Microporous and Mesoporous Materials 236 (2016) 250–259

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Optimal synthesis of amino-functionalized mesoporous silicas for the adsorption of heavy metal ions

Shiyou Hao [a], Antonio Verlotta [b], Paolo Aprea [b], Francesco Pepe [c, *], Domenico Caputo [b], Weidong Zhu [a, **]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Xingzi College & Institute of Physical Chemistry, Zhejiang Normal University, 321004 Jinhua, People's Republic of China

[b] ACLabs–Applied Chemistry Laboratories, Department of Chemical, Materials and Production Engineering, University Federico II, P.le V. Tecchio 80, 80125 Naples, Italy

[c] Department of Engineering, University of Sannio, Piazza Roma 21, 82100 Benevento, Italy

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form
3 September 2016
Accepted 7 September 2016
Available online 13 September 2016

Keywords:
Amino-functionalized material
Mesoporous silica
Heavy metal
Multi-component adsorption
Selective adsorption

ABSTRACT

Amino-functionalized mesoporous silicas (AFMS) were synthesized by a neutralization route using the anionic surfactant dodecanoic acid (DAA) as structure-directing agent (SDA), aminopropyltrimethoxysilane (APTMS) as co-structure-directing agent (CSDA), and tetraethoxysilane (TEOS) as silicon source. The synthesis parameters, which affect the structural properties and the amino loadings of the resultant AFMS, were optimized. Various techniques, such as FT-IR, XRD, N_2 adsorption-desorption, and TEM, were used to characterize the synthesized AFMS. The selective removal of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} from aqueous solutions in single-, binary-, ternary-, and quaternary-component systems by the synthesized AFMS was thoroughly investigated. The measured single-component adsorption isotherms of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} on the AFMS optimally synthesized can be well described by the Sips model, in which the extracted adsorption capacities are 2.34, 2.86, 1.71, and 1.36 mmol/g (0.149, 0.593, 0.192, and 0.089 g/g) for Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}, respectively, higher than those on other adsorbents reported in the literature. Furthermore, Pb^{2+} and Cu^{2+} can be more selectively removed by the synthesized adsorbent, compared to Cd^{2+} and Zn^{2+}, confirmed by the results on the multi-component adsorption.

1. Introduction

It is well known that heavy metals present high toxicity to the ecosystem and human beings, and tend to be accumulated in living tissues [1]. Heavy metals, such as Pb, Cu, Cd, and Zn, are the main toxic pollutants in industrial wastewater, and they have been found to be the major contaminants of surface and ground water, causing various diseases and disorders. Among heavy metals, Pb is one of the most toxic elements, even at rather low concentrations, causing mental disturbance, retardation, and semi-permanent brain damage [2]. Although Cu is an essential nutrient for humans, animals, and microorganisms, excess Cu may produce many toxic and harmful effects in living organisms [3]. Typically, itching and dermatitis, gastrointestinal diseases, alteration of liver and kidney functionalities, Wilson disease, hypoglycemia, and dyslexia can be caused by excess Cu [4]. Exposure to high levels of Cd has been related to respiratory, cardiovascular and renal problems, and furthermore to the notorious "itai itai" disease [5]. The accumulation of Zn in the human body can cause dehydration, electrolyte imbalance, stomach ache, nausea, dizziness and incoordination in muscles [6].

In general, the effluents from several industrial processes are characterized by the simultaneous presence of some heavy metal ions with significant concentrations. In particular, Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} can be simultaneously present in wastewaters from petroleum refining, fertilizer production, foundries, and pulp and paper production [7]. Consequently, it is necessary to find efficient methods to remove these heavy metals from the environment, even when present at very low concentrations.

* Corresponding author.
** Corresponding author.
E-mail addresses: francesco.pepe@unisannio.it (F. Pepe), weidongzhu@zjnu.cn (W. Zhu).

http://dx.doi.org/10.1016/j.micromeso.2016.09.008
1387-1811/

Compared with other technologies for the removal of heavy metal ions, such as ion exchange, precipitation, membrane separation, reverse osmosis, sedimentation, and electro-dialysis [8,9], the adsorption-based separation is a highly-efficient, cost effective method [10,11]. Up to now, many adsorbents, such as activated carbons [12], amino-functionalized materials [13], and biomass materials [14] etc., have been developed to remove heavy metal ions. Among these adsorbents, amino-functionalized mesoporous silicas (AFMS) appear to be particularly promising, due to their large adsorption capacities and high uptake rates for heavy metal ions [15]. Recently, the AFMS synthesized by an anionic surfactant-templated method have attracted much attention due to the extremely regular arrangement of the amino groups introduced by the co-structure directing method [16,17]. Moreover, anionic surfactants are used in greater volume than any other surfactants because of their highly potent detergency and low cost of manufacture [18], which makes the anionic surfactant-templated method more advantage in full scale application. Currently, both neutralization and double decomposition routes are applied to the preparation of AFMS, but the neutralization route is simpler, because organic acids used as anionic surfactants can directly interact with the free amino groups in co-structure-directing agent (CSDA), thus avoiding addition of another acid (such as hydrochloric acid) to protonate the free amino groups in CSDA during the double decomposition process [18]. In general, the amino content, especially on the surface of mesopores, and the textural properties, such as pore size, specific surface area, and pore volume, play an important role in the adsorption of heavy metal ions on AFMS. Although the neutralization method has been used to prepare AFMS, the optimization of the synthesis parameters, which significantly affect the amino content and textural properties, has not been carried out in detail.

