

Bi-functionalized xerogel adsorbent for selective removal of Pb^{2+} from aqueous solution

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Bi-functionalized adsorbents were successfully fabricated using polymeric polymethylhydrosiloxane (PMHS), tetraethylorthosilicate (TEOS), (3-mercaptopropyl)trimethoxysilane (MPTMS) and (3-Aminopropyl)trimethoxysilane (APTMS) as co-precursors via a facile one-pot sol-gel pathway. Experimental results showed that the as-prepared functional sample with developed pore frameworks could selectively adsorb Pb^{2+} from aqueous solutions and the removal efficiency was carefully evaluated using a simulated Pb^{2+} system with different concentrations.

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1. Introduction

Metal ions, especially heavy metals, are the most significant environmental pollutants found in wastewater and their effects on human health and natural ecosystems is a major concern [1]. At present, methods for metal ion removal include precipitation, flocculation, ion exchange, reverse osmosis, complexation/sequestration, electrochemical operation and biological treatment. Some limitations of these processes are high operating and energy costs [1,2]. In contrast, adsorption technology is one of the most popular methods to control such pollutants. Desirably, xerogel materials with high specific surface area have become an ideal adsorbent of removal heavy metal ions from aqueous solutions.

Recently, bi-functionalized silica adsorbents were the most widely studied materials for the purpose of metal removal. Zhao et al. developed thiol- and amino-functionalized SBA-15 silicas [3]. Furthermore, Burke et al. [4] synthesized large pore bi-functionalized mesoporous silica. However, some alkoxysilanes containing long-chain organic group (alkyl, amino or mercapto) were used as both silica sources and templates for preparing these bi-functionalized silica materials, but the syntheses of these alkoxysilanes are complicated and these compounds are expensive. In contrast, PMHS, a by-product of silicon industry, is inexpensive, nontoxic and stable to air/moisture and mainly used as a reducing agent for ketones, halogens, ethers, imines, and phosphine oxides [5].

In this work, a novel bi-functionalized xerogel adsorbent with developed pore structures was facilely assembled by co-condensation of APTMS, MPTMS and TEOS via a polymeric PMHS-assisted sol-gel method in the absence of traditional surfactants. The as-prepared xerogel material could selectively adsorb Pb^{2+} due to the presence of $-\text{SH}$ and $-\text{NH}_2$ groups in the developed frameworks.

2. Experimental

Polymethylhydrosiloxane (PMHS) (99%, $M_w = 2700 \sim 5400$), tetraethylorthosilicate (TEOS), (3-mercaptopropyl)trimethoxysilane (MPTMS) and (3-aminopropyl)-trimethoxysilane (APTMS) were supplied by Aldrich chemical company. Tetraethylorthosilicate (TEOS, 99%), ethyl alcohol and sodium hydroxide (NaOH) were provided by Tianjin chemical corporation of China. All the chemical agents were used as received without further purification.

For a typical synthesis, 0.6 mL of PMHS was dripped into a flask containing certain amount of ethanol (70 mL) and NaOH (0.10 g). The molar ratios of TEOS/ (MPTMS + APTMS) and MPTMS/APTMS are 4/1 and 1/1, respectively. After continuous stirring for 24 h, 4 mL deionized water was added into the system and kept vigorous stirring for another 3 h. After being aged for 1~2 d under ambient conditions, the sol converted into wet gel. The solvent were removal by treatment at 80 °C for 24h and hard glass solids were obtained, which can be used to adsorb Pb^{2+} after careful washing with deionized water.

For metal ion adsorption experiment, 0.1 g sample was added to 50 mL Pb^{2+} solution with different concentration and stirred for 12 h until saturation. The solution was then filtered and the remaining metal ions were determined using Atomic Adsorption Spectrum.

The morphology of the bi-functionalized gel was determined with a SEM (JEOL 6400). Transmission electron microscopy (TEM) image was obtained by a JEOL 2010 electron microscope with an acceleration voltage of 200KV. Nitrogen sorption was obtained by a Quantachrome SI analyzer at -196 °C after the treatment at 180 °C for 12 h in vacuum. Specific surface area was calculated by BET method, the total pore volume was determined by nitrogen adsorption $P/P_0 = 0.99$, and pore size distribution was determined from the desorption branch. ^{29}Si MAS NMR spectra was obtained on a Bruker

DSX400 spectrometer at room temperature with a 4 nm zirconia rotor spinning at 6 kHz.

