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Feasibility of metal–organic nanotubes $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$-coated fibers for solid-phase microextraction of polychlorinated biphenyls in water samples

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ABSTRACT

Metal-organic nanotubes (MONTs), a novel class of hybrid materials, have attracted considerable attention because of their uniform and fixed internal diameters, impressive topological structures, and versatile applications. However, to the best of our knowledge, no studies on MONTs coating fabrication for solid-phase microextraction are yet available. The aim of this work is to investigate the feasibility of using $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ as a solid-phase microextraction coating material to enrich trace levels of polychlorinated biphenyls in water samples. The novel $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$-coated fibers achieved large enhancement factors (396–1343), low limits of detection (3.9–21.7 pg L^{-1}), and wide linearity (0.1–500 ng L^{-1}) for detecting polychlorinated biphenyls. Relative standard deviations obtained ranged from 2.12 to 7.22%, and spiked PCBs recoveries (spiking concentrations of 1 and 5 ng L^{-1}) in four environmental water samples ranged from 71.3 to 104%. These findings indicate that $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ as a solid-phase microextraction coating material is an excellent alternative for the rapid and sensitive analysis of trace levels of polychlorinated biphenyls in the environment.

1. Introduction

As a sample pretreatment technique, solid-phase microextraction (SPME) can integrate sampling, extraction, concentration, and sample introduction into a single step [1]. SPME is widely used in many areas because of its clear advantages, which include simplicity, efficiency, fast operation, sensitivity, and lack of solvent consumption [2]. The technique is based on establishment of extraction equilibrium between a fiber coating and the sample matrix [3]. The fiber coating performs an important function in SPME [4]. Commercial coatings, such as polydimethysiloxane (PDMS) [4], PDMS/divinylbenzene (DVB) [5], and polyacrylate (PA) [6,7] have been successfully applied in many fields. Unfortunately, some of these coatings present several drawbacks, such as insufficient thermal or solvent instability and limited selectivity [8]. Therefore, development of novel coatings for SPME is of great significance for achieving high-enrichment efficiency and selectivity.

Metal–organic nanotubes (MONTs) are a novel class of hybrid materials that combine organic ligands and metal ions or metal-containing clusters [9]. MONTs bridge inorganic and organic nanotubes (NTs) and possess the advantages of carbon nanotubes (CNTs) and metal–organic frameworks (MOFs) [10]. These NTs have attracted considerable attention because of their uniform and fixed internal diameters, impressive topological structures, and versatile applications in catalytic reduction, ion exchange, gas adsorption and separation, and molecular sensing and recognition [10–14]. Various CNTs and MOFs, such as multi-walled CNTs (MWCNTs) [15], oxidized MWCNTs [16], MIL-88B [8], zeolitic imidazolate framework-90 [17], UiO-66 [18], and MIL-53 (Al) [19] have successfully been applied in SPME of various analytes. MONTs combine the excellent properties of MOFs and CNTs, such as a tunable pore size, open nanoporous structure, large specific surface area, and exceptional thermal and chemical stability. These properties indicate that MONTs are a promising fiber coating material for SPME development. However, to the best of our knowledge, no studies on MONTs coating fabrication for SPME are yet available.

Polychlorinated biphenyls (PCBs) are a class of industrial chemicals in which 1–10 chlorine atoms are attached to a biphenyl molecule [20]. The solubility, chemical stability, and apparent

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mobility of PCBs have resulted in environment movement comparable with that of several organochlorine insecticides [21]. PCBs can cause several negative effects on human health and the environment because of their toxicity and resistance to metabolic degradation [22,23]. Although PCBs manufacturing have been banned since the late 1970s, humans and animals are still exposed to these chemicals because of their long-range transport and good stability [24]. Therefore, monitoring PCBs in the environment is an important undertaking.

This study investigates the feasibility of using $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ MONTs (Cu-MONTs) as a SPME coating material to extract PCBs from water samples for gas chromatography–tandem mass spectrometry (GC–MS/MS) detection. The developed coating is used to analyze PCBs in real environmental water samples and evaluate its practicability.

2. Experimental

2.1. Chemicals and reagents

All chemicals used in the present study were of at least analytical grade. $Cu(NO_3)_2{\cdot}3H_2O$ was purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). 1,2,4-Triazole (Htz) and cyanuric acid (H_3CA) were obtained from Sigma-Aldrich Trading Co. Ltd. (Shanghai, China). Seven standards of PCB homologs (Congener Nos.: 28, 52, 101, 123, 137,153, 180) (1 mg L^{-1}) were obtained from Accu Standard (Connecticut, USA). A 5 μL GC microsyringe (Shanghai Gaoge Industrial and Trade Co. Ltd., Shanghai, China) was used to assemble the SPME device. A commercial SPME manual holder with fiber coatings of 100 μm PDMS or 50/30 μm DVB/CAR/PDMS (Supelco, Bellefonte, PA, USA) was used for comparison.

