



Mesoporous carbon–zirconium oxide nanocomposite derived from carbonized metal organic framework: A coating for solid-phase microextraction



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ABSTRACT

In this paper, a mesoporous carbon–ZrO₂ nanocomposite was fabricated on a stainless steel wire for the first time and used as the solid-phase microextraction coating. The fiber was synthesized with the direct carbonization of a Zr-based metal organic framework. With the utilization of the metal organic framework as the precursor, no additional carbon source was used for the synthesis of the mesoporous carbon–ZrO₂ nanocomposite coating. The fiber was applied for the determination of BTEX compounds (benzene, toluene, ethylbenzene and *m*, *p*-xylenes) in different water samples prior to gas chromatography–flame ionization detection. Such important experimental factors as synthesis time and temperature, salt concentration, equilibrium and extraction time, extraction temperature, desorption time and desorption temperature were studied and optimized. Good linearity in the concentration range of 0.2–200 μg L⁻¹ and detection limits in the range of 0.05–0.56 μg L⁻¹ was achieved for BTEX compounds. The intra- and inter-day relative standard deviations were in the range of 3.5–4.8% and 4.9–6.7%, respectively. The prepared fiber showed high capability for the analysis of BTEX compounds in different water and wastewater samples with good relative recoveries in the range of 93–107%.

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1. Introduction

Since the appearance of solid phase microextraction (SPME) technique by Pawliszyn and co-workers [1], several SPME coatings have been developed for the extraction and analysis of compounds in different samples [2–4]. Although commercial fibers such as polydimethylsiloxane (PDMS), polyacrylate, polydimethylsiloxane/divinylbenzene, Carboxen, and carbowax/divinylbenzene are widely used in the SPME technique, they have some deficiencies. In most commercial fibers, the extracting phase is coated on a fragile fused silica support. In addition, instability in organic solvents, high cost, the limited number of available fiber coatings, high thickness and memory effect problem are the other drawbacks of commercial SPME fibers. Therefore, most of the research articles in the field of SPME in the last decades have been devoted to the development of new SPME coatings [3,5–7].

Because of the exceptional chemical and physical properties of nanostructure materials, such as large surface area-to-volume ratio and high chemical and thermal stability, they have been widely

used as SPME coatings. So far, such different nanostructured metal oxides as ZnO, TiO₂, PbO₂, Co₃O₄ and Al₂O₃ have been applied as the sorbent in SPME [8–12]. Zirconium oxide is one of the metal oxides introduced as a sorbent in the preparation of SPME coatings due to its good extraction efficiency, high thermal and mechanical stability, and biocompatibility [13]. To increase surface area and provide more active sites, ZrO₂ coated on porous TiO₂ nanostructures has been used as the SPME fiber [14]. To improve the extraction efficiency of the sorbents, carbonaceous materials such as carbon nanotube and graphene have also been combined with different metal oxides [15–17].

In the past few years, mesoporous carbon has been applied as a SPME coating because of its high adsorption capacity, good thermal and chemical stability, uniform pore size, and the tendency to interact with aromatic molecules through π–π interaction. Generally, mesoporous carbon is synthesized using silica based materials as a template. Different materials such as MCM-48, SBA-15 and MSU-H have been used as the template for the synthesis of mesoporous carbon as the SPME coating. However, the synthesis methods are time consuming with multistep procedures requiring an additional carbon source [18–20].

Metal organic framework (MOF) is one type of organic-inorganic hybrid material in which a metal ion (inorganic part) is coordi-

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nated to a ligand (organic molecule). These porous materials have many applications in the field of drug delivery, gas storage, separation and catalysis [21–24]. Many studies have been focused on the application of metal organic frameworks as the template for the synthesis of mesoporous carbon because of their large surface area and nanoporous structure. These substances have been widely applied as catalyst supports, gas storage and supercapacitor materials [25–28]. Very recently, nanoporous carbon prepared by the carbonization of Co-based metal-organic framework has been applied as a solid-phase extraction adsorbent [29,30].

The synthesis of mesoporous carbon-metal oxide is performed in one step by the direct carbonization of a metal organic framework. In this process, under an inert atmosphere, the metal ion of MOF can be converted to the metal oxide nanoparticle, and the organic molecule (MOF ligand) is changed to the mesoporous carbon [31].

In this work, mesoporous carbon-ZrO₂ nanocomposite was synthesized by a simple one step procedure using a Zr-based MOF. This nanocomposite was coated on a stainless steel wire and used as a SPME fiber for the determination of BTEX compounds. Here, MOF acted as both a template and a precursor for the fabrication of mesoporous carbon ZrO₂ nanocomposite. Under the carbonization process, Zr-based MOF was converted to ZrO₂ nanoparticles and the mesoporous carbon. Besides the large surface area and high thermal stability of the nanocomposite, the mesoporous carbon has a high tendency to interact with the aromatic moiety of BTEX compounds through π - π interaction. Important factors including synthesis conditions (the time and temperature of synthesis), extraction conditions (salt concentration, extraction time and temperature) and desorption conditions (desorption time and temperature) were studied and optimized. The prepared fiber was used for the analysis of BTEX (as model compounds) in different water samples. In addition, the extraction efficiency of this fiber was compared to that of the commercial fiber (100 μ m PDMS fiber).

