

An inorganic–organic hybrid material based on ZnO nanoparticles anchored to a composite made from polythiophene and hexagonally ordered silica for use in solid-phase fiber microextraction of PAHs

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Abstract We report on an inorganic–organic hybrid nanocomposite that represents a novel kind of fiber coating for solid-phase microextraction (SPME) of polycyclic aromatic hydrocarbons (PAHs). The material is composed of ZnO nanoparticles, polythiophene and hexagonally ordered silica, and displays good extraction capability due to its nanostructure. The nanocomposite was synthesized by an in-situ polymerization technique, and the ZnO nanoparticles were anchored to the pores in the walls. The ZnO/polythiophene/hexagonally ordered silica (ZnO/PT/SBA-15) nanocomposite was then deposited on a stainless steel wire to obtain the fiber for SPME of PAHs. Optimum conditions include an extraction temperature of 85 °C (for 30 min only), a desorption temperature of 260 °C (for 2 min), and a salt concentration (NaCl) of 20 % (w/v). The detection limits are between 8.2 and 20 pg mL⁻¹, and the linear responses extend from 0.1 to 10 ng mL⁻¹. The repeatability for one fiber (for $n=5$), expressed as relative standard deviation, is between 4.3 and 9.1 %. The method offers the advantage of being simple to use, rapid, and low-cost (in terms of equipment). The thermal stability of the fiber and high relative recovery (compared to conventional methods) represent additional attractive features.

Keywords Polycyclic aromatic hydrocarbons · Polythiophene · Nanocomposite · Solid-phase microextraction · Gas chromatography–mass spectrometry

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. They are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. They are found throughout the environment in the air, water, and soil. PAHs have been of significant environmental concern over the past years due to their carcinogenic and mutagenic properties [1, 2]. Moreover, they show a high persistency and low biodegradability in the environment [3]. For these reasons, PAHs are listed as priority pollutants by United States Environmental Protection Agency [4] and World Health Organization drinking-water criteria. However, as PAHs are present in trace levels in environmental matrices, a suitable and sensitive extraction method is required. There have been numerous extraction methods developed over the years to assess PAHs concentration in environmental matrices [5, 6]. Among these methods, solid phase microextraction (SPME) has emerged as an innovative extraction technique devised by Pawliszyn in late 1989 [7]. Nowadays, Solid phase microextraction (SPME) is a new sampling and pre-concentration technique, which possesses solvent free, fast diffusion rate and high enrichment factor properties. SPME initially introduced for the analysis of volatile compounds at trace levels in the different matrixes. Especially, headspace solid phase microextraction (HS-SPME) is considered a suitable sampling mode for volatile organic compounds due to its indirect contact with the analytes and high enrichment factor. It is well known that the nature of SPME coatings determines the extraction performance. Many materials have been used as the coating of the extraction fibers, such as carbowax, poly-dimethylsiloxane (PDMS),

