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Talanta

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Carbon nanotube sponges as a solid-phase extraction adsorbent for the enrichment and determination of polychlorinated biphenyls at trace levels in environmental water samples



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ARTICLE INFO

Article history:

Received 5 April 2016

Received in revised form

21 June 2016

Accepted 2 July 2016

Available online 4 July 2016

Keywords:

Carbon nanotube sponges

Solid-phase extraction

Polychlorinated biphenyls

Gas chromatography–tandem mass spectrometry

ABSTRACT

Carbon nanotube (CNT) sponges has recently attracted considerable attention in numerous fields because of its excellent properties, such as high porosity, light weight, and large surface area. The potential of CNT sponges for the solid-phase extraction (SPE) of organic pollutants at trace levels was investigated in this study for the first time. Seven polychlorinated biphenyls (PCBs) were selected as analytes, and gas chromatography–tandem mass spectrometry was employed for the detection. We optimized important parameters that may influence the efficiency of SPE, including the kind and volume of elution solvent, sample pH, and sample flow rate and volume. Under optimized conditions, low limits of detection (0.72–1.98 ng L⁻¹), wide range of linearity (10–1000 ng L⁻¹) and good repeatability (2.69–6.85%, $n=5$) were obtained. CNT sponges exhibited higher extraction performance than other adsorbent materials under the optimized conditions. Real environmental water samples were analyzed, and satisfactory recoveries (81.1–119.1%) were achieved. All these results demonstrated that CNT sponges are suitable SPE material for the enrichment and sensitive determination of PCBs at trace levels.

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1. Introduction

Polychlorinated biphenyls (PCBs) had been widely used in various industries. PCBs are relatively stable, i.e., extremely difficult to be oxidized, reduced, or otherwise chemically transformed naturally [1,2]. These compounds can bio-magnify through the food chain and then pose a threat on human health [3,4]. Although PCB production has been banned since the late 1970s, humans are still exposed to these pollutants because of they have been widely distributed and are highly stable [5]. Thus, the determination of PCBs in the environment is urgently required for environmental impact and risk assessment [6]. Direct analysis of PCBs by modern chromatographic techniques, such as gas chromatography–mass spectrometry (GC–MS) [7] or GC–electron capture detection [8], is usually difficult because of the low concentrations or the complexity of sample matrixes. Therefore, suitable sample pretreatment steps are necessary prior to chromatographic determination [9].

To date, various pretreatment techniques have been developed

for the extraction and enrichment of PCBs at trace levels in the environment. These techniques include liquid–liquid extraction (LLE) [10], ultrasonic extraction (USE) [11], microwave-assisted extraction (MAE) [12], liquid-phase microextraction (LPME) [13,14], dispersive liquid–liquid microextraction (DLLME) [15], solid-phase microextraction (SPME) [16], and solid-phase extraction (SPE) [17]. Among these sample pretreatment techniques, LLE is the oldest sample preparation technique, which often requires large amounts of toxic solvent and time-consuming procedures. Compared with LLE, SPE offers several evident advantages, such as low consumption of solvents, high enrichment factors, simplicity, and ease of operation [18–20]. The selection of suitable adsorbents for SPE is crucial in obtaining high enrichment efficiency of targeted analytes. Multiwalled carbon nanotubes (MWCNTs) [18,19], bamboo charcoal [20], magnetic nanoporous carbon [21], C18-bonded silica [22], expanded graphite [23], and hydrofluoric acid-etched sand particles [24] have been investigated as SPE adsorbents.

Carbon nanotubes (CNTs) form unique nanostructures, thus enabling the use of the material in various applications, such as supercapacitors [25,26], artificial muscles [27], and superhydrophobic coatings [28]. A sponge-like material named CNT sponges has recently attracted considerable attention in numerous fields because of its excellent properties, such as high porosity

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(> 98%), large surface area, great sorption capacity and rate, and strong oleophilic and hydrophobic properties [29–31]. Furthermore, compared with other materials, CNT sponges show advantages, such as high flexibility of structure and thermal stability [32]. CNT sponges are promising candidates for environmental applications, such as adsorption, filtration, and separation, owing to their excellent properties, such as light weight, high porosity, and large surface area. Gui et al. used highly porous CNT sponges as an efficient adsorbent material for oil and organic reagents [33], in which the adsorption capacities were higher than 100 g g^{-1} [33]. Li et al. reported that porous sponge-like materials can scavenge and absorb large-area oil spill from water surface [32]. Then, the applications have been extended to the removal of organic dyes and nanoparticles from water by using the sponges as filtration membranes [32].

All applications of CNT sponges mentioned above mainly focus on the removal of nanoparticles and environmental pollutants from water samples and not on the enrichment and analysis of pollutants at trace levels in environmental water samples. To the best of our knowledge, the enrichment and analysis of pollutants in aqueous samples by using CNT sponges as SPE adsorbent has not been reported. This study aims to investigate the feasibility of using CNT sponges as an adsorbent for the enrichment and analysis of organic pollutants at trace levels in water samples. Seven PCBs were selected as analytes, and GC–MS/MS was used for detection. Surface morphology of CNT sponges was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The important parameters affecting the performance of SPE have been investigated and optimized in detail. Moreover, the possible extraction mechanism of CNT sponges was discussed. Finally, the developed method was used for the analysis of PCBs in real environmental water samples.