3. Results and discussions

Bi-functionalized xerogels with developed frameworks could be facily prepared by one-pot co-assembly of MPTMS, APTMS, TEOS and PMHS in absence of traditional templates. Firstly, the textural properties of as-prepared xerogel sample were investigated using N_2 sorption technique and the isotherms are shown in Fig. 1. According to the IUPAC classification^[5], the curves of sorption isotherms is characteristic of type IV profile with a sharp capillary condensation step at relative pressure range between 0.6 and 1.0, clearly indicating the presence of developed pore structures. Correspondingly, the pore size curve obtained from the desorption branch illustrates a quite uniform distribution at the range of 3~15 nm with an average pore diameter of 8.3 nm. Besides, the specific surface area and pore volume of this sample are 421 m^2/g and 0.77 cm^3/g , respectively, and this observation is similar to those reported results for silica xerogel-like samples synthesized at ambient pressure without using specific drying techniques like supercritical CO_2 fluid [5].

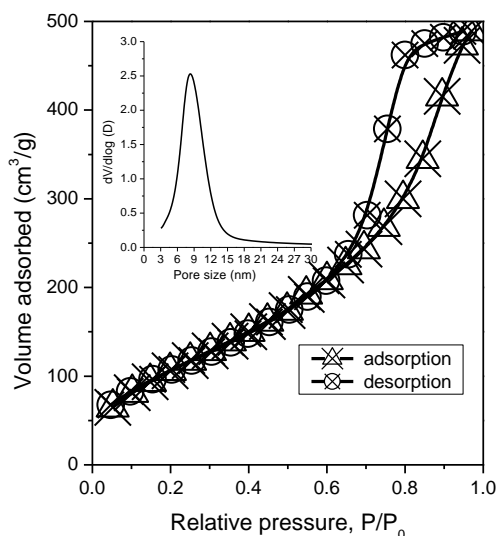


Fig.1. N_2 adsorption/desorption isotherms and pore size distribution of the bi-functionalized sample prepared with PMHS-assisted sol-gel method.

The morphology and pore structures of the bi-functionalized sample synthesized by the proposed facile pathway were characterized by SEM and TEM, and the images are shown in Fig. 2. On the one hand, irregular-shaped particles with several to tens micrometers in size are clearly observed in the SEM image shown in Fig. 2 (A), which is well in agreement with the sol-gel-processed siliceous xerogels prepared in alcohol-rich systems [6,7].

On the another hand, the TEM image in Fig. 2 (B) clearly elucidates a wormhole-like pore structures throughout the picture, clearly revealing a porous xerogel with relatively uniform mesopores have been facily prepared even though no traditional organic templates or salts were introduced in the assembly process. Combined with aforementioned N_2 adsorption/desorption analysis and TEM observations, it was demonstrated that a typical xerogel with developed pore structures could be easily assembled via co-condensation of silica precursors with different functionality.

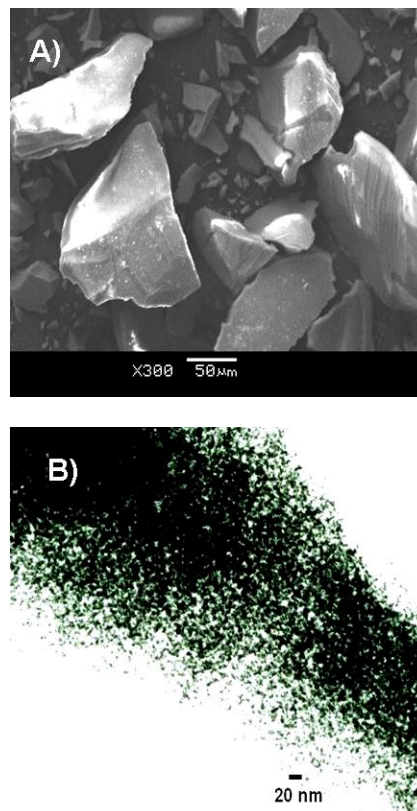


Fig. 2. SEM (A) and TEM (B) images of the studied sample.