polydimethylsiloxane–divinylbenzene (PDMS/DVB), carbowax–divinylbenzene (CW/DVB) and carboxen–PDMS, and polyacrylate [7–10]. However, these types of fibers are fragile and must be handled with great care also, these coatings showed poor selectivity and low extraction efficiency. To overcome this difficulty, so many recent researches on SPME have been focused on the preparation and characterization of new sorbents with remarkable chemical and mechanical stability, enhanced sensitivity and selectivity for specified analytes. Also new material such as Organic–inorganic nanocomposite and nanomaterials materials was synthesized and used as fiber coatings [8, 11–13]. ZnO nanomaterials have attracted much attention due to their importance in basic scientific research and their potential in manufacturing nanodevices [14–16]. Up to now, many nanodevices using ZnO nanostructures have been reported including nanolasers [17], solar cells [18], ultraviolet photodetectors [15], gas sensors [19], light emitting diodes [20], field-emission devices [21], and so on. Among the applications, gas sensors are different from the others. Gas sensors are based on good gas adsorption properties caused by the high surface to volume ratio of ZnO nanostructures. As gas adsorption materials, their application will not stop at gas sensors. But, few applications except gas sensors based on the gas adsorption properties of ZnO nanostructures have been reported. Therefore, it is interesting to find some new applications based on the gas adsorption properties of ZnO nanostructures. Organic–inorganic nanocomposites can be prepared by directly mixing nanoparticles with organic compounds or by sol–gel processes. A number of different metallic and metal oxide particles have been encapsulated into the shell of conducting polymers, giving rise to a host of nanocomposites [22, 23]. Among conducting polymers nanocomposites, the PT–metal oxide nanocomposites are attracting growing interest because of their advanced mechanical and chemical properties which are beneficial for many application fields [24]. The PT–metal interfacial structure is very important subject for various scientific and technological interests. These studies reveal to us that the fabrication of ZnO nanomaterials on the surface of PT would be suitable for the preparation of SPME coatings. By this approach, to prove and increase the surface area, and the sorption properties of polythiophene as a coating material for SPME fibers we used SBA-15 to fabricate PT/SBA-15 nanocomposites via chemical polymerization. In addition, the channels in the nanocomposite still have sufficient space. Therefore, ZnO nanomaterials were in situ anchored to the pore walls of the PT/SBA-15 composite and the ZnO/PT/SBA-15 nanocomposite was successfully prepared. The applicability of this nanocomposite coating was assessed using a laboratory-made SPME device and GC–MS for the extraction of some PAHs from the headspace of aqueous samples.

Experimental

Chemicals and reagents

Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (EO20–PO70–EO20 or Pluronic P123) as surfactant were purchased from Sigma (Buchs, Switzerland, www.sigmaaldrich.com). $\text{Zn}(\text{Ac})_2$, $\text{Li}(\text{OH})\cdot\text{H}_2\text{O}$, Methylene chloride, thiophene monomers, naphthalene, anthracene, fluorene, biphenyl, acenaphthene, fluoranthene, pyrene and all chemical solvents were obtained from the Fluka (Buchs, Switzerland, www.sigmaaldrich.com) or Merck (Darmstadt, Germany, www.merck.de) companies. The stock solution 1 mg mL^{-1} of PAHs was prepared in mixed methanol solvents. The working solutions of above compounds were prepared by diluting the stock solution with methanol and more diluted working solutions were prepared daily by diluting these solutions with deionized water. All solvents used in this study were of analytical reagent grade. Blank analyses were performed regularly to ensure that no PAHs were present in laboratory reagents, atmosphere, or fibers.

Apparatus

A Hewlett-Packard Agilent 7890A series GC equipped with a split/splitless injector and an Agilent 5975C mass-selective (Agilent Technologies, Palo Alto, CA, USA, <http://www.agilent.com/chem>) detector system were used for determination. The MS was operated in the EI mode (70 eV). Helium (99.999 %) was employed as a carrier gas, and its flow-rate was adjusted to 1 mL min^{-1} . The separation of PAHs was performed on a $30 \text{ m} \times 0.25 \text{ mm}$ HP-5 MS column (Agilent Technologies, Palo Alto, CA, USA) with $0.25 \text{ }\mu\text{m}$ film thickness. The column was held at $50 \text{ }^\circ\text{C}$ and increased to $180 \text{ }^\circ\text{C}$ at a rate of $15 \text{ }^\circ\text{C min}^{-1}$ and then raised to $260 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C min}^{-1}$ and kept at this temperature for 5 min. The injector temperature was set at $260 \text{ }^\circ\text{C}$, and all injections were carried out on the splitless mode for 2 min. The GC–MS interface, ion source and quadrupole temperatures were set at 280, 230 and $150 \text{ }^\circ\text{C}$, respectively. Compounds were identified using the Wiley 7 N (Wiley, New York, NY, USA) Mass Spectral Library. The mass spectra of target compounds were acquired and quantified in the selected ion monitoring (SIM) mode. The morphology of prepared nanocomposites was observed by using a Seron AIS-2100 scanning electron microscope (SEM). A home-made SPME device was used for holding and the injection of the fabricated fiber into the GC–MS injection port. The commercial SPME device and PDMS fiber ($100\text{-}\mu\text{m}$ film thickness) were purchased from Supelco (Bellefonte, PA, USA). The fiber was conditioned in the injection port of a GC for 1 h.

