obtained on a Bruker D8 Advance instrument equipped with a Cu Kα radiation source. Scanning electron microscopy (SEM) was obtained on a Zeiss DSM (960 A1 and 5KV). FT-IR spectra in KBr were recorded using a Bruker TENSOR 27 FT-IR spectrophotometer. The specific surface area was calculated from BET equation with an

automated DEL Japan apparatus at -200 $^\circ$C. The mercury amount was determined by using ICP-OES Varian Liberty.

3. Results and discussion

Fig.1 displays the IR spectrum of SilTu and TU-LUS-1. The bands at 696 cm^{-1} and 1542 cm^{-1} attributed to the oopbendig vibration mode of aromatic CH bond and the asymmetric stretching vibration mode of NCN bond, respectively. Also the band at 2972 cm^{-1} attributed to the asymmetric vibration mode of aliphatic CH bond. These results confirm the modification of the LUS-1 surface with Siltu.
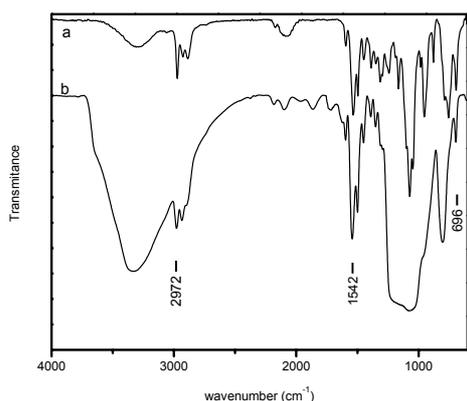
Fig. 1. IR spectrum of a) Siltu and b)TU-LUS-1.

The low angle XRD powder patterns of LUS-1 and TU-LUS-1 (fig.2) were showed typical of a hexagonal mesophase with the *P6mm* symmetry characteristic of MCM-41 [8]. The lower XRD intensity in TU-LUS-1 demonstrates the functionalization of LUS-1 with SilTu. No lattice change was observed between TU-LUS-1 and LUS-1. According to the BJH model, the pore size distribution of TU-LUS-1 and LUS-1 solid is still typical a MCM-41 and centered at 2.2 and 2.9 nm, respectively. The BET specific surface area (S$_{BET}$)

for TU-LUS-1 and LUS-1 were 760 m^{2}g^{-1} and 840 m^{2}g^{-1}, respectively. The decrease in S$_{BET}$ and average BJH pore diameter after functionalization can be interpreted due to the presence of organic ligand on the surface. The SEM image of TU-LUS-1 shows a texture form (fig.3).

The TGA analysis of TU-LUS-1 (fig.4) confirmed the amount of compound immobilized and also obtained information concerning the thermal stability. The reduction of the synthesis material weight in the temperature range between 150-700 °C indicated that the amount of organic ligand concentration was 0.8 mmol/g.
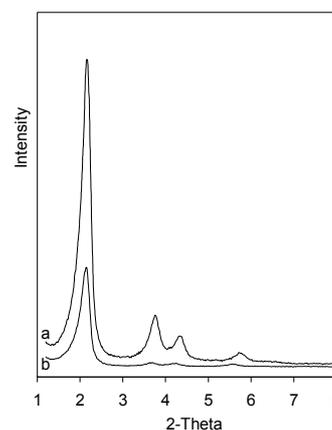
Fig. 2. XRD pattern of a) LUS-1 and b)TU-LUS-1.
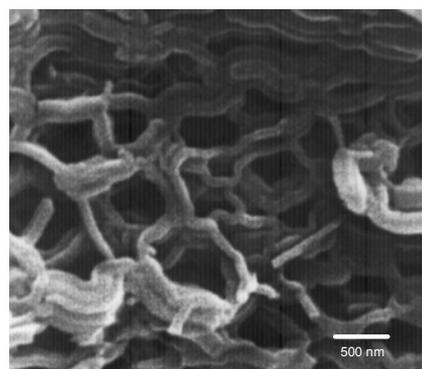
Fig. 3. Scanning electron microscopy (SEM) image of TU-LUS-1.
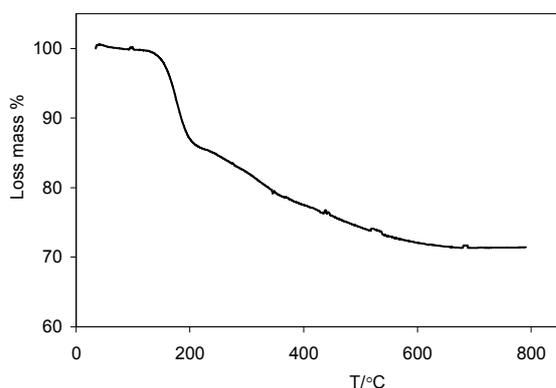
Fig. 4. Thermogravimetric analysis (TGA) of TU-LUS-1.

