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

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Facile synthesis of hierarchical porous carbon from crude biomass for high-performance solid-phase microextraction

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ARTICLE INFO

Article history:
Received 31 January 2018
Received in revised form 8 March 2018
Accepted 12 March 2018
Available online xxx

Keywords:
Solid-phase microextraction
Hierarchical porous carbon
Potassium hydroxide
Crude biomass
Chlorobenzenes

ABSTRACT

Porous materials have great prospective applications for solid-phase microextraction (SPME) technology because of their large specific surface area and pore volume. In this study, a hierarchical porous carbon (HPC) was synthesized by simple hydrothermal reaction and potassium hydroxide (KOH) activation of crude biomass and found to be an efficient adsorbent for SPME of organic pollutants. Results show that the as-prepared HPC has a partly graphitic amorphous-like structure with ultrahigh specific surface area (2551 m^2/g), high pore volume (1.53 cm^3/g), good pore size distribution (PSD) (mesopore/micropore ratio of 68%), and great thermal stability (>450 °C). When we utilized it as SPME fiber coating, the extraction capacities for chlorobenzenes (CBs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and phthalates (PAEs) were, respectively, 1.13–39.46, 2.40–7.78, 1.34–36.02, and 1.50–1.83 times higher than those of a commercial polydimethylsiloxane (PDMS) fiber. Under the optimized extraction conditions, an analytical method for CBs with low detection limits (0.01–0.24 ng/L), good repeatability (1.00%–4.93% for intra-day, 1.11%–6.94% for inter-day), and great reproducibility (1.48%–8.91%, n = 3) was developed. Moreover, we evaluated the practicality of the developed method for environmental water sample and obtained satisfactory recoveries (86.21%–104.34%). The findings provide a novel and promising HPC from crude biomass using a low-cost and facile synthetic route for SPME applications.

1. Introduction

Water pollution, an urgent global issue, has brought a great challenge to human health [1,2]. To guarantee the safety of water resources, a technology for highly sensitive analysis of typical toxic organic contaminants in water is necessary. Sample preparation, however, places a crucial limitation for the development of analytical technology [3]. Hence, attention to SPME, a promising sample pretreatment method, has increased [4,5]. SPME is simple, sustainable, and convenient method, and it integrates many steps, including extraction, concentration, purification, and injection, into one easy step. It uses a small sample volume, little time and less labor, and it obviates the use of organic solvent when coupled with gas chromatography (GC) [6]. Moreover, it imparts the advantage of high sensitivity. In general, the SPME fiber coating is a crucial point which determines the method's selectivity, sensitivity, life span, reproducibility, and application [7]. In the past decades, commercial SPME fibers have been introduced and applied, such as PDMS, polyacrylate, and carboxen, to improve SPME technology for analyzing trace levels of various compounds [8,9]. However, such fibers are costly and have poor thermal and mechanical stabilities, limiting its use. Hence, it is urgent to invent new fibers with low cost, great thermal and mechanical stabilities, high efficiencies in extraction, and high selectivity.

Recently, various porous materials have been studied and considered as suitable adsorbents for SPME fiber coatings because of their large specific surface area and pore volume. These include metal-organic frameworks [10], cross-linked polymer nanoparticles [11], powdery carbon aerogel [12], ordered mesoporous silica [13], and porous organic polymers [14]. They have shown high performance in SPME because of their abundant micropores or mesopores. Among these materials, porous carbon is desirable because of its good thermal and mechanical stabilities, potential π-π interaction, hydrophobic interaction, and dispersion forces [11,15]. However, previous reported studies have found that synthetic processes for porous carbon for SPME using a template agent are costly and complicated because of their multiple steps [12,16]. From a wide perspective, therefore, the fabrication of novel highly

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https://doi.org/10.1016/j.chroma.2018.03.019
0021-9673/

porous carbon materials with large specific surface area and wide PSD for SPME technology using easy and convenient routes is desired.