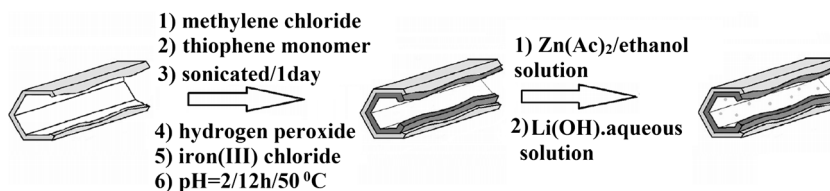
Preparation of ZnO/PT/SBA-15 nanocomposites

Preparation the ZnO/PT/SBA-15 nanocomposite was synthesized following the procedures described elsewhere [25]. Highly ordered mesoporous SBA-15 was synthesized using a procedure reported by Zhao and co-workers [26]. SBA-15 was thermally treated at 120 °C in a vacuum oven to remove the physically adsorbed water. Then, 0.50 g SBA-15 was immersed in a mixture of 10 ml methylene chloride and 5 ml thiophene monomers. The mixture was sonicated at ambient temperature for 1 h. When the methylene chloride and unadsorbed thiophene had been slowly evaporated at 30 °C for 24 h under a vacuum oven, the mixture was added to a solution of H₂O/ethanol (volume ratio: 5/1), which contained 5 ml 30 % hydrogen peroxide aqueous solution and 4 mg FeCl₃. The polymerization proceeded under nitrogen atmosphere and pH=2 for over 12 h at 50 °C. The remained product was directly precipitated into vigorously stirred methanol (six volumes), then filtered off and washed with methanol several times, and eventually dried under vacuum at 50 °C for 12 h to remove the physically adsorbed water molecules [27]. The PT/SBA-15 nanocomposite was directly immersed in Zn(Ac)₂/ethanol solution through sonication in order to adsorb Zn²⁺ adequately, and then Li(OH)·aqueous solution was added to form ZnO nanoparticles and the ZnO/PT/SBA-15 composite was successfully prepared [28]. The schematic of reactions is shown in Fig. 1.

Preparation of the SPME fiber

A piece of stainless steel wire with a 200- μ m diameter was twice cleaned with methanol in an ultrasonic bath for 20 min and dried at 70 °C. One centimeter of the wire was limed with epoxy glue and the ZnO/PT/SBA-15 nanocomposite was immobilized onto the wire. The coated wire was heated to 50 °C for 48 h in an oven, gently scrubbed to remove non-bonded particles and assembled to the SPME holder device. Finally, prepared SPME fiber was inserted into the GC injection port to be cleaned and conditioned at 260 °C for 1 h in a helium environment. Figure 2 shows the SEM image of a fabricated SPME fiber with a stainless steel core. The thickness of the uniform coating layer was calculated from the difference between the coated and uncoated stainless steel wire and come out to be about 20 μ m.

Fig. 1 Schematic representation of the synthesis of ZnO/PT/SBA-15



The headspace solid phase microextraction (HS-SPME) procedure

SPME was performed with the prepared nanocomposite fiber, mounted in its SPME device. During the headspace extraction, the aqueous samples were continuously stirred with a magnetic stir bar. The extraction temperature was controlled using a thermostated water bath. Thermal desorption of retained compounds on fiber was carried out at 260 °C while the split valve of injector on the GC kept closed at different period of times. In all experiments, 5 mL of double distilled water or wastewater was spiked with PAHs standards in a 20 mL vial and placed on a magnetic stirrer. After reaching the extraction time, the SPME probe containing analytes from the sample, was withdrawn from the vial and inserted into the GC injection port for thermal desorption.

Water and waste water samples

Water samples were collected (on July 2013) from Tabriz, Iran (polluted part of the Aji River (at Polsangi bridge)) and Chichih River near the Ahar city. The samples were stored at 4 °C before the analysis.

