Journal of Chromatography A, xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Preparation of porous zinc ferrite/carbon as a magnetic-assisted dispersive miniaturized solid phase extraction sorbent and its application

Shujun Xia[a], Zhixiong Cai[a], Jing Dong[a], Shuya Wang[a], Yiru Wang[a,*], Huaizhi Kang[c], Xi Chen[a,b,**]

[a] Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
[b] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, Fujian 361005, China
[c] Pen-Tung Sah Institute of Micro-Nano Science and Technology of Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Received 30 January 2018
Received in revised form 17 June 2018
Accepted 1 July 2018
Available online xxx

Keywords:
M-DμSPE
Organochlorine pesticide
$ZnFe_2O_4$/carbon

ABSTRACT

In this study, porous $ZnFe_2O_4$/carbon, derived from Zn-Fe zeolitic imidazolate framework (Zn-Fe-ZIF), was employed as a novel sorbent for magnetic-assisted dispersive miniaturized solid phase extraction (M-DμSPE). The Zn-Fe-ZIF derived magnetic porous $ZnFe_2O_4$/carbon was easily prepared using a one-pot solvothermal method, and its morphology, structure and magnetic characteristics were evaluated via scanning electron microscopy, powder X-ray diffraction, Raman spectroscopy and vibrating sample magnetometry. The extraction ability of $ZnFe_2O_4$/carbon is evaluated by different kinds of compounds including organochlorine pesticides, pyrethroid insecticides, aldehydes, nerolidol, benzoic acid and sorbic acid. A M-DμSPE method was developed for the analysis of organochlorine pesticides. Several parameters affecting the extraction efficiency were systematically investigated. The calibration curves ranged from 0.05 to 100 ng g^{-1} and the limits of detection were 0.005–0.3 ng g^{-1}. The intra-day and inter-day relative standard deviations were lower than 2.3 and 5.2%. The recoveries of spiked organochlorine pesticides were in the range of 86.1–109.4%.

1. Introduction

Sample pretreatment plays a key role in the whole analytical procedure, and solid phase extraction (SPE) is a commonly used sample pretreatment approach. Magnetic-assisted dispersive miniaturized solid phase extraction (M-DμSPE) is an SPE-based method, which has drawn a great deal of attention in the field of sample pretreatment. The nature of M-DμSPE endows it with the benefit of time saving, ease of operation and excellent extraction efficiency. Suitable sorbents can determine their affinity to the target analytes, thus improving the extraction capability [1,2].

The magnetic sorbents used in M-DμSPE have included Fe_3O_4 nanoparticles [3], magnetic carbon nanotubes [4,5], magnetic graphene [6], magnetic metal-organic frameworks (MOFs) [7] and so on. In general, functionalized Fe_3O_4 nanoparticles have been widely used in the magnetic separation process for the improvement of the stability and dispersity. However, the time-consuming synthesis of the nanoparticles needs several steps. Therefore, it is desirable to develop an efficient sorbent with a simple and rapid synthesis method.

A new member of highly porous carbon materials and composites derived from MOFs, MOFs-derived carbons (MDCs), have drawn a great deal of attention in various fields, such as catalysis, drug delivery, electronics, gas storage and adsorption [8–12]. Compared to the conventional materials, MDCs exhibit larger surface area, higher hierarchical porosity, more excellent electron mobility, and more extraordinary thermal and chemical stability, which make them a promising candidate for efficient enrichment [13]. Zinc ferrite ($ZnFe_2O_4$), an important member of the magnetic nanomaterials, is of great interest due to its advantages of excellent

* Corresponding author at: Department of Chemistry, Xiamen University, No. 422, Siming South Road, Xiamen, Fujian 361005, China.
** Corresponding author at: Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.
E-mail addresses: yrwang@xmu.edu.cn (Y. Wang), xichen@xmu.edu.cn (X. Chen).