Given the points mentioned above, one-pot synthesis of porous carbon using a chemical agent, which is simple, rapid, convenient, and inexpensive, is a desirable strategy [17]. KOH is a suitable chemical agent for generating a high-porosity structure with large specific surface area and pore volume [18]. But narrow PSD is detrimental to SPME. To overcome this obstacle, we used crude biomass as starting material for porous carbon because of its multi-element components, whose inorganic salts were beneficial for hierarchical porous structure [17,19]. Crop wastes are typical crude biomasses that not only low cost but also available everywhere. Among them, oilseed rape straw (OSRS) is an important crop waste. Its yield has increased remarkably because of the high demand for rapeseed for green and sustainable oil production [20]. However, few studies have reported the use of OSRS as a potential carbon precursor for porous carbon. We aimed to synthesize a promising porous material for the SPME fiber coating and to provide basic data for porous carbon production from OSRS for its applications in gas carriers, energy conversion, storage, and purification.

In this study, the synthesis of HPC from OSRS and its application as SPME fiber coating were investigated. The extraction capacity of the HPC-coated fiber was evaluated by comparison the performance of commercial PDMS fiber using CBs, PCBs, PAHs, and PAEs, typical persistent organic pollutants. Using the optimum extraction temperature, salt concentration and extraction time, a new method was established to rapid determine trace levels of CBs. The HPC-coated fiber was developed and applied to actual water sample.

2. Materials and methods

2.1. Substances and materials

OSRS was obtained from a local farmland in Jiangsu, China. KOH and cyclohexane were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). CBs (1,2-Dichlorobenzene (1,2-DCB), 1,3-Dichlorobenzene (1,3-DCB), 1,3,5-Trichlorobenzenes (1,3,5-TCB), 1,2,4-Trichlorobenzenes (1,2,4-TCB), 1,2,3-Trichlorobenzenes (1,2,3-TCB), 1,2,3,4-Tetrachlorobenzene (1,2,3,4-TeCB), 1,2,4,5-Tetrachlorobenzene (1,2,4,5-TeCB) and Pentachlorobenzene (PeCB)), PCBs (2,4′-Dichlorobiphenyl (PCB-8), 2,5-Dichlorobiphenyl (PCB-9), 2,2′,5-Trichlorobiphenyl (PCB-18), 2,3,3′-Trichlorobiphenyl (PCB-20), 2,4,4′-Trichlorobiphenyl (PCB-28)), PAHs (Naphthalene (NAP), Acenaphthylene (ANY), Acenaphthene (ANA), Fluorene (FLU), Phenanthrene (PHE)), chromatographic grade *n*-hexane, and acetone were obtained from Accustandard Inc. (New Haven, CT, USA). PAEs (Dibutyl phthalate (DBP), Diisobutyl phthalate (DIBP), Dipropyl phtalate (DPRP), Diisopropylo phthalate (DIPRP)) were obtained from ChemService Inc. (West Chester, PA, USA). Silicone sealant was bought from Sika Ltd. (Beijing, China). Stainless steel wire (Φ 127 μm) was purchased from Small Parts (Miami, FL, USA). A 30 μm PDMS fiber and a SPME manual holder were obtained from Supelco (Bellefonte, PA, USA). An empty SPME needle was purchased from XTrust Instruments (Shanghai, China).

2.2. Synthesis of hierarchical porous carbon from oilseed rape straw

Typically, 10 g OSRS was dried in a conventional oven and then ground into powder. After mixing with ultrapure water (40 mL) in a hydrothermal reactor and heating at 250 °C for 4 h, a brown-black solid residue was collected by filtration and dried at 105 °C for 12 h. Subsequently, the residue was mixed with KOH (KOH/residue ratio of 4) in a corundum crucible. It was then carbonized and activated at 850 °C (temperature was increased at 5 °C/min) for 1 h under N_2 flow (400 mL/min). The resulting black solid residue was washed ultrasonically with 1 M hydrochloric acid solution to remove metallic compounds. After the residue was dried at 120 °C for 12 h, a novel and promising HPC was obtained.

