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Analytical Methods

Preparation of magnetic metal organic frameworks adsorbent modified with mercapto groups for the extraction and analysis of lead in food samples by flame atomic absorption spectrometry

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ABSTRACT

A novel magnetic metal organic frameworks adsorbent modified with mercapto groups was synthesized and developed for extraction and spectrophotometric determination of trace lead. The adsorbent was characterized by Fourier transforms infrared spectrometer, X-ray diffraction, scanning electron microscopy and vibrating sample magnetometry. The results indicated the adsorbents exhibited high adsorption capacities for lead due to the chelation mechanism between metal cations and mercapto groups. Meanwhile, the lead sorption onto the adsorbents could be easily separated from aqueous solution using a magnetic separation method. Under the optimal conditions, a linear calibration curve in the range from 1 to 20 μg L^{-1} was achieved with an enrichment factor of 100. The limits of detection and quantitation for lead were found to be 0.29 and 0.97 μg L^{-1}, respectively. The developed method was successfully applied to the determination of trace amounts of lead in food samples and certified reference material with satisfactory results.

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1. Introduction

Environmental pollution nature of heavy metals and metalloids has received considerable attention. Among these heavy metals, lead is critical for human health. Due to its low excretion rate, lead can accumulate both in the soft tissues and the bones and thus is poisonous to the nervous system and causes brain disorders (Blake et al., 2001; Rodriguez, Bolbot, & Tothill, 2004; Shetty et al., 2003). The intake of lead can occur in human by breathing air, drinking water, and eating food. However, as the levels of lead in food and environmental samples are low, there is a crucial need for the enrichment and preconcentration of trace elements before their analysis (Ferreira et al., 2007; Sitko, Gliwinska, Zawisza, & Feist, 2013).

Solid-phase extraction (SPE) is a widely used approach for sample pretreatment due to its high recovery, short extraction time, high enrichment factor, and ease of automation (Fornieles, Garcia de Torres, Vereda Alonso, & Cano Pavón, 2013; Parham, Pourreza, & Rahbar, 2009; Yang, Liu, Liu, Chen, & Wang, 2012). The choice of appropriate adsorbent is an important factor to obtain good recovery and high enrichment factor in SPE procedure. Recently, numerous adsorbents including activated carbon, SBA-15 silicas, mesoporous manganites and mesoporous titania–silica–phosphonate have been employed as adsorbents in SPE techniques due to their unique large surface areas, well-defined pore sizes, high pore volume and great diversity in surface functionalization (Chouyyok et al., 2010; Lin, Ma, & Yuan, 2011; Liu, Hidajat, Kawi, & Zhao, 2000; Nandi, Sarkar, Seikh, & Bhaumik, 2011). However, the application of such adsorbents often requires post-treatment after adsorption. Sometimes the complete separation and removal of adsorbents from aqueous solutions can be difficult and can cause additional environmental problems. Magnetic solid-phase extraction (MSPE) using magnetic composites as adsorbents are one of the latest developments in SPE techniques. The inherent characteristic of magnetic properties ability has promoted an increasing application of magnetic composites in many fields (Daneshvar Tarigh & Shemirani, 2013; Huo & Yan, 2012; Mashhadizadeh, Amoli-Diva, Shapouri, & Afruzi, 2014). For MSPE, the dispersed magnetic composites can be separated from the matrix quickly in a magnet, and redispersed in the eluent once the external field is removed.

Metal organic frameworks (MOFs), forming by the coordination of a metallic center and an organic ligand, have proved to be a new class of materials. The high porosity and specific surface of MOFs has directed their potential applications toward catalysis, sensors, separation, and drug delivery (Dhakshinamoorthy, Alvaro, &

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Garcia, 2011; Huxford, Rocca, & Lin, 2010; Petit, Levasseur, Mendoza, & Bandosz, 2012; Yu et al., 2014). Moreover, MOFs also show great promise in the analytical applications such as the capture of heavy metal ions by the chelation coordination effect between metal ions and functional group in the linker (Fang et al., 2010; He et al., 2013; Yang et al., 2013). However, the use of functional linkers is limited by the conventional solvothermal procedure of MOFs. Postsynthetic modification has been utilized as a powerful tool for introducing functionality to MOFs by covalent reactions. The incorporation of functional groups on the linking ligands can provide an opportunity to develop MOFs with a variety of functionalities (Bernt, Guillerm, Serre, & Stock, 2011; Gadzikwa et al., 2008; Jung et al., 2011).

Herein, we report the preparation of mercapto groups modified magnetic metal organic frameworks (SH-Fe_3O_4/$Cu_3(BTC)_2$) adsorbents and the potential application for the extraction of trace heavy metal ions followed by flame atomic absorption spectroscopy (FAAS). The adsorbent possesses large a surface area because of the nanometer size. The superparamagnetic Fe_3O_4 contributes to the rapid separation of the adsorbent from the matrix solution. Mercapto groups provide more bonding sites for heavy metals. Based on these considerations, extracting trace heavy metals from water solutions can be readily achieved. To the best of our knowledge, no research on the application of SH-Fe_3O_4/$Cu_3(BTC)_2$ composites for extraction and determination of trace lead in food samples and certified reference material has been reported.