https://doi.org/10.1016/j.chroma.2018.07.001
0021-9673/

magnetic, electrical, optical and catalytic properties [14]. Furthermore, the high surface area of $ZnFe_2O_4$ makes it possible to improve the adsorptive efficiency [15]. In general, the surface modification of magnetic particles is an essential way to extend their practical applications. $ZnFe_2O_4$ magnetic particles can be introduced into nanoporous three dimensional graphene, thus creating a magnetic porous carbon material that has excellent adsorption capability for nine bisphenol analogs from a water sample [16]. The hybrid materials of $ZnFe_2O_4$ and MDCs present a high specific surface area, and possess sufficient magnetism. Zn-Fe zeolitic imidazolate framework (Zn-Fe-ZIF) is expected to be a highly interesting precursor to prepare MOF-derived carbon materials, because Zn-Fe-ZIF (2-imidazole as organic linkers and zinc and ferric ions as metallic nodes) derived carbon composites can be easily gained in one-step synthesis, incorporating magnetic property and the advantages of porous carbon. Furthermore, the crystalline ZIFs can be transformed into the proposed product using a simple direct calcination process, which enhances their potential applications in the field of adsorption. Compared with other magnetic sorbents, this synthesis method is easier and more convenient without layer-by-layer assembling or a template process [17–19].

In this study, magnetic porous $ZnFe_2O_4$/carbon was synthesized using one-pot solvothermal and direct pyrolysis method, and its morphology, structure and magnetic characteristics were evaluated via scanning electron microscopy, powder X-ray diffraction, Raman spectroscopy and vibrating sample magnetometry. Organochlorine pesticides, pyrethroid insecticides, aldehydes, nerolidol, benzoic acid and sorbic acid were chosen as model analytes to evaluate the extraction ability of $ZnFe_2O_4$/carbon. Additionally, the prepared magnetic dispersive material was applied to the determination of organochlorine pesticides in fresh pepper samples to evaluate the tolerance of $ZnFe_2O_4$/carbon composites in complex sample matrixes.

2. Experimental

2.1. Chemicals and reagents

Organochlorine pesticides (o, p'-DDT, p, p'-DDE, chlordane, heptachlor, lindane, aldrin) were purchased from China Standard Technology Development Corporation (Beijing, China). All analytical grade reagents, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), zinc oxide (ZnO), N, N-dimethylformamide (DMF) and ethanol were from the National Medicines Corporation (Shanghai, China). 2-Methylimidazole was obtained from the Aladdin Reagent Company (Shanghai, China). Iron(III) acetylacetonate and terephthalic acid were obtained from Sigma (Shanghai, China). The stock solutions of organochlorine pesticides and pyrethroid insecticides were prepared by diluting a 100 mg L^{-1} solution of each compound to 10 mg L^{-1} using acetone (HPLC grade). 1000 mg L^{-1} stock solutions of aldehydes, nerolidol, benzoic acid and sorbic acid were prepared by dissolving these compounds in methanol (HPLC grade). Ethyl acetate, acetone and hexane were purchased from Tedia (Ohio, USA). Pure water from a Millipore Autopure WR600 A system (Millipore Ltd., USA, 18.2 MΩ) was used throughout the experiments. All the solutions mentioned above were sealed and stored at 4 °C. Pepper samples were collected from local supermarkets, and pepper has a lot of fat or oil, which may result in high residue of persistent organic pollutants like organochlorine pesticides.

