



Postsynthetic modification of copper terephthalate metal-organic frameworks and their new application in preparation of samples containing heavy metal ions



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ARTICLE INFO

Article history:

Received 25 November 2014

Received in revised form

9 February 2015

Accepted 15 February 2015

Available online 25 February 2015

Keywords:

Copper terephthalate metal-organic frameworks

Postsynthetic modification

Heavy metal ions

Tea

ABSTRACT

In this paper, a novel thiol-functionalized porous metal-organic frameworks (MOFs), namely thiol-functionalized $[\text{Cu}_4\text{O}(\text{BDC})_n]$ (BDC = Terephthalic acid), was synthesized. The successful modification was certified by Fourier transform infrared spectroscopy and X-ray powder diffraction. The modified MOFs were further characterized by scanning electron microscopy and thermogravimetric measurements. The adsorption of the modified MOFs for both common and heavy metals was investigated. The modified MOFs showed remarkable and selective adsorption for four heavy metals (Hg^{2+} , Cr^{6+} , Pb^{2+} , Cd^{2+}), especially for Hg^{2+} . The dynamic and static adsorption tests showed that the modified MOFs exhibited high adsorption capacity and selectivity for Hg^{2+} , and offered a fast kinetics for the adsorption of Hg^{2+} . The as-synthesized modified MOFs were successfully used as adsorbents to selectively enrich the above four heavy metals in preparation of a tea sample. The results indicate that functionalized MOFs by postsynthetic modification have a promising potential in preparation of samples containing heavy metal ions.

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1. Introduction

Heavy metal pollution in soil is one of the main environmental global hazards and they may easily enter the human food chain through the crops. Heavy metals are stable in environment and their contents in agricultural products are far beyond the safety standards. They accumulate in human bodies gradually and cannot be metabolized, which can affect human health. Thus, the monitoring of heavy metals in agricultural products is very important [1]. Traditionally, atomic absorption spectrometry (AAS) is a powerful tool for the determination of heavy metals. A sample preparation is usually needed prior to their detection. Many pretreatment methods for determination of heavy metals in samples, including liquid–liquid extraction, electrodeposition, chelation, and magnetic separation, etc, have been reported [2–5]. However, these methods suffer from issues involving complex operations, low efficiency. Recently, solid phase

extraction (SPE) shows greater potential in heavy metals sample preparation. Several kinds of materials like organic copolymer [6], magnetic nanoparticles [7], nanoporous silica [8] and Portland cement and zeolite [9], were used as adsorbents of SPE to remove heavy metals. However, these materials also have some disadvantages such as lack of selectivity and relatively poor adsorption capacities for heavy metals due to their structural defects.

In last few decades, metal-organic frameworks (MOFs) have emerged as promising materials in the design of advanced multifunctional materials owing to their unique structures [10–14]. The most attractive features of MOFs are porous and large surface areas. Based on these advantages, MOFs are widely used in gas storage [15], catalysis [16,17] and removal of hazardous gas [18,19]. In recent years, some interests have been focused on the removals of heavy metal ions in water with MOFs [20,21]. The studies showed that the adsorption performance of MOFs for heavy metal ions was undesirable. Consequently, postsynthetic modification (PSM) method was developed to improve the adsorption efficiency of MOFs for heavy metal ions. Zou et al. synthesized HKUST-1 first, and then functionalized the MOFs with phosphotungstic acid to

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form HKUST-1-@H₃PW₁₂O₄₀. The modified MOFs showed selective adsorption for heavy metal ions [20]. Most notably, the thiol-functionalized [Cu₃(BTC)₂]_n prepared by Ke et al. had a remarkable adsorption capacity for Hg²⁺ [21]. Up to date, there has been no report about the application of MOFs as adsorption material in the pretreatment of samples containing heavy metals.

Herein, [Cu₄O(BDC)]_n, a crystalline, highly porous copper terephthalate MOF, [Cu₄O(BDC)]_n, (BDC = Terephthalic acid) was thiol-functionalized for the first time by a simple, efficient PSM method. The functionalized MOF showed selective adsorption for heavy metal ions, and was finally used as the adsorbent to prepare a tea sample prior to the detection of Hg²⁺, Cr⁶⁺, Pb²⁺ and Cd²⁺ in the tea sample.

2. Experimental section

2.1. Materials

Terephthalic acid (H₂BDC) and copper nitrate trihydrate were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Dithioglycol and mercuric chloride were purchased from Xiya Reagent Co. Ltd. (Chengdu, China). N, N-dimethylformamide (DMF) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and dried before use. Other chemicals were purchased commercially and used without further treatment.