Results and discussion

Mesoporous silica SBA-15 is an inorganic material, which does not have good interaction with nonpolar organic compounds. Therefore, the use of nanostructure silica for extraction of volatile organic compounds is rather inconsiderable. To overcome this problem, the polymerization of SBA-15 with polythiophene was performed to modify the surface of the SBA-15 particles. Since polythiophene contains a conjugated π structure, there is an expectation that it efficiently extracts aromatic compounds easily through π - π and hydrophobic interactions. In addition, the channels in the PT/SBA-15 nanocomposite have sufficient space. Therefore, ZnO nanoparticles that have good gas adsorption properties anchored to the pore walls of the PT/SBA-15 nanocomposite and the ZnO/PT/SBA-15 nanocomposite was successfully prepared. The SEM images of this nanocomposite were recorded, and the results confirmed the previous report [25]. As it is shown in Fig. 3 the nanocomposites have a homogeneous structure, which could significantly increase the available surface area for adsorption.

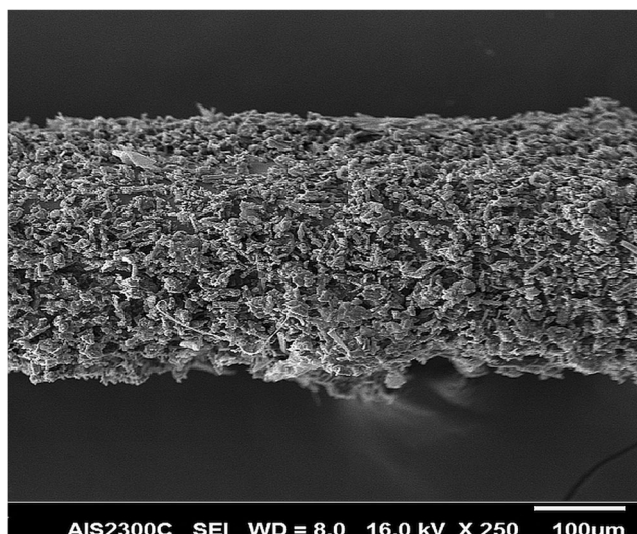


Fig. 2 SEM image of a fabricated SPME fiber

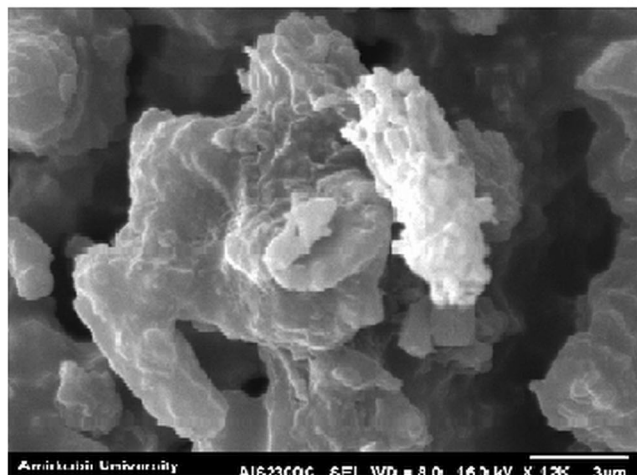
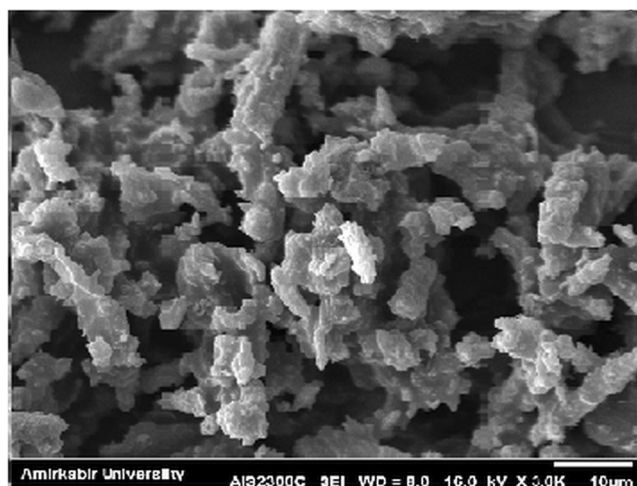


