Contents lists available at ScienceDirect



Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece



Synthesis of thiol-functionalized mesoporous calcium silicate and its adsorption characteristics for heavy metal ions



Lihua Liu^{a,b,c,*}, Tong Li^a, Ganggang Yang^a, Yifeng Wang^a, Anping Tang^{a,b,c}, Yulin Ling^a

^a School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

^b Key Laboratory of Theoretical Organic Chemistry and Function Molecule, Ministry of Education, Xiangtan 411201, China

^c Hunan Province College Key Laboratory of QSAR/QSPR, Xiangtan 411201, China

ARTICLE INFO

Keywords: Thiol-functionalized mesoporous calcium silicate Heavy metal ion Adsorption performance Adsorption thermodynamics and kinetics Adsorption mechanism

ABSTRACT

Thiol-functionalized mesoporous calcium silicate (MCS-SH) was synthesized using post-grafting with calcium nitrate tetrahydrate and sodium metasilicate nonahydrate as raw materials, cetyl trimethyl ammonium bromide as template, and (3-mercaptopropyl)trimethoxysilane as modifying agent. The structure and composition were characterized using X-ray diffraction, Fourier-transform infrared spectroscopy, Brunauer-Emmett-Teller surface analysis, thermogravimetry-differential thermal analysis, scanning electron microscopy, transmission electron microscopy, and energy-dispersive X-ray spectrometry. The adsorption performance and thermodynamic and kinetic characteristics of MCS-SH for Cd^{2+} , Cu^{2+} , Pb^{2+} , and Cr^{3+} were investigated. Results showed that MCS-SH possessed a slit-pore structure with a specific surface area of $129.32 \text{ m}^2 \text{ g}^{-1}$ and pore size that was mainly distributed in 5–49 nm, which reduced by 28.81 m² g⁻¹ and 2 nm compared with those of unmodified mesoporous calcium silicate (MCS), respectively. The amount of -SH grafted to MCS-SH was 0.4594 mmol g⁻¹, according to the determined sulfur content. The maximum adsorption capacities for Cd^{2+} , Cu^{2+} , Pb^{2+} , and Cr^{3+} were 601.51, 509.56, 618.09, and 334.81 mg g⁻¹ at 293 K, respectively, which were much higher than those reported in the literature, and follow the order of $Pb^{2+} > Cd^{2+} > Cu^{2+} > Cr^{3+}$. The equilibrium data of the four heavy metal ions adsorbed by MCS-SH fitted the Langmuir model and, especially, the Redlich-Peterson model well. The adsorption processes were all endothermic, entropy increasing, and spontaneous. The adsorption of MCS-SH for Cd^{2+} , Cu^{2+} , Pb^{2+} , and Cr^{3+} was rapid and attained equilibrium within 60 min. The adsorption kinetics can be well fitted by the pseudo-second-order model, and the adsorption activation energy followed the order of Cr^{3+} (29.7526 kJ mol⁻¹) > Pb²⁺ (21.5840 kJ mol⁻¹) > Cu²⁺ $(19.6988 \text{ kJ mol}^{-1}) > \text{Cd}^{2+}$ (18.5377 kJ mol⁻¹). The adsorption mechanisms include physical adsorption, chemical adsorption (especially surface complexing adsorption), and ion exchange, with chemical adsorption being the dominant mechanism. MCS-SH exhibited an excellent performance as adsorption material for Cd²⁺, Cu^{2+} , Pb^{2+} , and Cr^{3+} .

1. Introduction

With the rapid development of modern industry, a large amount of heavy metal wastewater, especially that containing Pb^{2+} , Cd^{2+} , Cr^{3+} , Cu^{2+} , and Hg^{2+} , is produced during the commercial production and has caused serious environmental pollution and threatened human health [1]. Given the toxicity of these metals, the World Health Organization restricts the maximum acceptable concentration of Pb^{2+} , Cd^{2+} , Cr^{3+} , Cu^{2+} and Hg^{2+} in drinking water to be 0.01, 0.003, 0.05, 2.0 and 0.001 mg L⁻¹, respectively [2]. The problem motivated the scientific community to develop new methods to detect and remove

toxic contaminants from wastewater in efficient and economically practicable approaches. Although various methods, such as conventional chemical precipitation [3], chelating–flocculation method [1], ion exchange [4], electrochemical method [5,6], flotation [7,8], membrane filtration [9–12], liquid membrane separation [13], and adsorption method [14–17], have been used to manage heavy metal wastewater, these strategies present several disadvantages [9,15]. For example, in conventional chemical precipitation, emission standards are difficult to meet, a large amount of sludge is easily produced, and the heavy metal could be released and thus produce secondary pollution. With chelating–flocculation, the chelating flocculant cannot be

* Corresponding author at: School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China.