To the best of our knowledge, although many studies have been focused on the single-component adsorption of Pb^{2+} and Cu^{2+} on AFMS, few have examined the binary adsorption of Pb^{2+} and Cu^{2+} as well as the effects of co-existing metal ions such as Zn^{2+} and Cd^{2+} on the adsorption of Pb^{2+} and/or Cu^{2+} [19–21]. In fact, the chemical composition of heavy metal ions in the polluted wastewater is rather complicated, because more than one contaminant are often detected at different concentrations. Therefore, it is important to characterize the adsorption behaviors of heavy metal ions on an adsorbent toward multi-component solutions.

In the present study, a series of AFMS were prepared by the neutralization route. In order to obtain AFMS with high amino contents and desired textural properties, the synthesis parameters were optimized. Then we investigated the single-, binary-, ternary-, and quaternary-component adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} on the optimally synthesized AFMS sample as adsorbent. In particular, we focused on investigating the competitive adsorption effects on the removal efficiencies of the heavy metal ions from their aqueous solutions.

2. Experimental

2.1. Chemicals and synthesis

Dodecanoic acid (DAA), tetraethoxysilane (TEOS), and aminopropyltrimethoxysilane (APTMS) were purchased from Merck, Acros, and Aldrich, respectively. $Cu(NO_3)_2\cdot 3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2\cdot 3H_2O$, $Cd(NO_3)_2\cdot 4H_2O$, methanol, ethanol, propanol, butanol, ethanol amine, NaOH, sodium ethylenediaminetetraacetic acid (EDTA), and 37% fuming hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai. All aqueous solutions were prepared at room temperature using deionized water as solvent. 0.1 M single-component Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} aqueous solutions were prepared from the precursors $Cu(NO_3)_2\cdot 3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2\cdot 3H_2O$, and $Cd(NO_3)_2\cdot 4H_2O$, respectively, and the obtained solutions were used as atomic absorption spectrometry standards and as stock solutions. The single-component solutions with different concentrations for adsorption experiments were then prepared by dilution of the stock solutions just prior to use, and their pH values were adjusted to the required ones using 0.1 M HCl or 0.1 M NaOH solution.

AFMS were prepared by a neutralization method [18]. The typical synthesis process was carried out as follows: 2 mmol (0.4013 g) of DAA was dissolved into a mixture of 30 ml H_2O and 30 ml alcohol (one among methanol, ethanol, propanol, and butanol) at 60 °C. To the above-prepared solution, a mixture of 3.0 ml TEOS and x ml ($0.2 \leq x \leq 3.0$) APTMS was added drop by drop under vigorous stirring in a period of 30 min. In order to investigate the effects of the alcohol composition on the mesostructure of the resultant AFMS, different water/alcohol ratios were used while keeping the total volume of water and alcohol constant as 60 ml. The resulting mixture was then aged hydrothermally without agitation in a closed 100 ml reaction kettle placed in an oven at 80 °C for 2 days. The product was filtered and the solid was washed with deionized water several times. The washed solid was then dried for 600 min at 80 °C prior to a further analysis or use.

The surfactant in the dried sample was removed by an extraction method. Typically, 1.0 g of the dried solid was dispersed in a solution containing 25.2 g of 3.3 M ethanolamine and 100 ml ethanol at room temperature under agitation. Afterwards, the mixture was refluxed at 90 °C for 720 min. The solid was then recovered by filtration, washed with ethanol, and dried. The above extraction procedure was repeated twice.

2.2. Characterization

The FT-IR spectra were recorded on a Nicole Nexus 670 spectrometer with a resolution of 4 cm^{-1} using a KBr compression method. The powdered X-ray diffraction (XRD) patterns were performed on a PHILIPS PW3040/60 powder diffractometer using Cu$K\alpha$ radiation (λ = 0.15406 nm). The morphology and particle sizes of the synthesized samples were examined with transmission electron microscopy (TEM) technique. The TEM images were obtained on a 2100 JEOL instrument working at 200 kV. The nitrogen contents of the synthesized AFMS samples were measured by a Vario ELIII elemental analyzer. The adsorption-desorption isotherms of N_2 on AFMS at −196 °C were performed on a Micromeritics ASAP 2020 apparatus, and the specific surface areas were then calculated using the multiple-point Brunauer-Emmett-Teller (BET) method in the relative pressure range of $p/p_0 = 0.05–0.3$. The pore size distribution (PSD) curves were computed using the Barrett-Joyner-Halenda (BJH) method and the average pore sizes were obtained from the peak positions of the PSD curves. Zeta potential analysis was conducted in ethanol solvent under a Malvern Zetasizer Nano ZS90 with MPT-2 autotitrator.

2.3. Adsorption

2.3.1. Single-component adsorption

0.02 g of the dried AFMS adsorbent was suspended into 20 ml of 2.0 mM $Cu(NO_3)_2$ solution, also applied to $Pb(NO_3)_2$, $Zn(NO_3)_2$, and $Cd(NO_3)_2$ solutions having a concentration of 2.0 mM, with an initial pH value of 5.07, under vigorous stirring at 25 °C for different periods ranging from 2 to 120 min. The mixture was then quickly