2. Experimental

2.1. Reagents and materials

Copper nitrate, ferrous chloride, ferric chloride, 1,3,5-benzene tricarboxylic acid (H_3BTC, 98%), dithioglycol, anhydrous ethanol, dimethylformamide (DMF), sodium hydroxide, hydrogen peroxide, lead nitrate, ammonium hydroxide, perchloric acid and nitric acid were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The lead stock solution of 1000 mg L^{-1} was prepared by dissolving 33.12 g of $Pb(NO_3)_2$ in 100 mL deionized water. Working standard solutions of lead were prepared by stepwise dilution of the stock solution with deionized water. Reference materials GBW10017 (Milk powder) was purchased from the BHH Biotechnology Co., Ltd (Beijing, China). Rice, pig liver and tea leaves were purchased from the local market. Water sample was collected from the laboratory. Double deionized water (18 MΩ cm) was used throughout the experiments.

2.2. Apparatus

The FTIR spectra were collected using a Cary 610/670 infrared microspectrometer (America Varian). The powder X-ray diffraction (XRD) patterns were collected with a D8 Advance X-ray diffractometer (Bruker Co., Germany) from 5° to 50°. The morphology of the composites was recorded by Hitachi S-4800 microscope (Japan) with ethanol spitting and then sonicated for 30 min. The magnetic property was analyzed by using a vibrating sample magnetometer (VSM, LDJ9600). An atomic absorption spectrometer (AEEnit 700) with flame was used for testing lead and the instrumental parameters were adjusted according to the manufacturer recommendations. A continuous flow atomic fluorescence spectrometer (AFS-3100) was employed for the method validation. For atomic fluorescence spectrometer, the sample solutions were analyzed under the following conditions: lamp current (30 mA), atomizer height (8 mm), negative high voltage of the PTM (300 V), flow rate of carrier gas (400 mL min^{-1}), flow rate of shield gas (900 mL min^{-1}), injection volume (1 mL), read mode (peak area). A permanent magnet was used for the isolation of the analytes from the complicated matrix.

2.3. Synthesis of Fe_3O_4

The magnetic nanoparticles were prepared according to the previous report with small modifications (Kang, Risbud, Rabolt, & Stroeve, 1996). 10.8 g $FeCl_3 \cdot 6H_2O$ and 4.2 g $FeCl_2 \cdot 4H_2O$ were completely dissolved in 25 mL of HCl (6 mol L^{-1}). Then 50 mL NH_4OH (25% wt) was quickly added to the above aqueous solutions at 60 °C for 30 min. After cooling to ambient temperature, the black precipitation was separated by a magnet and further washed with distilled water and dried at 60 °C for 6 h. N_2 was used as the protective gas throughout the experiment.

2.4. Synthesis of Fe_3O_4/$Cu_3(BTC)_2$

1.0 g H_3BTC dissolved in 80 mL mixture solutions (DMF: anhydrous ethanol = 1:1) was transferred into a 250 mL flask. Under magnetic stirring, 0.15 g Fe_3O_4 dissolved in 20 mL anhydrous ethanol was added and refluxed for a while at 70 °C. Afterwards, 2.0 g $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in 40 mL deionized water was slowly added to the above solution and this was refluxed for 4 h. After cooling to ambient temperature, the product was filtered off, washed several times with deionized water (50 mL) and ethanol (10 mL), and then dried at 120 °C for 10 h.

2.5. Synthesis of SH-Fe_3O_4/$Cu_3(BTC)_2$

0.11 g prepared Fe_3O_4/$Cu_3(BTC)_2$ sample was dried at 150 °C for 12 h, and then suspended in 10 mL anhydrous toluene. 0.6 mL dithioglycol solution (0.24 mol L^{-1}) was added into the mixture solution and stirred 24 h. Finally, the blue-green powder was collected by filtration, washed with 15 mL ethanol five times, and dried 24 h at room temperature.

2.6. Sample preparation

(1) 10 g of rice sample was triturated and homogenized. Then a portion of 3.0 g was dried in an oven at 110 °C to constant weight. The dried sample was placed in a furnace and heated to 450 °C, and concentrated nitric acid was added dropwise until white ashes appeared. After that, the sample was dissolved in 1 mL 1 mol L^{-1} nitric acid and diluted to 10 mL with deionized water. (2) Pig livers were heated in an oven at 80 °C for 3 h. After drying, 1.0 g sample was dissolved 5 mL of nitric acid and transferred into a digestion tube at room temperature overnight. Then the tube was heated at 160 °C until the contents nearly dried. After cooling, 2 mL perchloric acid was added, and the contents were further heated to dryness at 210 °C. Finally the residue was dissolved with 10 mL deionized water when the tube was cooled down. (3) Water sample was filtered using a 0.45 μm filter prior to analysis. (4) 1.0 g of tea leaves was added in a solution including 5 mL of concentrated HNO_3 and 2 mL of 30% H_2O_2. Then the mixture was transferred into a 10 mL flask, and heated 200 °C for 20 min. After cooling to the room temperature, the samples were transferred to a 50 mL volumetric flask and diluted to the mark. (5) 1.0 g certified reference material GBW10017 (milk powder) was carbonized in 10 mL concentrated H_2SO_4 with another 10 min heating. After cooling, the sample was dissolved in 15 mL 1 mol L^{-1} HNO_3 and diluted to 100 mL with deionized water.

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