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Metal-organic framework-199/graphite oxide hybrid composites coated solid-phase microextraction fibers coupled with gas chromatography for determination of organochlorine pesticides from complicated samples

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ABSTRACT

The hybrid material of a copper-based metal-organic framework (MOF-199) and graphite oxide (GO) was explored as the solid-phase microextraction (SPME) coating for the first time. This fiber was fabricated by using 3-amino-propyltriethoxysilane (APTES) as the cross-linking agent, which enhanced its durability and allowed more than 140 replicate extractions. With the incorporation of GO, the MOF-199/GO fibers with GO contents ranging from 5 to 15 wt% exhibited enhanced adsorption affinity to organochlorine pesticides (OCPs) compared to MOF or GO individually. This improvement was linked to the enhanced dispersive forces (increased volume of small pores) that provided by the dense carbon layers of GO. Combining the superior properties of high porosity of MOFs and the unique layered character of GO, the MOF-199/GO (10 wt%) fiber exhibited higher adsorption affinity to some OCPs than commercial polydimethylsiloxane (PDMS) and polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibers. This new fiber was developed for headspace (HS) SPME of eight OCPs followed by GC/ECD analysis. The limits of detection were 2.3–6.9 ng/L. The relative standard deviation (RSD) for five replicate extractions using one fiber ranged from 5.3% to 8.8%. The fiber-to-fiber reproducibility was 5.2–12.8%. This method was successfully used for simultaneous determination of eight OCPs from river water, soil, water convolvulus and longan with satisfactory recoveries of 90.6–104.4%, 82.7–96.8%, 72.2–107.7% and 82.8–94.3%, respectively. These results indicated the MOF-199/GO composite provided a promising alternative in sample pretreatment.

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1. Introduction

Metal-organic frameworks (MOFs), first introduced by Yaghi and coworkers [1,2], are formed by the self-assembly between metal ion and organic ligands (mainly derivatives of benzene carboxylate) [3]. MOFs are thermal stable and their porosity can reach up to 60% [4]. Compared to conventional porous materials such as zeolites and activated carbon, they possess higher surface area (up to 4500 m²/g for MOF-177) [5] and chemical tunable structures (via the diversity of metallic component and organic linkers). These features make them the promising materials in gas adsorption, separation and purification [4,6–12]. Recently, MOFs have been proved to be effective adsorption materials for in-field sampling and preconcentration of formaldehyde, solid-phase microextraction for benzene homologs [13,14], and separation media for *n*-alkanes, xylene isomers, substituted aromatics and some persistent organic pollutants [15–18].

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Graphite oxide (GO) is derived from the oxidative exfoliation of graphite using strong oxidizing agents. It bears a considerable amount of hydroxyl and epoxy groups within the interlayer space and carboxyl groups mainly located on the edges of the layers [19]. GO is a multilayer system with the interlayer distance varying from 6 to 12 Å depending on the level of hydration [20]. Owing to its unique layered character, large specific surface area [21] and good dispersibility in aqueous solution, GO can participate in a wide range of bonding interaction and has been used recently as a component in several composite materials with promising photochemical, electronic and adsorptive properties [22–24].

In previous studies [25–29], MOFs/GO composites have been synthesized and used for gas adsorption. These hybrid materials exhibited improved adsorption equilibrium capacity for NO₂, H₂ or NH₃ compared to the parent materials, which is linked to the increased dispersive forces in new pores located between the two components [25–30]. Owing to the high specific surface area of MOFs and the enhanced dispersive forces provided by GO, such a class of new porous material is an ideal choice in sample pretreatment.

Solid-phase microextraction (SPME), introduced in the early 1990s [31], is a simple sample preparation method that integrates sampling, extraction and sample introduction into one step with less solvent consumption. Generally, the stationary phase coated onto the fiber is critical in improving the extraction performance. However, the commercially available SPME coatings, such as polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polyacrylate (PA), polyethylene glycol/divinylbenzene (PEG/DVB), carboxen/poly(dimethylsiloxane) (CAR/PDMS), and carbowax/divinylbenzene (CW/DVB), suffer from the drawbacks of instability at high temperature, swelling in organic solvents, or stripping from the substrate [32]. Thus, they are not always satisfactory for the extraction of large numbers of varied analytes.

In this paper, a new porous material formed rapidly by a combination of MOF-199 (copper-based MOF) and GO at room-temperature was initially explored as the SPME coating via a chemical-bonded strategy. GO was expected to enhance dispersive forces due to its dense carbon layers, and MOF-199 was expected to increase the porosity of the hybrid material. MOF-199/GO SPME fibers with different GO contents were fabricated, and their extraction performance for organochlorine pesticides (OCPs) was investigated. The results showed that their adsorption affinity to OCPs was significantly higher than MOFs and GO, respectively. This new fiber was successfully used to simultaneously determine eight OCPs from different samples prior to gas chromatography/electron capture detector (GC/ECD) analysis. To the best of our knowledge, it is the first example of the utilization of this hybrid material for trace substances analysis from complicated samples.