2.2. Preparation of $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$

$[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ was synthesized via a hydrothermal growth method according to Huang et al. [12]. Briefly, $Cu(NO_3)_2{\cdot}3H_2O$ (0.880 g, 3.60 mmol), Htz (0.168 g, 2.00 mmol), NaCl (0.116 g, 2.00 mmol), H_3CA (0.260 g, 2.00 mmol), and aqueous NH_3 (25%, 12.0 mL) were added to an ethanediol–H_2O (v/v = 1:1, 12.0 mL) solution. This mixture was stirred for 15 min at room temperature, transferred to and sealed in a 100 mL Teflon-lined reactor, and then heated to 160 °C for 70 h in an oven. The oven was gradually cooled to room temperature, and the resultant blue powders were obtained by centrifugal washing with water and ethanol for several cycles and then overnight drying at 80 °C in an oven.

2.3. Fabrication of $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$-coated solid-phase microextraction fibers

A 20 cm-long stainless steel wire was used as the SPME substrate. One side of the stainless steel wire (2.0 cm long) was roughened by corrosion using 37% HCl solution for approximately 30 min. The corroded surface was washed with ultrapure water and then dried in air. The etched stainless steel wire was vertically immersed in silicone glue for 30 s and then pulled out quickly. The redundant silicone glue was scraped by a knife to yield a homogeneous glue film on the surface of the etched stainless steel wire. The gummed portion of the wire was inserted into a 2.5 mL centrifuge tube filled with $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ powders for 60 s and then pulled out. Finally, the stainless steel wire coated with $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ was dried in air for 24 h to allow the MONTs to solidify on the stainless steel wire. The stainless steel wire coated with Cu-MONT was installed in a 5 μL GC syringe by hand to produce a home-made SPME device. The coated fiber was conditioned in the GC injector at 300 °C for aging under nitrogen until a stable GC baseline was obtained.

2.4. Instrumentation

An Agilent GC system (7890A, Palo Alto, USA) equipped with a triple quadrupole mass spectrometer (7000B, Agilent, USA) was used for this experiment. GC separation was performed using a methylpolysilicone HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) (Abel Bonded, USA). The oven temperature was held at 130 °C for 3 min, programmed to increase by 8 °C min^{-1} to 300 °C, and then held for 5 min. Helium (99.999%) flowing at a rate of 2.25 mL min^{-1} was used as the carrier gas. The mass spectrometer was operated in electron impact ionization mode with an ionizing energy of 70 eV. Both interface and ion source temperatures were set to 230 °C and analysis was performed in MRM mode.

XRD patterns were recorded on a D/max-r8 diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å). TGA experiments were performed on an STA 449F3-QMS403C system (Netzsch, Germany) from room temperature to 400 °C at a ramp rate of 10 °C min^{-1}. SEM images were recorded on a SUPPA™ 55 instrument (Zeiss, Germany).

2.5. Solid-phase microextraction procedure

All SPME experiments were performed under direct SPME mode. Approximately 10 mL of the sample solution was added to a glass vial that was then capped with a butyl rubber stopper. The needle of the home-made SPME device was inserted into the stopper and the fabricated fiber was completely pushed into the sample solution. The fiber was retracted into the needle, removed from the vial, and then detected by GC–MS/MS after extraction. The fiber was aged at 300 °C for 5 min in the GC inlet before each use.

2.6. Environmental water samples

Tap water, river water, underground water, and pond water were selected as real samples. Tap water was collected from our laboratory, river water was collected from the Yellow River (Jinan, China), underground water was collected from Dezhou (Shandong, China), and pond water was collected from our center. All water samples were stored in brown glass bottles at 4 °C and filtered through 0.45 μm micropore membranes prior to analysis.

3. Results and discussion

3.1. Characterization of the $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$-coated stainless steel fiber

A high-magnification SEM micrograph of the prepared $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ is shown in Fig. 1(A). A large number of $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ with general diameters of 100–200 nm may be observed. Other $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ with diameters beyond the above range were also observed. Fig. S1 (ESI) shows that the XRD pattern of the MONTs agrees with that reported literature [12], which demonstrates successful fabrication of $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$. The material is stable in air and insoluble in water and common organic solvents [12]. TGA was used to evaluate the thermal stability of the epoxy resin, $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$-coating, and Cu-MONT powders. The decomposition temperature of the Cu-MONT powders is approximately 325 °C. Epoxy resin adhesion enabled the decomposition temperature of $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$-coating to increase to nearly 340 °C, which is beneficial to thermal stability. SEM images in Fig. 1(C) and