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Multiwall carbon nanotube- zirconium oxide nanocomposite hollow fiber solid phase microextraction for determination of polyaromatic hydrocarbons in water, coffee and tea samples

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ABSTRACT

The purpose of this study was to evaluate the application of hollow fiber solid-phase microextraction (HF-SPME) followed by HPLC-UV to determine the ultra-trace amounts of polycyclic aromatic hydrocarbons (PAHs) as model analytes in complex coffee and tea samples. HF-SPME can be effectively used as an alternative to the direct immersion SPME (DI-SPME) method in complex matrices. The DI-SPME method suffers from serious limitation in dirty and complicated matrices with low sample clean-up, while the HF-SPME method has high clean-up and selectivity due to the high porosity of hollow fiber that can pick out analyte from complicated matrices. As a hollow fiber sorbent, a novel multiwall carbon nanotube/zirconium oxide nanocomposite (MWCNT/ZrO_2) was fabricated. The excellent adsorption of PAHs on the sorbent was attributed to the dominant roles of π–π stacking interaction and hydrophobic interaction. Under the optimized extraction conditions, the wide linear range of 0.1–200 $\mu g\,L^{-1}$ with coefficients of determination better than 0.998 and low detection limits of 0.033–0.16 $\mu g\,L^{-1}$ with satisfactory precision (RSD < 6.6%) were obtained. The relative recoveries obtained by spiking the PAHs in water, coffee and tea samples were in the range of 92.0–106.0%. Compared to other methods, MWCNT/ZrO_2 hollow fiber solid phase microextraction demonstrated a good capability for determination of PAHs in complex coffee and tea samples.

1. Introduction

Modern trends in analytical chemistry are moving toward simplified and miniaturized sample preparation methods providing simultaneous sample clean-up and analyte preconcentration. Among different extraction methods, solid phase microextraction (SPME), introduced in 1990 by Pawliszyn, is a fast alternative technique for conventional extraction systems [1]. SPME technique involves two typical modes, the exposure of a coated fused silica fiber in a liquid sample (direct immersion (DI-SPME)) or in the headspace of the sample. The extraction ability of SPME is primarily determined by the nature of the sorbent coated on the fiber [2,3]. However, commercial SPME fibers present some serious problems, such as fiber consubstantial properties, low thermal and chemical stability, high cost, breakage, instability, and the possibility of carry-over [4]. In addition, DI-SPME is compatible with simple and less complicated matrices and the selectivity of DI-SPME is low. Recently, in order to overcome these drawbacks and fiber fabrication, porous polypropylene hollow fiber (HF) was used as protection membrane for SPME or used as SPME fiber due to its low cost, high surface area, simple operation, high porosity, high extraction recovery, and high sample clean-up [5,6]. In HF-SPME (HF as SPME fiber), the sorbent is placed into the pores of porous polypropylene hollow fiber that increase the selectivity and omit the carry-over; thus, this method can be used in complex matrices [7–9].

Among different coating materials, carbon nanotubes (CNTs) have many remarkable characteristics, such as rich stacking π electron, hollow tube structure, dispersion forces, high surface area (150–1500 m^2/g), and hydrophobic interactions with organic compounds to exhibit good affinity toward organic compounds [10–12]. However, challenges in CNTs include rigidity, chemical inertness, and strong π–π interactions of nanotubes and formation of aggregates. Also pure CNTs are difficult to dissolve or disperse into solutions or polymers [13]. Therefore, modification of their surface or structure can improve physical and chemical properties and their dispersion for a diverse set of applications.

One approach to enhance CNT properties and improve these drawbacks is synthesis nanocomposite of CNTs and inorganic mate-

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rials, such as metal oxides (MnO_2, TiO_2, Fe_2O_3, SnO_2, ZnO, etc.). In comparison with their traditional nanofibers, these nanocomposites have remarkable advantages, including dimensional stability, good mechanical properties, simple synthesis, high chemical resistance, high adsorption capability, and low toxicity. Among these metal oxides, zirconium oxide (ZrO_2) is a material of excellent technological significance because of its excellent mechanical and thermal stability, wear and corrosion resistance, good extraction efficiency, high toughness, and biocompatibility. The crystal morphology of zirconia is monoclinic, tetragonal, and cubic [14,15]. Their outstanding properties make them useful materials in the field of ceramic, solid electrolytes, gas sensors, extraction, and catalysis [16]. Here, a rapid and convenient approach to fabricating of MWCNT/ZrO_2 is reported. The composite of MWCNT/ZrO_2 was placed inside the pores of hollow fiber and used for extraction of organic pollutants in complex matrices such as tea and coffee samples.

Coffee and tea are the most popular beverage in the world that are consumed several times a day by millions of people. Consumption of tea and coffee can cause benefit health however, contamination of these plants by organic pollutants such as pesticides, polycyclic aromatic hydrocarbons (PAHs) and heavy metals is a threat to human health [17,18]. PAHs are known as potent carcinogenic compounds. These environmental pollutants are considered as ubiquitous byproducts of incomplete combustion or pyrolysis such as coal, wood, soil, garbage, tobacco, organic foods, and other human activities. PAHs are the key components of the 189 hazardous air pollutants (HAPs) in the U.S. Clean Air Act Amendments [19]. The occurrence of PAHs in coffee and tea samples are mainly due to environmental sources, such as deposition from the air on the surface of plants, intake by marine organisms in polluted zones, and food preparation (for instance grilling, roasting, or smoking) [20–23]. Generally, the drying process increases the concentration of PAHs by more than 200 times compared to fresh tea leaves [24]. PAH contamination of coffee samples is also due to the roasting step in the production of coffee beans [25–27].