2. Experimental

2.1. Materials

Terephthalic acid, *N,N*-dimethylformamide (DMF), benzene, toluene, ethylbenzene and xylenes (*m*, *p*-xylenes) were obtained from Merck (Darmstadt, Germany). Zirconium chloride (ZrCl₄) was purchased from Fluka (Buchs, Switzerland). Other compounds and reagents were also obtained from Merck. An individual stock standard solution of each analyte (2000 mg L⁻¹) was prepared in methanol. A mixture of standard solution of the analytes (BTEX) at the concentration of 200 mg L⁻¹ was prepared by diluting each individual solution in methanol. The other working solutions of BTEX were prepared in pure water just before use. Purified water was prepared by OES (Overseas Equipment & Services) water purification system (OK, USA). A stainless steel wire (0.30 mm o.d.) was used as substrate for preparing SPME fiber.

2.2. Instrumentation

Chromatographic separation and analysis was performed by a SP-3420 gas chromatograph with a flame ionization detector (BEIFEN, Beijing, China) and a split/splitless injector. A VOC-HP (19091R-303) fused silica capillary column (30 m \times 0.2 mm \times 1.12 μ m) was purchased from Agilent (Palo Alto, CA, USA); and used for separation. Temperature programming of GC column was as follows: 1 min at 60 °C and then raised to 200 °C with a rate of 20 °C min⁻¹ (held 5 min). The injector and detector temperatures were 250 °C and 260 °C, respectively. The injector was equipped with a low volume insert designed for analysis by

SPME (Restek Bellefonte, PA, USA). Make up and carrier gas (nitrogen, 99.999%) flow rates were 30 and 1 mL min⁻¹, respectively. A homemade SPME holder constructed in our laboratory, was used to perform experiments. The SPME device for commercial fiber (100 μ m PDMS) was purchased from Supelco (Bellefonte, PA, USA). Field emission scanning electron microscopy (HITACHI, S-4160, Tokyo, Japan) and transmission electron microscopy (Philips CM30, Eindhoven, The Netherlands) were used to investigate the morphology of the prepared fiber coating. The XRD pattern of zirconium oxide was obtained with a Philips XRD (Model XPERT, Eindhoven, The Netherlands) equipped with Cu K α radiation. Thermogravimetric analysis (TGA) was done with a NETZSCH STA 449 F3 Jupiter (Netzsch Company, Selb, Germany) under nitrogen atmosphere with a flow rate of 10 °C min⁻¹.

2.3. Synthesis of mesoporous carbon-ZrO₂ nanocomposite

Zirconium-based metal organic framework was synthesized according to a previous report [32]. According to the synthesis method, 0.159 g of zirconium chloride and 0.102 g of terephthalic acid were mixed with 20 mL of DMF. Then, the mixture was ultrasonicated for 1 min and transferred to a Teflon-lined bomb. The Teflon-lined bomb was sealed and placed at 120 °C for 24 h. After that, the obtained MOF was collected with centrifugation at 3000 rpm for 5 min. The precipitate was washed with ethanol and dried at 100 °C. For the synthesis of mesoporous carbon-ZrO₂ nanocomposite, the resulting metal organic framework was placed in a furnace at 750 °C for 4 h under nitrogen flow.

2.4. Fabrication of mesoporous carbon-ZrO₂ coated SPME fiber

To fabricate the SPME fiber, a 3-cm stainless steel wire was cleaned in an ultrasonic bath with methanol and pure water and then air-dried. 1.5 cm of the stainless steel wire was vertically immersed into silicon glue for 30 s and then pulled out. The fiber was then inserted into the prepared ZrO₂-carbon powder for 60 s. The constructed fiber was dried in an oven at 70 °C for 15 min. This process was repeated twice. Before use, the fiber was conditioned in a GC injection port at 280 °C for 2 h.

2.5. SPME procedure

The extraction was performed in the headspace mode by using 10 mL aqueous standard solution of BTEX. Extraction was done in a 15-mL glass vial capped with a silicon septum. The aqueous solution containing the appropriate amount of Na₂SO₄ (0.2 g mL⁻¹) was stirred on a magnetic stirrer at the rate of 1300 rpm for 5 min at 30 °C. The fiber was then introduced into the headspace of sample solution and stirred for 15 min. The fiber was then removed from the sample vial and inserted into the GC injection port for analysis.

2.6. Real sample preparation

Water sample was obtained from Zayandeh-rood river (Isfahan, Iran). Wastewater samples 1 and 2 were obtained from wastewater treatment plants of Isfahan Mobarakeh Steel Company (Isfahan, Iran). Wastewater sample 3 was obtained from the municipal wastewater treatment plant of shahinshahr (Shahinshahr, Iran). Wastewater sample 4 was acquired from wastewater treatment plant of LAB Company (Isfahan, Iran). The water samples were filtered with a nylon membrane filter (0.45- μ m, Millipore, Bedford, MA, USA) to removed solid particles.

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