E-mail addresses: llh213@163.com, liulihualj@sina.com.cn (L. Lihua), 1546044226@qq.com (T. Li), 214909296@qq.com (G. Yang), 735857488@qq.com (Y. Wang), anpingxt@126.com (A. Tang), lyl931@126.com (Y. Ling).

https://doi.org/10.1016/j.jece.2017.11.046

Received 16 September 2017; Received in revised form 10 November 2017; Accepted 16 November 2017 Available online 21 November 2017 2213-3437/ © 2017 Elsevier Ltd. All rights reserved. recycled, and the cost is relatively higher than other methods. Ion exchange method is only suitable for low-concentration wastewater, and resin exchange capacity is limited. Moreover, the approach presents poor resistance to organic matter pollution and oxidation; it easily produces high concentrations of eluent and thus causes secondary pollution. The disadvantages of membrane filtration are high cost, complex process, membrane fouling, and low permeation flux. Flotation is of huge initial investment and requires expensive maintenance and operation. The electrochemical method offers the advantages of a fast process, good control, absence of chemicals, and relatively low sludge quantity, but the investment and power consumption are large. These disadvantages limit the practical applications of these approaches. Compared with other methods, adsorption is widely applied in the treatment of heavy metals because of its simple operation, high efficiency, and low cost [11,15,17-20]. However, numerous conventional adsorbents, such as activated carbons, molecular sieves, and porous polymers, show low adsorption efficiency and are difficult to prepare or modify, thus limiting their application in heavy metal wastewater treatment. Among adsorption materials, inorganic porous materials have recently become the subject of considerable interest because of its advantages of ion exchange, selective adsorption, and high chemical and biological stability. These materials have received considerable attention in the field of heavy metal wastewater treatment because of their large specific surface area; good chemical stability; and controllable structure, size, and composition. In addition, they possess nano- and microchannels that are adjustable and easily modified. At present, inorganic porous materials that are used to treat heavy metal wastewater primarily include mesoporous silica, such as SBA-15 [21], MCM-41 [22], MCM-48 [23], thiol-functionalized mesoporous silica [24], and thiol-functionalized SBA-15 [25]. Furthermore, mesoporous zirconium phosphonate hybrid materials [26], ordered macroporous titanium phosphate [27], Cu-exchanged ZnS nanoadsorbents [28], mesoporous magnetic iron oxide carbon coating materials [29], ordered mesoporous carbon materials [30], Al₂O₃/carbon composites [31], and tetragonal nanostructured zirconia-modified hematite mesoporous composites [32] are available. However, the previously mentioned mesoporous adsorption materials suffer from complex operation, high cost, and difficulty in synthesis, modification, and scale production. Porous calcium silicate is a type of porous inorganic silicate material synthesized using calcium hydroxide or calcium salt and silicate under certain conditions. Its application in water treatment is gaining increasing attention from the researchers because of its many distinctive properties, such as high whiteness, high specific surface area, porosity, and negative charge strength [33-35]. Porous calcium silicate is mainly used for the removal of phosphorus in wastewater [34,36-38], surface water treatment with low nutrient concentration [39], dibutyl phthalate adsorption [40], and fluoride recovery [41]. However, its application in heavy metal wastewater is rarely reported. Studies mainly included a mesoporous calcium silicate material (MCSM) from coal fly ash [42] and ultrathin calcium silicate hydrate nanosheets [43]. The former work only investigated the adsorption performance and preliminary isotherm and kinetics for Co(II) and lacked thermodynamic and kinetic parameters, whereas the latter study only investigated the preliminary adsorption effects for Cr³⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Pb^{2+} . In the research on modified calcium silicate application in heavy metal adsorption, chitosan-coated calcium silicate hydrate (CSH/chitosan) mesoporous microspheres were reported [44], but thermodynamic and kinetic parameters were lacking, such as enthalpy change (ΔH) , entropy change (ΔS) , Gibbs free energy (ΔG) , and activation energy of adsorption (E_a) .