In this work, due to the toxicity, carcinogenic and mutagenic properties of PAH compounds and low concentration of PAHs in coffee and tea as well as the complex matrices of them, hollow fiber as SPME fiber and MWCNT/ZrO_2 nanocomposite as HF-SPME sorbent was applied for clean-up and extraction of PAHs as a model analytes from tea and coffee samples. The effect of different parameters on the extraction efficiency of the analytes were investigated and optimized. To the best of our knowledge, there is no report about the synthesis of a nanostructured MWCNT-ZrO_2 composite coating as the extracting phase in HF-SPME.

2. Experimental

2.1. Chemicals and reagents

Standards of PAHs (naphthalene 99% (NAP), acenaphthylene 98% (ACY), acenaphthene 99% (ACP), 4-Hcyclopenta[def]phenanthrene 97% (CPP), fluoranthene 98% (FLU), and carbazole ≥ 95% (CAR)) were purchased from Aldrich (Milwaukee, WI, USA). Under the Safe Drinking Water Act, EPA sets legal maximum limits of PAHs in drinking water in the range of 0.1–0.4 $\mu g\,L^{-1}$ [28]. Stock standard solutions of PAHs were prepared in HPLC grade acetonitrile. The individual stock solutions were prepared at a concentration of 1000 $mg\,L^{-1}$ and stored at 4 °C protected from light. The working standard solution was prepared by combining aliquots of each individual stock solution in acetonitrile and diluting to obtain the desired concentration. HPLC-grade methanol and acetonitrile were purchased from Caledon (Georgetown, ON, Canada). *n*-Hexane and 1-propanol were obtained from Merck (Darmstadt, Germany). MWCNTs of 95% purity with average diameter 3–20 nm, length 1–10 mm, and number of walls 3–15 were purchased from Plasma Chem GmbH (Berlin, Germany). Zirconyl nitrate ($ZrO(NO_3)_2$. $6H_2O$ and ethylenediamine ($H_2NCH_2CH_2NH_2$) were obtained from Merck. Plastic and glassware used for the experiments were previously washed with acetone and rinsed carefully with doubly distilled water. The Accurel Q3/2 polypropylene hollow fiber membrane (600 μm i.d., 200 μm wall thickness, and 0.2 μm pore size) was supplied by Membrana (Wuppertal, Germany).

2.2. Apparatus

The chromatographic analysis was performed with a HPLC instrument including a Varian 9012 HPLC pump (Walnut Creek, CA, USA), a six-port Chem inert HPLC valve from Valco (Houston, TX, USA) with a 20 μL sample loop, and equipped with a Varian 9050 UV–vis detector. Chromatographic data were recorded and analyzed using Chromana Software (version 3.6.4). The separations were carried out on an ODS-3 column (250 mm × 4.0 mm, with a 5 μm particle size) from MZ-Analysentechnik (Mainz, Germany). PAHs were eluted by acetonitrile (solvent A) and water (solvent B) under gradient elution conditions at a flow rate of 1.0 $mL\,min^{-1}$. The gradient elution program was 60: 40% (A:B) from 0 to 7 min; 80:20% from 7 to 9 min; and 100:0% from 9 to 20 min. The analytes were detected at 210 nm. The particle size and morphology of the synthesized NPs were determined by a scanning electron microscope (SEM) model EM3200 from KYKY Zhongguancun (Beijing, China). In addition, Fourier-transform infrared (FT-IR) spectra (4000–400 cm^{-1}) were recorded on a Thermo Scientific Nicolet IR100 (Madison, WI, USA). The KBr pellets with a ratio sample/KBr of 1:100 by mass were used to obtain FT-IR spectra.

2.3. Synthesis of ZrO_2 nanoparticles

To synthesize ZrO_2 nanoparticles, 1 mmol of ethylenediamine was dissolved in 50 mL of distilled water and added drop-wise into 1 mmol of $ZrO(NO_3)_2$. $6H_2O$ dissolved in 50 mL of distilled water under ultrasound irradiation. Then, the obtained hydroxide precipitate was filtered and washed with distilled water three times. The final product was dried at 80 °C for 24 h and calcined at 600 °C for 4 h [29].

2.4. Synthesis of MWCNT/ZrO_2 nanocomposite

In a typical synthesis, 100 mg of MWCNT was dispersed in 50 mL of distilled water and sonicated for 90 min (solution A). Solution B was prepared by dispersing a certain amount of ZrO_2 nanoparticles in 50 mL of distilled water. The different ratios of ZrO_2 to MWCNT including 0:1, 1:0, 1:1, 1:2, 1:3 and 2:1 were applied. The A and B solutions were mixed quickly. Finally, the resulting precipitate was aged at 80 °C for 12 h and the final product was collected by centrifuge (4000 rpm for 5 min, RCF = 2810 × *g* and Max RCF = 4190 × *g*)., washed with water and ethanol five times, and dried at 70 °C for 6 h.

2.5. Preparation of MWCNT/ZrO_2 nanocomposite film-coated SPME hollow fiber

Fabrication of MWCNT/ZrO_2 nanocomposite on hollow fiber is as follows: the Accurel Q 3/2 polypropylene hollow fibers (3 cm) were washed with acetone to remove impurities and were dried in air. 20 mg of MWCNT/ZrO_2 was first dispersed in 2 mL of methanol and sonicated for 5 min to mix the adsorbents. Then, polypropylene hollow fiber was put into this mixture and was sonicated for 30 min. As a result, the adsorbent was placed on the wall of hollow fiber