



Synthesis and characterization of sulfur-functionalized silica materials towards developing adsorbents for mercury removal from aqueous solutions



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ABSTRACT

Three methods were used to synthesize sulfur-functionalized silica materials with spherical morphology: (a) impregnation of CS₂ and S₈ onto preformed silica support (MCM-TEOS); (b) co-condensation of TEOS and BTESPT/MPTMS; and (c) direct use of BTESPT and MPTMS as precursors. The presence of sulfur functional groups in the synthesized adsorbents was confirmed by the FTIR and EDX analyses. Lower pore arrangements and pore characteristics of sulfur-functionalized silicas were found which were observed from the XRD and nitrogen adsorption desorption analysis. However, these samples showed higher adsorption capacity than silica without sulfur. The highest Hg(II) adsorption capacity (47.50 mg/g) was obtained by the MPTMS-SMs(I) adsorbent synthesized through the co-condensation method.

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1. Introduction

The past decade has seen extensive studies in developing functionalized silica as alternative materials for catalysis [1,2], separation medium [3,4], membranes [5,6], drug delivery systems [7,8], immobilization host for enzymes [9] and for environmental technology applications [10]. These are due to the physical and chemical characteristics of the silica materials such as good mechanical strength, do not swell and can sustain high temperatures; thus they become the most researched heavy metal adsorbent [11–16]. Another advantage of using silica materials is that they are easy to modify and functioned in many ways due to the existence of free hydroxyl groups (O–H) on their surfaces, which can be utilized as points of attachment with functional agents.

The functionalization of silica materials could be done using various strategies to improve the availability of functional groups in the silica matrices namely impregnation [17,18], post-synthesis grafting [11,12,16,19–25], co-condensation of alkoxysilane and organoalkoxysilanes [13–15,26–31] and direct use of organoalkoxysilanes as precursors [32–34]. At the beginning, post-synthesis grafting method is widely used. It can produce materials with

organic residues anchored covalently onto the pore walls or to the mat rice surfaces. This method gives better control of the modification process and can avoid unnecessary pore blockage [25]. However, a large excess of functionalization agent is needed in order to obtain a high density of the functional group. In comparison, co-condensation provides shorter synthesis time, and high content and good dispersion of the functional groups compared to the grafting method [31].

The introduction of sulfur containing organoalkoxysilanes (e.g. MPTMS and BTESPT) [13,14,16,22,24,26–28] and organosulfurs (e.g. mercaptobenzimidazole and dithiocarbamate) [15,19–21,25] into silica frameworks has been found to result in high adsorption capacity and selectivity towards mercury ions. Thiol compounds such as MPTMS, mercaptobenzimidazole and dithiocarbamate are the most widely used functionalization agents. The availability of terminal sulfur groups in its molecular structure is the main reason for the high Hg(II) adsorption. Other types of sulfur such as elemental sulfur (S₈), carbon disulfide (CS₂) and hydrogen sulfide (H₂S) are normally functionalized through impregnation. These types of sulfur are commonly used to functionalize onto carbon materials, leading to higher adsorption performance for elemental mercury [35–37] and mercuric ion [38,39]. So far, there is no report on the impregnation of mesoporous silica using these sulfur compounds.

The synthesis of sulfur-functionalized silicas using direct use of organoalkoxysilanes as precursors had been reported previously

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[32–34]. For instance, Miller et al. [34] prepared the thiol-functionalized silica using MPTMS via surfactant-free synthesis route. Deng et al. [32] proposed a new and simple technique for synthesizing hybrid silica spheres using only water as a solvent, ammonia as a catalyst, and MPTMS, vinyltriethoxysilane (VTES) and phenyltriethoxysilane (PTES) as organoalkoxysilane precursors. In the late 1990s, the periodic mesoporous organosilicas (PMOs) were synthesized using bridged organoalkoxysilane precursors containing saturated aliphatic [40,41], ethene [42] and aromatic bridges [43]. Organoalkoxysilane having bridged active group such as bis(triethoxysilyl propyl) urea (BSPU) was used as a precursor, under basic condition and CTAB as an organic template to produce a material possessing irregular particle shapes, uniform hexagonal mesostructure with high surface area [33]. Apart from these, other uses of organosilanes as precursors for synthesizing uniform hybrid organic–inorganic mesoporous organosilica microsphere particles having active sulfur atom or sulfur bridges have not been reported by any publications.

Besides the types of sulfur compounds and functionalization methods, the morphology of the adsorbents also plays an important role in the adsorption process. Spherical particles tend to have higher surface area, thus providing more binding sites for the interaction with metal ions. In addition, they can be easily packed into the existing reactors, column or fixed and fluidized-beds in various reaction systems and can be used to reduce the pressure drop in the column [30]. The spherical silica particles are basically prepared based on the modified Stöber method [44], which involves hydrolysis of alkoxides in mixed alcohol–water solvent system using aqueous ammonia as a catalyst. It was reported that the synthesis parameters such as silica sources, temperature and pH of the solutions can drastically change the morphology and size of the particles. This is due to the fact that during the silica formation, the respective kinetics of the nucleation and aggregation processes depends on the quantity of nucleation seeds and the concentration of the reagents [23].