In this study, a thiol-functionalized mesoporous calcium silicate (MCS-SH) was synthesized using post-grafting with calcium nitrate tetrahydrate and sodium metasilicate nonahydrate as raw materials, cetyl trimethyl ammonium bromide (CTMAB) as template, and (3-mercaptopropyl)trimethoxysilane (MPTMS) as modifying agent. The structure, morphology, and composition were characterized using X-ray

diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetry-differential thermal analysis (TG-DTA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDX). and Brunauer-Emmett-Teller (BET) surface analysis. Detailed experimental investigations on the adsorption isotherm and kinetics of MCS-SH for Cd^{2+} , Cu^{2+} , Pb^{2+} , and Cr^{3+} were conducted over a wide range of experimental conditions. This study aimed to investigate the adsorption performance of MCS-SH for heavy metals, obtain the corresponding thermodynamic and kinetic parameters, ascertain the adsorption mechanism, and thereby provide a fundamental basis for improvement and application. Results showed that MCS-SH possessed extremely high adsorption capacity and rapid adsorption ability for various heavy metal ions. Therefore, MCS-SH is an excellent adsorption material for the treatment of heavy metal wastewater.

2. Experimental

2.1. Materials

Calcium nitrate tetrahydrate was purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. Sodium metasilicate nonahydrate was purchased from Shantou Xilong Chemical Co., Ltd. CTMAB and toluene were purchased from Sinopharm Group Chemical Reagent Co., Ltd. MPTMS was purchased from Shanghai Aladdin Biological Technology Co., Ltd. Triethylenetetramine, ethylenediaminetetraacetic acid (EDTA), and anhydrous ethanol were obtained from Tianjin Fuchen Chemical Reagent Factory. Cadmium chloride and chromium sulfate were obtained from Shenyang Xinguang Chemical Factory. Lead nitrate enneahydrate, copper sulfate pentahydrate, hydrochloride acid, nitric acid, and sodium hydroxide were purchased from Tianjin Damao Chemical Reagent Co., Ltd. All reagents were of analytical grade and used as purchased. Deionized water was used in the experiments.

2.2. Preparation of MCS-SH

The synthetic route of MCS-SH is shown in Scheme 1.

The synthesis procedure was as follows. Sodium metasilicate nonahydrate (18.5 g) was dissolved completely into 300 mL distilled water under constant stirring for 1 h. CTMAB (0.925 g) was then added gradually to the solution according to the mass ratio of m(CTMAB):m(Na₂SiO₃·9H₂O) = 0.05:1. The white gel appeared gradually with the addition of CTMAB. Then, the solution was stirred for 1 h. Calcium nitrate solution, which was obtained by dissolving 15.4 g calcium nitrate tetrahydrate into 100 mL distilled water (in accordance with the 1:1 molar ratio of calcium nitrate tetrahydrate and sodium metasilicate nonahydrate), was added dropwise. With the addition of calcium nitrate tetrahydrate, a white glue gradually formed. The intermediate product (MCS) was obtained by filtering after a 5 h reaction, washing 3–4 times with distilled water, extraction for 24 h with anhydrous ethanol, and drying in a vacuum oven at 50 °C for 24 h.

Then, 2.5 g of the mesoporous calcium silicate (MCS) was dispersed into 40 mL toluene solution under constant stirring for 1 h. The dispersion was added with 5 mL MPTMS dropwise and then reacted for 24 h at 120 °C. The final product (MCS-SH) was obtained by filtering, washing with ethanol and distilled water three times sequentially, and then drying in a vacuum oven at 40 °C for 12 h.

2.3. Adsorption study

Adsorption studies were performed to evaluate the adsorption performance of MCS-SH for Cd^{2+} , Pb^{2+} , Cu^{2+} , and Cr^{3+} . Given the concentration range of some actual heavy metal wastewaters and similar heavy metal adsorption study samples, simulated heavy metal wastewater samples containing 25, 50, 75, 100, 125, and 150 mg L⁻¹ Cd²⁺, Download English Version:

https://daneshyari.com/en/article/6664252

Download Persian Version:

https://daneshyari.com/article/6664252

Daneshyari.com