2. Experimental

2.1. Instruments

An HP 4890D gas chromatography (Agilent, Palo Alto, USA) equipped with a ^{63}Ni electron capture detector (ECD) was used for all experiments. An AE.SE-54 (Lanzhou Atech Technologies, Lanzhou, China) capillary column (30 m long \times 0.25 mm i.d. \times 0.33 μm film thickness) was used for the chromatographic separation. The GC conditions were set as follows: the injector temperature was 280 $^{\circ}\text{C}$, and the detector temperature was 300 $^{\circ}\text{C}$. The column temperature was maintained at 100 $^{\circ}\text{C}$ for 2 min, and then increased to 200 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C}/\text{min}$, finally increased to 246 $^{\circ}\text{C}$ at a rate of 2 $^{\circ}\text{C}/\text{min}$. Splitless injections were used throughout. The high-purity nitrogen (99.999%) was used as carrier gas with the flow rate of 1.6 mL/min. Additional make-up gas was also high-purity nitrogen with the flow rate of 60 mL/min.

Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet Avatar 330 spectrometer. X-ray diffraction (XRD) measurements were performed on a D-Max 2200 VPC diffractometer (Japan) using Cu K α radiation. Scanning electron microscopy (SEM) images were recorded on a JSM-6300F SEM instrument (Japan). Thermogravimetric (TG) curves were obtained using a Netzsch-209 thermal gravimetric analyzer (Bavaria, Germany). An ultrasonicator (KQ 5200, Kunshan, China) was used for the preparation of GO dispersions. An IKA RET magnetic stirrer (Germany) was employed for all experiments. Commercial 100- μm PDMS SPME fiber and 65- μm PDMS/DVB SPME fiber (Supelco, St. Louis, MO) were utilized for the comparison study.

2.2. Materials and reagents

The OCPs standard solutions included hexachlorobenzene (HCB), aldrin, heptachlor epoxide, *trans*-chlordane, α -endosulfan, *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE), dieldrin and *p,p'*-

p'-dichlorodiphenyldichloroethane (*p,p'*-DDD) were purchased from Agro-Environment Protection Institute (Tianjin, China). The chemical structures of the eight OCPs are listed in Supporting information (SI), Fig. S1. HPLC grade *n*-hexane was obtained from Fuchen Chemical Reagents (Tianjin, China). Distilled water was used throughout the study. The fused-silica fibers (120 μm i.d.) were obtained from Fiber Home Telecommunication Technologies (Wuhan, China). Graphite powder (99.95%) was purchased from Alfa Aesar. 1,3,5-Benzenetricarboxylic acid (H_3BTC) and 3-aminopropyltriethoxysilane (APTES) were purchased from Aladdin Chemistry. Other chemicals were of analytical grade.

2.3. Preparation of MOF-199/GO composites

2.3.1. Synthesis of GO

GO was synthesized by oxidation of graphite using Hummers method [33,34]. Briefly, graphite was treated by an 80 $^{\circ}\text{C}$ mixture of concentrated H_2SO_4 , $\text{K}_2\text{S}_2\text{O}_8$ and P_2O_5 . The obtained pre-oxidized graphite was added into concentrated H_2SO_4 in an ice bath, and then KMnO_4 was added slowly. The mixture was stirred at 35 $^{\circ}\text{C}$ for 2 h and then slowly diluted with water, finally H_2O_2 was added to terminate the reaction. The mixture was filtrated, washed with HCl solution, and finally dried. The obtained brown solid was GO.

2.3.2. Synthesis of MOF-199

MOF-199 was synthesized according to Ref. [35] H_3BTC (250 mg, 1.19 mmol) was added to 40 mL of dimethyl formamide/ethanol (DMF/EtOH) solution (v/v, 1:1). $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (430 mg, 2.16 mmol) was dissolved in 20 mL water. The two solutions were mixed with stirring. Triethylamine (0.25 mL) was added to the mixture and then stirred for 3 h. The product was collected by filtration, washed with DMF, and finally dried. After that, the MOF-199 powder was sieved to particle size less than 106 μm , which was used for the preparation of SPME coating.

2.3.3. Synthesis of MOF-199/GO composites

H_3BTC (250 mg) was dissolved to 40 mL of DMF/EtOH solution (v/v, 1:1). $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (430 mg) was dissolved in 20 mL water. GO (38.8 mg) was exfoliated by 30 min ultrasonication in 10 mL water to form stable aqueous dispersion. Then, the GO dispersion and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ solution were orderly adding into H_3BTC solution with stirring. Triethylamine (0.25 mL) was then added and stirred for 3 h. The product was collected by filtration, washed with DMF, dried, and finally sieved to particle size less than 106 μm . The added GO consists of 10 wt% of the final material weight. Three MOF-199/GO composites with various GO contents (5, 10, and 15 wt%) were synthesized, which were referred to as MG-5, MG-10 and MG-15, respectively.

2.4. Preparation of MOF-199/GO composites coated SPME fibers

GO possesses a considerable amount of carboxyl groups mostly at the sheet edges. The organic linkers of MOF-199 contain dangling carboxyl groups [36]. The carboxyl groups offer opportunities for the preparation of chemical-bonded MOF-199/GO SPME fibers using APTES as the cross-linking agent.

The silica fiber with a length of 17 cm was used to fabricate the SPME fiber. The schematic fabrication process is shown in Fig. 1. Firstly, its one tip (1.0 cm) was immersed into acetone for 20 min to remove the protecting polyimide layer, followed by alkaline treatment using 1 mol/L NaOH solution for 1 h to expose the maximum number of silanol, and then washed with water. After that, this fiber was dipped into APTES for 5 min, pulled out and immediately immersed into the powder of MOF/GO composite. Subsequently, it was taken out and placed into an oven at 70 $^{\circ}\text{C}$ for

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