As indicated above, a wide range of sulfur compounds and methods have been used to synthesize mercury adsorbents, which cannot be simply compared due to different experimental conditions used by researchers. The present study will thus address this by examining the effect of precursors, sulfur ligands and functionalization methods on the physical and chemical properties of the respective adsorbents towards mercury adsorption affinity. The synthesis was carried out using TEOS, MPTMS and BTESPT as precursors, which were expected to have a spherical morphology and be structurally porous. The MPTMS and BTESPT were also used as functionalization agents during the co-condensation synthesis, with TEOS as a primary silica source. The functionalization by impregnation process was carried out onto MCM-TEOS using S_8 and CS_2 as sulfur ligands. The effectiveness of MPTMS, BTESPT, S_8 and CS_2 , as being reported to have high affinity towards mercury, was investigated.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, 99%), ammonium hydroxide (NH_4OH , 25%), nitric acid (HNO_3 , 70%), *n*-cetyltrimethylammonium bromide (CTAB, 99%), elemental sulfur (S_8 , 99–101%), carbon disulfide (CS_2 , 99.9%) and sodium hydroxide (NaOH pellets, 99%) were purchased from Merck (Germany). Ethanol (99.5%) and mercury nitrate monohydrate ($Hg(NO_3)_2 \cdot H_2O$, 98.5%) were obtained from Fluka (Germany). The organoalkoxysilanes; 3-mercaptopropyl trimethoxysilane (MPTMS, 99%) were bought from ACROS (Belgium), while bis(triethoxysilylpropyl) tetrasulfide (BTESPT)

was obtained from Power Chemical Corporation (China). All chemicals used were of analytical grades except BTESPT, which was of industrial grade; all were used as received. Deionized water used throughout this work was produced by the Purite Water System (UK) which is available in our laboratory.

2.2. Material synthesis

2.2.1. Preparation of MCM-TEOS adsorbent

The MCM-TEOS adsorbent synthesis was carried out according to the method as described by Walcarius and Delacôte [14] with some modifications. First, the CTAB solution was prepared by dissolving 2.5 g of CTAB in 100 ml of deionized water. 14.5 ml of aqueous ammonia and 60 g of ethanol were then added into the CTAB solution, while stirring for 15 min to form a homogeneous solution. Then, 5 ml of TEOS was added drop-wise into the homogeneous solution with rapid stirring. After 2 h of stirring, the product was filtered, washed using deionized water and dried at room temperature (30 ± 1 °C). The dried synthesized adsorbent was then ground into powder form and placed in an oven at 105 ± 0.5 °C for 2 days. Lastly, the CTAB template was removed through calcination at 550 ± 0.5 °C in the furnace for 5 h.

2.2.2. Preparation of MCM-TEOS(S_8) and MCM-TEOS(CS_2) adsorbents

The MCM-TEOS was functionalized with elemental sulfur (S_8) and CS_2 through the impregnation process. For elemental sulfur, this was carried out by using dry impregnation procedure as described by Hsi et al. [35]. The MCM-TEOS was physically mixed with S_8 at a mass ratio of 1:6. The mixture was placed in a ceramic boat, which was then placed in the tabular furnace. Before heating, N_2 gas was flowed into the furnace for 15 min. After that, the furnace was heated up to 200 °C and this condition was maintained for 3 h. The temperature was then increased up to 600 °C and this temperature was maintained for another 5 h. The furnace was then cooled naturally and the sample was taken out and ground into powder form. This final product was denoted as the MCM-TEOS(S_8) adsorbent. The CS_2 was functionalized through wet impregnation procedure as described by Silva et al. [39]. 2 g of MCM-TEOS was soaked in 25 ml of CS_2 solution and the mixture was stirred overnight at room temperature (30 ± 1 °C). The mixture was then dried by passing nitrogen gas onto it for an hour. The dried sample was ground into powder form and this final product was denoted as the MCM-TEOS(CS_2) adsorbent.

2.2.3. Preparation of MCM-BTESPT(1) and MCM-MPTMS(1) adsorbents

Co-condensation method was conducted according to the procedure as reported by Gaslain et al. [45] and Walcarius and Delacôte [14]. 2.5 g of CTAB was dissolved in 100 ml of deionized water to form a CTAB solution. 14.5 ml of ammonia and 60 g of ethanol were then added into the CTAB solution while stirring to form a homogeneous solution. After 15 min of stirring, 6 ml of precursor solutions (TEOS containing 10% of BTESPT or MPTMS) was added drop-wise into the homogeneous solution under rapid stirring. After 2 h of stirring at room temperature (30 ± 1 °C), the product was recovered by filtration, then washed several times using deionized water and dried at room temperature. The dried product was then ground into powder form and further dried in an oven at 105 ± 0.5 °C for 2 days. Calcination at high temperature to remove CTAB template would not be suitable since the BTESPT or MPTMS in the silica frameworks would be degraded. In this case, the CTAB template was removed by suspending the powdered product in ethanol, with a ratio of 1 g of the powdered product in 140 ml of ethanol. The mixture was then refluxed for 48 h. After cooling, the product was filtered and washed several times using ethanol and deionized water. The product was then dried at 105 ± 0.5 °C for 2 days. The product obtained from the synthesis using TEOS

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