2.2. Instrumentation

The determination of organochlorine pesticides and pyrethroid insecticides were carried on a Shimadazu GC-2010 gas chromatograph (GC) system equipped with an electron capture detector (ECD), and in the determination of aldehydes, nerolidol, benzoic acid and sorbic acid, a flame ionization detector (FID) was used. A DB-5 column (30 m × 0.25 mm I.D., 0.25 μm, J&W Scientific, California, USA) was used for the separation of all the targeted compounds. The column temperature program applied for the separation of organochlorine pesticides was set as follows: an initial temperature of 100 °C, kept 1 min, then increased to 180 °C at 20 °C min^{-1}, stayed 1 min, finally increased by 10 °C min^{-1} to 270 °C and held for 3 min. The temperatures of the injector and ECD detector were set at 220 °C and 300 °C. The carrier gas of nitrogen (99.999%) kept at a flow rate of 1.0 mL min^{-1}. X-ray powder diffraction (XRD) results were obtained by a Rigaku Model Ultima IV XRD diffractometer (Rigaku, Japan) with Cu Kα radiation (35 kV, 15 mA, λ = 1.54051 Å). The magnetization curve of microspheres was obtained at room temperature with a vibrating sample magnetometer (VSM, Lake Shore). The morphology of the sorbent was investigated using scanning electron microscopy (SEM, Zeiss Sigma). Thermogravimetric analysis (TGA) was performed on an SDT Q600 TG/DTA thermogravimetric analyzer. Raman spectra were recorded on an X-Plora Raman instrument (Jobin Yvon-Horiba, France) with a 638 nm laser. 10 μL of microliter syringe was purchased from Shanghai high pigeon industry &trade company.

2.3. Preparation of $ZnFe_2O_4$/carbon and ZnO/$ZnFe_2O_4$/carbon

2.3.1. Synthesis of $ZnFe_2O_4$/carbon

Zn-Fe-ZIF was prepared following earlier reports [20,21]. In a typical process, 2.1280g $Zn(NO_3)_2{\cdot}6H_2O$ (7.16 mmol) and 0.9953g $FeSO_4{\cdot}7H_2O$ (3.58 mmol) were added into 80 mL DMF solvent under vigorous stirring until completely dissolved. Then, this solution was added to the DMF solution of 2-methylimidazole (80 mL, 0.08 M) and stirring was maintained for another 30 min. The obtained mixture was then transferred into a sealed Teflon-lined stainless steel vessel and heated at 140 °C for two days. After cooling down to room temperature, the precipitate was collected by centrifugation and washed thoroughly with DMF and ethanol. The products thermally treated in a flow of ultrapure Ar and kept for 2 h under 600 °C with the heating rate of 5 °C min^{-1}, and the final product of porous $ZnFe_2O_4$/carbon nanocomposites was obtained.

2.3.2. Preparation of ZnO/$ZnFe_2O_4$/carbon

ZnO/$ZnFe_2O_4$/carbon was prepared from Fe^{III}-MOF-5 templates following the reported procedure [22]. In brief, 3.05 mmol of iron(III) acetylacetonate, 2.81 mmol of $Zn(NO_3)_2{\cdot}6H_2O$, 1.02 mmol of terephthalic acid, and 0.065 mmol of polyvinylpyrrolidone (Mw = 55 000) were dissolved in a DMF/ethanol mixture solvent (150 mL DMF and 90 mL ethanol). The resulting mixture was stirred for 20 min and then transferred into a sealed Teflon-lined stainless steel vessel and heated at 150 °C for 6 h. The precipitate was obtained with centrifugation, washed several times using ethanol and DMF, and then dried at 80 °C for 24 h. Finally, the obtained Fe^{III}-MOF-5 was calcined under 800 °C at a heating rate of 5 °C min^{-1} in Ar for 3 h. After that, it was cooled to room temperature to obtain porous ZnO/$ZnFe_2O_4$/carbon nanocomposites.

2.4. Magnetic-assisted dispersive miniaturized solid phase extraction (M-DμSPE)

The schematic M-DμSPE procedure is illustrated in Fig. 1. All the extraction experiments were conducted in a 20 mL centrifuge tube. 30 mg of $ZnFe_2O_4$/carbon was added to 10 mL of the aqueous solution containing organochlorine pesticides (5 ng mL^{-1}). Then, the tube was shaken using an oscillator for 20 min. Subsequently, $ZnFe_2O_4$/carbon was collected using an extra magnet in a few seconds. The aqueous solution was removed, and the

Please cite this article in press as: S. Xia, et al., Preparation of porous zinc ferrite/carbon as a magnetic-assisted dispersive miniaturized solid phase extraction sorbent and its application, J. Chromatogr. A (2018), https://doi.org/10.1016/j.chroma.2018.07.001