The pH value of the medium is one of the most important factors controlling the limit of extractability of metal ions by the proposed modified silica gel due to the competitive reactions between chelate forming groups and hydrogen ions in solution. The effect of pH values on $\log(K_d)$ was shown in Fig.5. $\log(K_d)$ of mercury in TU-LUS-1 increased with increase in pH up to 5 and then decreased until 7. The observed decrease in $\log(K_d)$ at pH values lower 5 can be attributed to protonation of the nitrogen atoms of the TU group, which was responsible for coordination of the mercury ion. The maximum capacity was observed in the pH=5. This can be explained by high strength of the thiol-mercury bond [31, 32].
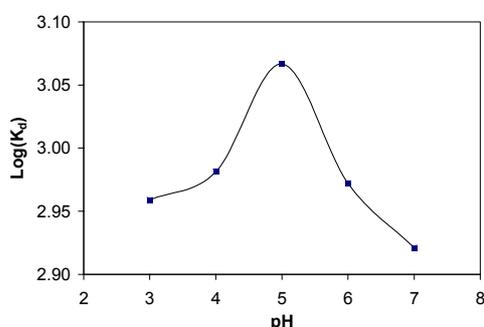
Fig. 5. Variation of logarithmic values of distribution coefficient log (K_d) of Hg(II) (5×10^{-5} M) with pH at 25 °C.

The percentage sorption of mercury as a function of time is shown in fig.6. It is observed that there is a very rapid sorption in the early stages of the experiment followed by slower uptake. Nearly 75-95% of the mercury is adsorbed within 4 min of equilibration. This could be due to the characteristic property of LUS-1 exhibiting high surface area and wide porosity, facilitating the immediate accessibility of sorption sites by mercury thus resulting in sorption of mercury within a short time of 4 min.

Fig.7 shows the plot of $\log K_d$ against $1/T$ for the sorption of Hg(II). The slope of the line suggests that the sorption process is endothermic and the enthalpy change (ΔH) for adsorption can be estimated from the slope of the line by using the following equation:

Log K_d = (-ΔH / 2.303 RT) + Constant

When the initial concentration of mercury increases from $4H10^{-5}$ to $5H10^{-3}$ M, ΔH decreases from 130 to 9 kJ/mol (Table 1). It is observed that the ΔH is endothermic and it decreases with increase in the initial concentration of mercury.
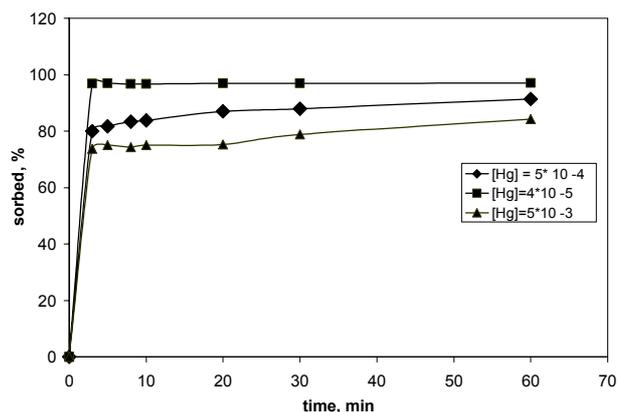
Fig. 6. Variation of percentage sorption of Hg (II) with time
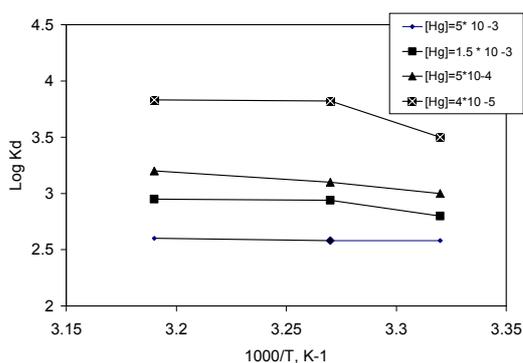
Fig. 7. Variation of log K_d with 1/T for the sorption of Hg(II) by TU-LUS-1

Table 1. Enthalpy changes by sorption of mercury from 0.1 M HCl on TU-LUS-1 at 25 $^{\circ}$C.

[Hg],M	ΔH, kJ/mol
4×10^{-5}	130
5×10^{-4}	85
1.5×10^{-3}	59
5×10^{-3}	9

4. Conclusion

The phenylthiourea-substituted triethoxysilane (SilTu) was synthesized and characterized. The silyant agent SilTu was grafted on LUS-1 with a texture morphology and hexagonal structure. This material (Tu-LUS-1) was contained 0.8 mmol/g of soft base TU group and surface area 760 m^2g^{-1} and characterized by FTIR and TGA. The TU-LUS-1 was able to adsorb 0.75 mmolHg/g in endothermic reaction.

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