Fig. 3 The SEM images of ZnO/PT/SBA-15 nanocomposite at various magnifications

Optimization of the HS-SPME apparatus

To evaluate the ability of prepared nanocomposite for extracting aromatic compounds from water samples, a mixture of PAHs including naphthalene, biphenyl, anthracene, fluorene, acenaphthene, fluoranthene and pyrene was used. The extraction of these selected analytes from spiked water solutions was performed using the headspace SPME (HS-SPME) mode. The use of headspace is usually preferred as the extent of damage to the fiber caused by the sample matrix is quite limited. Also, PAHs have sufficient vapor pressure to be analyzed by headspace mode. Effects of different parameters such as the extraction temperature, stirring rate, the ionic strength and extraction time on the amounts of extracted PAHs from water samples were investigated using SPME fiber. Before optimization of the extraction parameters, complete desorption of the collected analytes in the GC–MS injection port, and their proper separation over the column had been optimized. For this purpose, different injector temperatures and desorption times were tested. The upper temperature that can be used for desorption of the analytes from a fiber is limited by the thermal stability of its coating. A temperature of 260 °C was found to be appropriate for the efficient desorption of analytes from the fabricated nanocomposite fiber without damaging its coating. Desorption times from 1 to 5 min were investigated at optimum temperature (260 °C); 2 min was selected for a complete desorption with no memory effect.

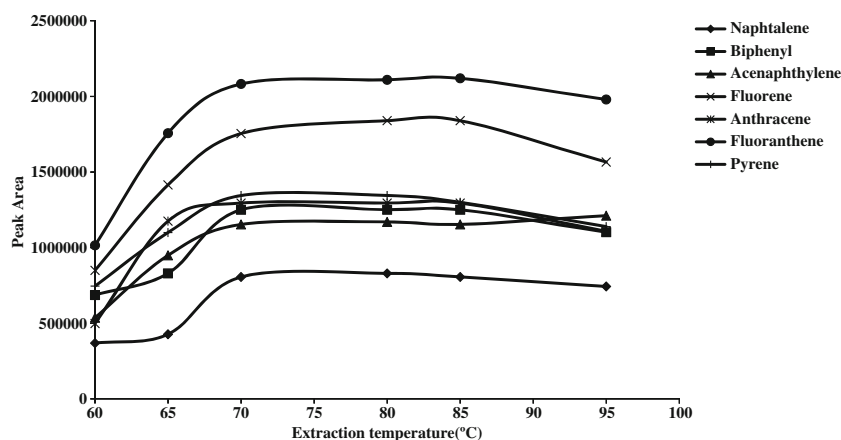
Temperature effect

For HS-SPME, the sample temperature is a very important factor because it can affect the rate and equilibrium of extraction. The effect of temperature on the extraction of the PAHs compounds, present in 5 mL aqueous solution in the range of 60–95 °C, was investigated. Figure 4 presents the effect of sample temperature on the extraction ability of volatile compounds. As can be seen, the extraction ability increases, with increasing temperature, up to 65 °C, due to the increasing distribution constant of analytes between the sample phase and headspace; However, for most of the compound a slight decrease in adsorption capacity was observed when temperature increased up to 100 °C. This is most probably due to a decreased partition coefficient of analytes between headspace and fiber because adsorption is generally an exothermic process. On the basis of these experimental observations, the optimum sample temperature was chosen to be 85 °C.