2.3. Fabrication of hierarchical porous carbon-coated fiber

Fastening of the HPC by silicone sealant via a solidification reaction was adapted with some modifications [11,21]. In brief, a 2 cm stainless steel wire was washed with acetone and ultrapure water for 10 min using ultrasound. After the cleaned wire was dried in an oven, it was immersed into cyclohexane-diluted silicone sealant (1 mL per 0.25 g). Followed taking fiber out immediately and wiping with weighing paper, a homogeneous thin film of silicone sealant remained on the surface of the wire. This fiber was further rotated in the powdered HPC. After conditioning at 90 °C for 10 min to solidified the mixture for avoiding the falling of HPC from the fiber, a well-distribution HPC layer was remained on the surface of the silicone sealant-coated wire. The above steps were repeated twice to avoid pore blocking that might be caused by the sol-gel technique used for obtaining the HPC-coated fiber.

2.4. Solid-phase microextraction procedure and gas chromatography analysis

Before installation in the SPME manual holder, the SPME fiber was conditioned at 250 °C for 2 h. The water sample was transferred to a brown bottle with rotor, and then the SPME fiber was held over the water sample. After extraction, the SPME fiber was taken out and inserted into the injection port of the GC (310 °C, 5 min for HPC-coated fiber). Then, physical adsorbed pollutants on the SPME fiber were desorbed under a high temperature, diffused from SPME coating, and ran into chromatographic column via N_2 blowing. An Agilent Technologies 7890A GC with Electron Capture Detector (ECD) was used to analyze CBs and PCBs, and 5975 Mass Spectrometer (MS) were performed to analyze PAHs and PAEs. A J&W 123–5631 column (30 m × 0.32 mm i.d. × 0.25 μm) and an Agilent 19091S-433 column (30 m × 0.25 mm i.d. × 0.25 μm) were coupled with the GC-ECD and GC–MS systems, respectively. N_2 and He (purity >99.999%) were used as the carrier gases for GC-ECD and GC–MS, respectively. For CBs, the column oven temperature was initially set at 60 °C, held for 1 min, increased to 230 °C at 15 °C/min, increased to 300 °C at 20 °C/min, and then held at 300 °C for 4 min. For PCBs, the column oven temperature was initially set at 100 °C and then increased to 250 °C at 10 °C/min. For PAHs, the column oven temperature was initially set at 80 °C for 2 min, increased to 170 °C at 35 °C/min, increased to 190 °C at 15 °C/min, kept at 190 °C for 2 min, and finally increased to 220 °C at 10 °C/min. For PAEs, the column oven temperature was initially set at 50 °C for 1 min, increased to 200 °C at 30 °C/min, kept at 200 °C for 1 min, increased to 240 °C at 8 °C/min, and then held at 240 °C for 1 min.

2.5. Structure characterization

Scanning electron microscope (SEM) and transmission electron microscope (TEM) were performed using a Zeiss EVO18 and JEM-2100 (HR), respectively. N_2 adsorption/desorption isotherms were obtained on a Micromeritics model ASAP 2020 sorptometer. X-ray diffraction (XRD) was performed with a SmartLab X-ray diffractometer operated at 45 kV and 200 mA. An InVia-Reflex apparatus was used to record Raman spectra using a 532 nm laser. Fourier transform infrared (FT-IR) spectroscopy analysis was performed on a Nexus 870 FT-IR. Thermogravimetry (TG) and differential scan-

Please cite this article in press as: H. Cheng, et al., Facile synthesis of hierarchical porous carbon from crude biomass for high-performance solid-phase microextraction, J. Chromatogr. A (2018), https://doi.org/10.1016/j.chroma.2018.03.019