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Chemically functionalized silica gel with alkynyl terminated monolayers as an efficient new material for removal of mercury ions from water

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ABSTRACT

An efficient new material for removal of mercury from water was prepared by the chemically functionalization of silica gel. Various monolayers were grafted on the silica gel surface to attach terminal alkynyl groups. All modified surfaces were characterized by XPS, ATR-IR and elemental analysis while Hg^{2+} concentrations were determined by ICP-OES. The Hg^{2+} adsorption reached equilibrium within 2 h with maximum adsorption capacities of 174.3 mg g^{-1} for alkynyl monolayers functionalized silica gel. Due to relatively lower price of silica gel, it can be efficiently used after functionalization on large scale to remove Hg^{2+} ions from the wastewater.

Introduction

Water is the source of life and energy. Rapid industrialization and unplanned urbanization are the main reasons for the severe water pollution. The main sources of water pollution can be attributed to the discharge of untreated toxic industrial wastes into the water sources [1,2]. Metals and other elements present in the wastewater can enter into the food chain causing severe health effects. Mercury is considered as one of the most harmful pollutants because, along with environmental pollution, it can accumulate in biological tissues, a process known as bioaccumulation [3].

Mercury is released from the industrial processes like chloralkali production, paint, pulp, fertilizer, oil refineries, etc. [3–5]. Various processes like chemical precipitation, coagulation, ion exchange, ultrafiltration, reverse osmosis and electrolytic processes are used for the removal of mercury from the wastewater [2,6–9]. Among these methods, the adsorption using solid materials as adsorbents is considered the most reliable, convenient and simple method [3,10]. For excellent efficiency, adsorbent material should have good chemical affinity towards heavy metals, high adsorption speed and low cost [3]. Different materials like agricultural waste e.g. saw dust, rice husk, seeds [11–16], industrial wastes e.g. fly ash [17] and blast furnace slag [18], natural materials like chitosan, starch and synthetic materials like polymer resins and mesoporous silica are used as adsorbents [9,19–21] for mercury removal. Activated carbon is the most widely used adsorbent [22] but commercially activated carbons and synthetic mesoporous materials are expensive or their production involves the use of toxic materials. Therefore, search for alternative and cheaper adsorbents is of particular interest [3,9]. There are some reports where silica micro/nanoparticles were used for removal of heavy metals from water

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[3] but cost of such particles is normally very high. In this study, we used silica gel to decrease the cost of the adsorbent and to make it possible to apply at commercial scale.

Keeping in view the above, the present study was undertaken to investigate the adsorption of mercury using silica gel functionalized with terminal acetylenes. Terminal acetylenes are interesting products themselves and also as intermediates to introduce a number of further functionalities. The geometry of the acetylenic function corresponds to a rigid carbon rod with acidic hydrogen at the tip. Such terminal acetylenic groups can act both as a hydrogen bond acceptor and donor [23] and can complex various metal ions. In our previous studies, we dialyze pentynyl ether of dextran against $AgNO_3$ solution under exclusion of light and results show that 23.3 g of Ag per 100 g of pentynyl dextran was bound as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Same experiment (using per acetylated pentynyl ether of dextran) with Fe_2O_3 gives product with 9.4 g Fe per 100 g of the pentynyl dextran [23]. In another study [24], we functionalized terminal alkynyl monolayers on glass discs and after complexation with Ag was used as an antibacterial surface and results proved that it was much more effective against different pathogens as compared to other traditional antibacterial surfaces mostly used for this purpose. These results suggest that terminal alkynyls have very strong ability to make complexation with various metals and encouraged use to apply these new types of materials as adsorbent for heavy metals. Here we report on the surface functionalization of silica gel-60 with terminal acetylene groups and their application for removal of mercury from the water solution.

Experimental

Materials

Silica gel 60 (0.040–0.063 mm) was from Merck (Darmstdat, Germany). *N*-[2-Aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPTMS, 97%), (3-aminopropyl)trimethoxysilane (APTMS, 97%), (3-glycidyloxypropyl)trimethoxysilane (GOPTMS, ≥98%), 5-chloro-1-pentyne (98%), mercury(II) chloride ($HgCl_2$, 99.5%), triethylamine (Et_3N, 99%) and dichloromethane (anhydrous, ≥99.8%) was from Aldrich (St. Louis, MO, USA). Methanol (99.9%, anhydrous) was from Alfa Aesar (Ward Hill, MA, USA). Silica gel was dried before use while other chemicals were applied without further purification or any other treatment.