Extraction time

HS-SPME is an equilibrium-based technique, and there is a direct relationship between the amount extracted and the extraction time. The adsorption time profiles were studied

Fig. 4 Influence of the extraction temperature on the peak area of PAHs. Conditions: PAH concentration: 5 ng mL^{-1} , extraction time: 30 min, stirring rate: 500 rpm, NaCl: 20 %

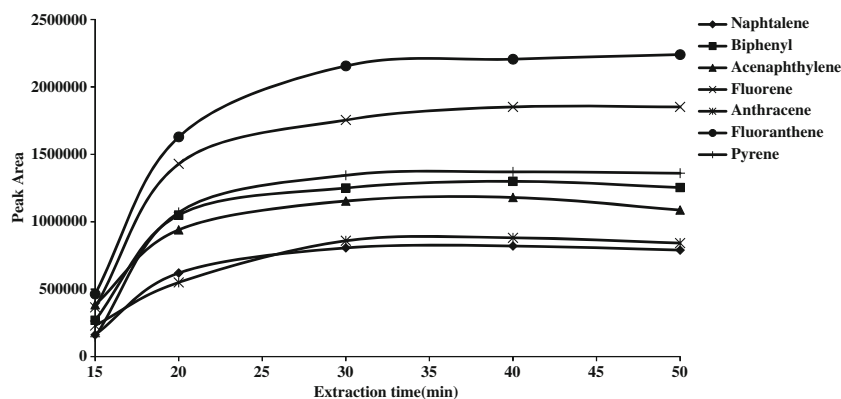


by monitoring the GC/MS peak area as a function of extraction time, while the fiber was exposed to standard solutions of the PAHs at a concentration of 5 ng mL^{-1} for a time ranging from 15 to 50 min. Figure 5 shows that at constant temperature the extraction efficiency increases with extraction time and reaches a plateau when equilibrium is established. The equilibrium times for the PAHs increased with increasing molecular mass. Thus, an extraction time of 30 min was selected to shorten the analysis time.

Effect ionic strength

The addition of salt often increased the ionic strength and thus increased the extraction efficiency due to the salting out effect. For this purpose, the influence of the NaCl concentration on the extraction efficiency was investigated by preparing solutions of PAHs in a range of 0–30 % (W/V). The results indicated that the extraction efficiency increases with increasing concentration of NaCl, reaches a maximum in the presence of 20 % NaCl and remains constant thereafter. The best results obtained for an aqueous sample containing 20 % NaCl, which was three to seven times greater than that obtained for an aqueous sample with no added NaCl.

Fig. 5 Effect of the extraction time on the peak area of PAHs. Conditions: PAHs concentration: 5 ng mL^{-1} , extraction temperature: $85 \text{ }^\circ\text{C}$, stirring rate: 500 rpm, NaCl: 20 %



Therefore, all further extractions were conducted with 20 % NaCl added.

Stirring rate

Agitation of the sample improve mass transfer in the aqueous phase and induces the convection in the headspace, and consequently, the between the aqueous phase and headspace can be achieved more rapidly. In other words, sample stirring reduces the time required to reach the equilibrium by enhancing the diffusion of the analytes towards the fiber, especially for higher molecular mass analytes. Extraction efficiency of the studied compounds was measured from 5 ml of the model sample solutions containing 20 % (W/V) NaCl and 30 min extraction times at various stirring speeds. The results revealed that extraction efficiency reaches a maximum and remains constant above 500 rpm.

Quantitative evaluation and real sample analysis

Figures of merit of the method including dynamic linear range (DLR), the correlation coefficient of the calibration graph, and relative standard deviation are listed in Table 1. Calibration

Table 1 Some analytical data obtained for microextraction of PAHs using the ZnO/PT/SBA-15 SPME fiber

| Compound | DLR ^a (ng mL ⁻¹) | Regression coefficient | LOD ^b (pg mL ⁻¹) ZnO/PT/SBA-15 | Reproducibility R.S.D. %, (5 ng mL ⁻¹) | Repeatability R.S.D. ^c %, (5 ng mL ⁻¹) |
|--------------|---|------------------------|---|--|---|
| Naphthalene | 0.1–10 | 0.994 | 20.1 | 17.1 | 9.1 |
| Biphenyl | 0.1–10 | 0.988 | 10.2 | 14.3 | 6.3 |
| Acenaphthene | 0.1–10 | 0.996 | 9.2 | 12.5 | 7.8 |
| Fluorene | 0.1–10 | 0.998 | 8.2 | 13.4 | 6.3 |
| Anthracene | 0.1–10 | 0.997 | 10.3 | 15.3 | 5.9 |
| Fluoranthene | 0.1–10 | 0.994 | 9.0 | 16.2 | 6.2 |
| Pyrene | 0.1–100 | 0.997 | 9.8 | 14.1 | 4.3 |

^aDynamic linear range^bLimit of detection calculated as three times the baseline noise^cRelative standard deviation

curves were drawn using 10 spiking levels of PAHs in the concentration range of 0.1–10 ng mL⁻¹. For each level, three replicate extractions and determination were performed at optimal conditions. The values of the correlation coefficient obtained were between 0.988 and 0.998, showing an acceptable linearity in the dynamic ranges represented in Table 1.