2.2. Physical measurements

The scanning electron microscopy (SEM) images were taken using an S-3400N II scanning electron microscopy (Hitachi, Japan). The thermogravimetric (TGA) measurements were performed using a Pyris 1 DSC unit (PerkinElmer, USA). Fourier transform infrared spectra (FT-IR) were recorded on a Tensor 27 FT-IR instrument (Bruker, Germany). The powder X-ray diffraction (XRD) patterns of the samples were collected using a X'TRA diffractometer (ARL, Switzerland) and using CuK α radiation (40 kV, 40 mA) at the desired temperature. The concentrations of all metal ions (except for Hg²⁺) were determined with a Contra AA 700 atomic absorption spectrophotometer (AAS) (Jena, Germany). The concentrations of Hg²⁺ were determined with an AFS-930 atomic fluorescence spectrometry (AFS) (Jitian, China). The tea sample was ashed in GSL-1100X high-temperature vacuum furnace (KMT, China).

2.3. Synthesis of thiol-functionalized [Cu₄O(BDC)]_n

[Cu₄O(BDC)]_n was prepared according to the reported method with some modification [22]. 0.4832 g of copper nitrate trihydrate and 0.3324 g of terephthalic acid were dissolved in 40 mL of DMF. The mixture was transferred to a teflon flask after magnetic stirring for 30 min. The flask was then sealed and put in an oven at 100 °C for 24 h. Solvothermal reaction of copper nitrate trihydrate and terephthalic acid led to the formation of blue precipitated crystals. After centrifugation, the crystals were washed with DMF for several times, and the yield of 82% was obtained. The crystals were dried at 150 °C overnight before use.

To synthesize thiol-functionalized [Cu₄O(BDC)]_n, 400 mg of as-synthesized [Cu₄O(BDC)]_n was suspended in 20 mL of dehydrated alcohol. And then 6 mL of dithioglycol in dehydrated alcohol (0.24 mol/L) was added to the suspension. The mixture was then stirred magnetically at room temperature for 24 h. The blue crystals were collected by filtration and washed with dehydrated alcohol for several times. The product was dried at 100 °C overnight before use.

2.4. Selectivity of adsorption of the thiol-functionalized [Cu₄O(BDC)]_n for heavy metals

Six common metal ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe³⁺, Zn²⁺) were selected as controls to investigate the adsorption capacities and selectivity of thiol-functionalized [Cu₄O(BDC)]_n for four heavy metal ions (Hg²⁺, Cr⁶⁺, Pb²⁺, Cd²⁺). The concentration of each metal ion solution was 0.40 mg/mL. 10 mg of the thiol-functionalized [Cu₄O(BDC)]_n was added to 5 mL of the above mentioned metal ion solutions. The suspension was shaken at room temperature for 1 h, and then centrifuged. The concentration of Hg²⁺ was detected by AFS and the other metal ions were detected by AAS.

2.5. Adsorption performance of the thiol-functionalized [Cu₄O(BDC)]_n for Hg²⁺

Typically, 10 mg of the thiol-functionalized [Cu₄O(BDC)]_n was added to 5 mL of the Hg²⁺ solutions with a series of concentrations, respectively. The suspension was then shaken at room temperature for 1 h, and then centrifuged. The concentrations of Hg²⁺ in the solutions were tested by AFS. As a control, the MOFs without modification were performed in the same way.

2.6. Application

A tea sample was ground and weighed accurately after dried at 105 °C overnight. The powder of the sample was ashed in high-temperature vacuum furnace at 500 °C for 3 h. After cooled to room temperature, the ash was digested with HCl (36%), and then diluted to 25 mL with deionized water. The pH of the solution was adjusted to pH 7.0 with 1 mol/L NaOH before adsorption. The adsorption experiment was measured according to the procedure in Section 2.4.

After adsorption, the suspension was centrifuged and the crystals were distributed with 5 mL of 2 mmol/L EDTA solution, and shaken at room temperature for 10 min. Then, the suspension was centrifuged and the concentrations of the four heavy metal ions (Hg²⁺, Cr⁶⁺, Pb²⁺, Cd²⁺) desorbed by EDTA solution were tested. The concentration of Hg²⁺ was detected by AFS and the other metal ions were detected by AAS.

3. Results and discussion

3.1. Characterization

The crystal size and morphology of the MOFs were determined by SEM. The crystals were tetrahedron, which was consistent with the literature [22], and had an average size of 5 μ m with a smooth surface as shown in Fig. 1a. However, the surface of MOFs after PSM got rougher than that of the original MOFs, but the shape and size almost had no changes (Fig. 1b). There was some crystalline defect after modification as a result of the addition of dithioglycol. This phenomenon was also recorded by Ke et al. [21].

The crystals of the MOFs before and after PSM were evaluated by XRD, and the result is shown in Fig. 2. The XRD pattern of the as-synthesized [Cu₄O(BDC)]_n crystals (Fig. 2a) coincided well with the literature data [22], suggesting the successful formation of the desired material. The diffraction peaks of the thiol-functionalized [Cu₄O(BDC)]_n (Fig. 2b) were almost the same as that of the [Cu₄O(BDC)]_n, which indicated that the crystals of [Cu₄O(BDC)]_n were retained after modification with dithioglycol.

TGA analysis was performed using the powdered MOFs under nitrogen atmosphere. The TGA result of the as-synthesized [Cu₄O(BDC)]_n (Fig. 3a) showed that the first mass loss was in the

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