More convincing supports for the successful incorporation of organic moieties into the siliceous network come from ^{29}Si MAS NMR analysis. The technique was used to clarify the basic structural unit in the as-prepared sample. As shown in Fig. 3, the spectrum exhibits four distinct signals at -111, -100, -64 and -56 ppm, corresponding to Q^4 ($Si^*(OSi)_4$), Q^3 ($(OH)Si^*(SiO)_3$), T^3 ($(SiO)_3Si^*-C$), and T^2 ($(OH)(SiO)_2Si^*-C$) environments of silicon atoms, respectively^[8]. The appearance of strong signal of T^2 and T^3 clearly indicates that organic functional groups ($-CH_2CH_2CH_2SH$, $-CH_2CH_2CH_2NH_2$) have been chemically bonded to the skeleton via co-condensation of silica species, which is identical to those reported studies for bi-functionalized mesostructures prepared by co-condensation method in the presence of traditional surfactants that must be remove by tedious extraction procedures.

In contrast, the present bi-functionalized sample with developed porosity could be facily prepared using the

proposed PMHS-assisted sol-gel method, which favorably avoided time-consuming procedures as template removal related process. It should be noted that, however, different from those typical mesoporous materials like SBA15 or MCM41, the pore structures occluded in the xerogel are wormhole-like, which may be mainly associated with the unique PMHS-assisted one-pot assembly process^[5]. And this method is helpful to the scaleable synthesis of functional materials for specific applications as selective adsorbents for heavy metals or organic pollutants.

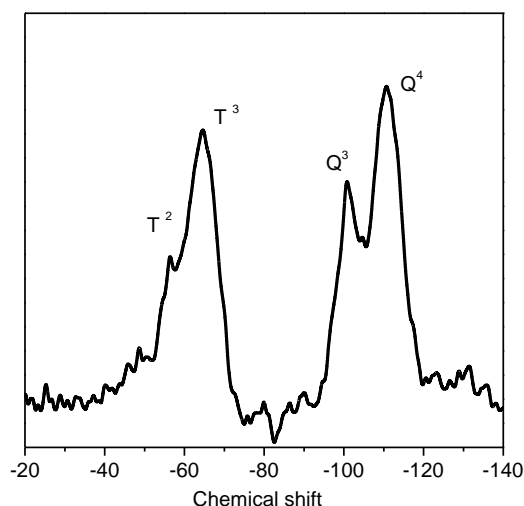


Fig. 3. ²⁹Si MAS NMR spectrum of as-prepared bi-functionalized xerogel sample

To evaluate the affinity of -NH₂/-SH groups to metal ions, the bi-functionalized xerogel was tested for selective adsorption of Pb²⁺ from simulated solution with different concentrations, and the analysis results are illustrated in Fig. 4. Clearly, this xerogel adsorbent shows remarkable adsorption properties toward Pb²⁺ ions under studied conditions, even though the removal efficiency slightly decreases with the increase of Pb²⁺ concentration. The observation illustrates that the removal efficiency of as-prepared adsorbent gradually reduced due to the adsorption equilibrium between organic moieties and metal ions^[8-11]. However, the adsorbent still exhibited considerable removal efficiency over 35% at the highest Pb²⁺ concentration of 500 mg/L. It is thus thought that, in combination with the selective capture property and facile preparation process with upscale synthesis potentiality, the bi-functionalized xerogel adsorbent with developed frameworks possess expected adsorption capacity to heavy metals and it may have bright future in the filed of wastewater treatment.

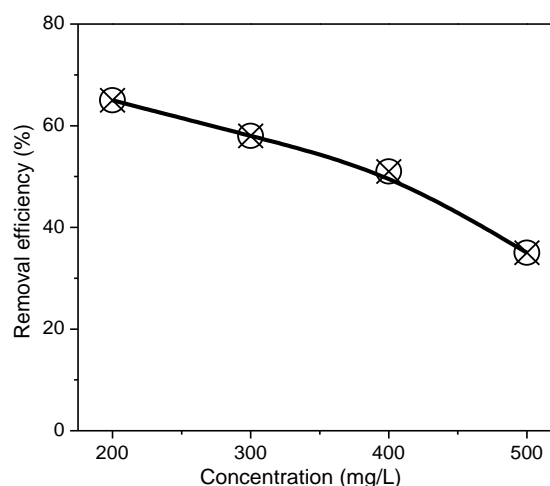


Fig. 4. Removal efficiency of as-prepared xerogel adsorbent toward different Pb²⁺ systems

4. Conclusions

This study demonstrates that novel bi-functionalized xerogel samples with developed porosity could be easily assembled via a PMHS-assisted one-pot pathway in the absence of traditional templates. The as-prepared hybrid gel exhibited remarkable adsorption properties for heavy metal of Pb²⁺ due to the presence of -SH and -NH₂ functionalities in the porous frameworks, and the maximum Pb²⁺ adsorption capacity was 142 mg/g.

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