In order to assess the repeatability (for one fiber) and reproducibility (fiber-to-fiber), we constructed five fibers under the same conditions and five repeated experiments were carried out using each fiber. The R.S.Ds. for each fiber and for fiber-to-fiber were calculated and are summarized in Table 1. These data show that repeatability of the method is good. Relatively high fiber-to-fiber R.S.D. ($\leq 17.1\%$) indicates that, most likely, the coating volume varies significantly between fibers. Consequently, the coating procedure needs to be improved to ensure the thickness is more uniform and reproducible. On the other hand, the prepared SPME fiber is mechanically stable and there is no need to use different fibers in analysis.

The extraction capabilities of the fabricated fiber for sampling PAHs in water at trace levels were compared with a commercial solid coated based SPME fiber, polydimethylsiloxane 100 μm [29], under similar conditions. The observed results showed that chromatographic response of the prepared fiber is 2–3 times higher than the results acquired by using the commercial PDMS fiber.

The ZnO/PT/SBA-15 fibers were applied to the determination of PAH₅ compounds in polluted river water and water samples. Since the concentrations of most of the PAH₅ compounds in the real samples were lower than the detection limit

of the method, the samples were spiked with the PAH₅ compounds. Table 2 shows the satisfactory results obtained for the real samples.

The lifetime of homemade SPME device

The lifetime of the homemade SPME device was evaluated after more than 20 analyses, using a 5 ng spiked sample as the performance test sample. No significant variance was observed in the obtained results which indicate the stability of the mentioned device. The lifetime of this device should be longer than the commercial SPME fiber.

Conclusion

In the present study, novel SPME sorbent based on ZnO/PT/SBA-15 nanocomposite material was fabricated. One obstacle to using SBA-15 nanostructure silica is low interaction with nonpolar organic compounds. In this work, we developed a method that overcomes this hurdle and provides ZnO/PT/SBA-15 for HS-SPME. As-prepared composites were successfully used in the process of pre-concentration and extraction of PAHs from water samples. The enhanced sorbent capacity was originated from the properties of the composites, including porous structure, small particle size, and homogeneous framework. The porous structure, easy preparation, long lifetime, strong interaction, high thermal stability, and simplicity of the coating to the steel wire are among the clear advantages of the proposed fiber coating. The presented

Table 2 The results obtained for the analysis of the spiked water samples (5 ng mL⁻¹) by the proposed method, under the optimized conditions

| Sample | Added (ng mL ⁻¹) | Found ^a (ng mL ⁻¹) | | | | | | |
|---------------|------------------------------|---|----------|------------|----------|--------------|--------------|----------|
| | | Naphthalene | Biphenyl | Anthracene | Fluorene | Acenaphthene | Fluoranthene | Pyrene |
| Aji river | 5.0 | 5.2 (0.6) | 5.7(0.7) | 5.2(0.1) | 5.6(0.7) | 5.3(0.8) | 5.9(0.4) | 5.7(0.3) |
| Chichih river | 5.0 | 5.1(0.9) | 5.2(0.3) | 5.3(0.7) | 5.6(0.9) | 5.7(0.7) | 5.1(0.2) | 5.1(0.5) |

^aThe figures within parentheses are standard deviations for three replicates

experimental results clearly demonstrate that prepared fibers are suitable for HS-SPME of PAHs analyses. The combination of HS-SPME using ZnO/PT/SBA-15 fiber with GC-MS can achieve low LODs and can be applied to determine PAHs in real samples.

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