2. Experimental

2.1. Reagents and materials

CNT sponges, MWCNTs, and single-walled CNTs were purchased from XFNANO Materials Tech Co., Ltd (Nanjing, China). Activated carbon was purchased from Sigma-Aldrich (USA), and the Oasis HLB 6 cc (200 mg) extraction cartridge was sourced from Waters Technology Co., Ltd. (Milford, USA). Methanol (HPLC grade), *n*-hexane (HPLC grade), and dichloromethane (pesticide grade) were supplied by Oceanpak Alexative Co., Ltd. (Sweden). Acetone (HPLC grade) was obtained from Duksan Pure Chemicals Co., Ltd. (Korea). Other reagents were of analytical grade unless otherwise stated. A soil standard substance (GBW08307) was obtained from Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (Beijing, China). PCBs standard solution with $10 \mu\text{g mL}^{-1}$ concentration of each component was purchased from AccuStandard, Inc. (New Haven, USA). The solution contained 2,4,4'-trichlorobiphenyl (PCB-28), 2,2',5,5'-tetrachlorobiphenyl (PCB-52), 2,2',4,5,5'-pentachlorobiphenyl (PCB-101), 2',3',4,4',5-pentachlorobiphenyl (PCB-118), 2,2',3,4,4',5'-hexachlorobiphenyl (PCB-138), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153) and 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB-180). A stock solution ($100 \mu\text{g L}^{-1}$) was prepared in methanol. Fresh working solutions were prepared daily by appropriate dilution of the stock solution using double-distilled water. All solutions were stored at 4°C in the dark prior to use.

2.2. Instrumentation

In this work, a gas chromatography system (436 GC, Bruker, USA) coupled with a triple quadrupole mass spectrometer (SCION

Table 1
Analytical parameters of the proposed method.

Analytes	Linear range (ng L^{-1})	R	LOD (ng L^{-1})	LOQ (ng L^{-1})	RSD-Intra-day (%, $n=5$)
PCB-28	10–1000	0.9953	0.95	3.17	6.34
PCB-52	10–1000	0.9938	0.79	2.63	3.16
PCB-101	10–1000	0.9982	1.98	6.60	6.85
PCB-118	10–1000	0.9960	1.94	6.47	3.59
PCB-138	10–1000	0.9988	0.72	2.42	2.69
PCB-153	10–1000	0.9951	1.67	5.55	4.67
PCB-180	10–1000	0.9936	1.93	6.43	4.90

TQ, Bruker, USA) was used in multiple reaction monitoring (MRM) mode. GC separation was conducted with a fused silica DB-5MS capillary column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$) (Agilent Technologies, USA). Oven temperature was held at 150°C for 1 min, programmed at $10^\circ\text{C min}^{-1}$ to 290°C , and was held for 4 min. The GC carrier gas was helium, and the flow rate was 1 mL min^{-1} . The injection port temperature and transfer line temperature were 280°C and 290°C , respectively. Other GC–MS parameters, such as retention time, precursor ions, product ions, and collision energy, are presented in Table 1S. In the experiment, external standard calibration was employed. Six different concentrations (10, 20, 50, 100, 500, and 1000 ng L^{-1}) in methanol were used as calibration standards.

The micrographs of CNT sponges were recorded by SEM (Carl Zeiss Microimaging Co., Ltd., Germany) and high-resolution TEM (HRTEM, JEM-2100, JEOL, Japan). An accelerated surface area and porosimetry system (ASAP2020 HD88, Micromeritics, USA) was used for the determination of specific surface area and pore size distribution.

An adsorbent material packed cartridge (CNT sponges, MWCNTs, SWCNTs, activated carbon, or Oasis HLB) was prepared by modifying a Waters Oasis SPE C18 cartridge (60 mg, 3 mL, polypropylene) [18–20]. An 21.8 mg portion of adsorbent material (CNT sponges, MWCNTs, SWCNTs, activated carbon, or Oasis HLB) was packed into the cartridge after evacuating the C18 packing of the cartridge. The 1.5 mm polypropylene upper and lower partition remained at both ends of the cartridge to keep the adsorbent packing in place. Afterwards, the outlet tip of the cartridge was connected to a model SHB-3 (III) vacuum pump (Great Wall Scientific Industrial and Trade Co., Ltd., Zhengzhou, China), and the inlet end was connected to a polytetrafluoroethylene suction tube. The other end of the PTFE tube was inserted into working solutions or water samples. The SPE system was washed with ample methanol prior to use.

2.3. SPE procedure

An SPE cartridge packed with CNT sponges was washed with 6 mL of methanol and 6 mL of ultrapure water. Then, working solutions or water samples were passed through the SPE cartridge at a constant flow rate. Subsequently, the SPE cartridge was dried by negative pressure for 5 min. After this step, target compounds were eluted by dichloromethane in an optimum volume. The eluent was blown with a mild stream of nitrogen gas to dryness at room temperature. The residue was dissolved in $100 \mu\text{L}$ of methanol, and $1 \mu\text{L}$ of the solution was injected for analysis.

2.4. Water samples

Four real environmental water samples, including ground water, pond water, tap water, and mine water, were used to verify the proposed method. Ground water was collected from WangZhuangXinCun (Taian, China). Pond water was taken from

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