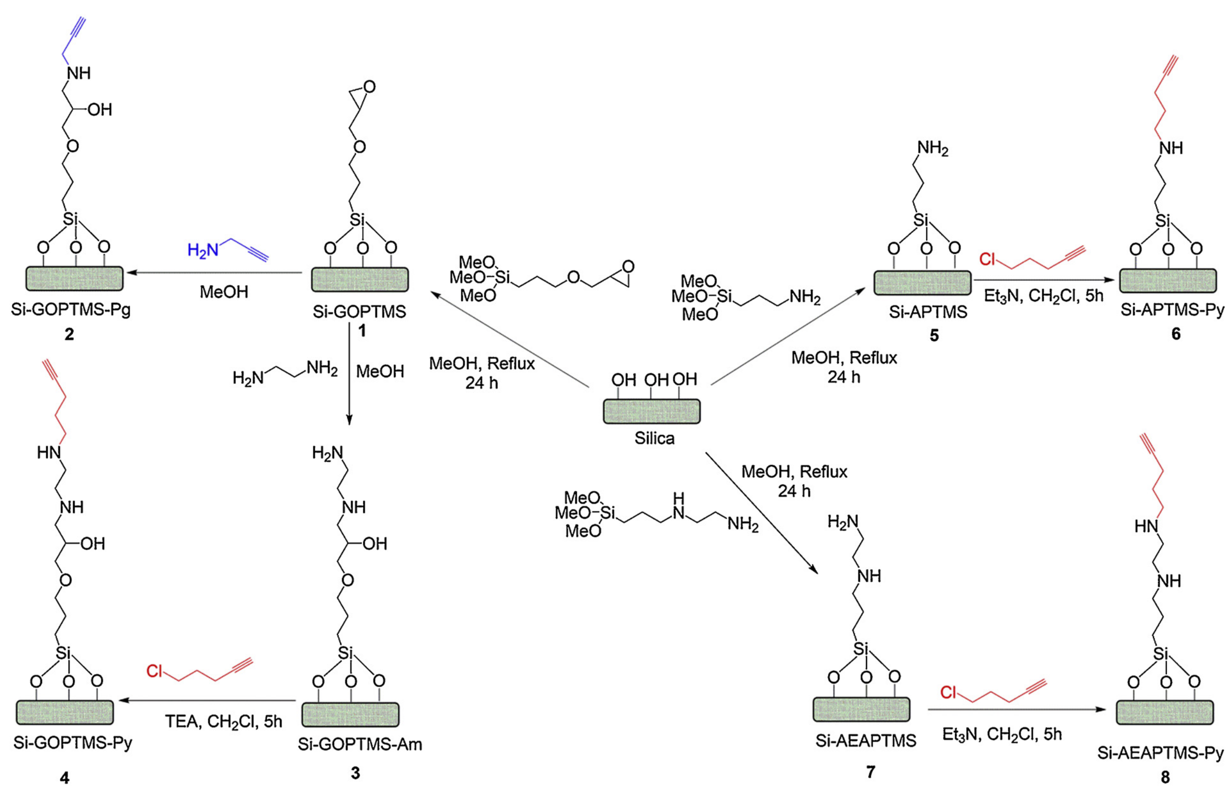
Surface functionalization of silica gel

Silica gel (10 g) was dried under vacuum at 130 °C for 24 h and added in a dried flask followed by addition of one of the trimethoxysilane reagent (AEAPTMS, APTMS, GOPTMS, 10 mmol) and refluxed in methanol (100 ml) for 24 h under continuous stirring. Modified silica gel (Si-GOPTMS (**1**), Si-APTMS (**5**), Si-AEAPTMS (**7**)) was filtered and washed several times with methanol and acetone and dried under vacuum.

Si-GOPTMS (**1**, 5 g) was converted to Si-GOPTMS-Pg (**2**) by reacting with propargylamine (5 mmol) in methanol (50 mL) at room temperature for 24 h. Si-GOPTMS (**1**) was also reacted with ethyleneamine under the same conditions as described above (for synthesis of **2**) to prepare Si-GOPTMS-Am (**3**) which in next step was converted into Si-GOPTMS-Py (**4**) by reacting with 5-chloro-1-pentyne (1 mL), Et_3N (2 mL), dry dichloromethane (15 mL) and stirring at 40 °C for 5 h. Same method of pentynylation was used to convert Si-APTMS (**5**) into Si-APTMS-Py (**6**) and Si-AEAPTMS (**7**) into Si-AEAPTMS-Py (**8**) as shown in Scheme 1. Washing and drying as described above were followed after each step.

X-ray photoelectron spectroscopy (XPS)

XPS spectra were recorded by using a Sigma Probe (ThermoVG, UK) photoelectron spectrometer. High-resolution spectra were obtained using monochromatic *Al-Kα* X-ray radiation at 15 kV and



Scheme 1. Functionalization of silica gel with terminal acetylene-, amine-, epoxide- and thio-functional groups.