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Carbon fibers modified with carbon nanoparticles by a facile and fast flame preparation for in-tube solid-phase microextraction



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KEYWORDS

Carbon nanoparticles; Carbon fibers; Flame preparation method; Solid-phase microextraction; Polycyclic aromatic hydrocarbons **Abstract** Carbon fibers (CFs) were modified with carbon nanoparticles (CNPs) by a facile and fast flame preparation method. CNPs-CFs were observed by scanning electron microscope, and the nano-scaled granular structure on the surface was found. This material was also characterized by Raman microscope and X-ray photoelectron spectroscope. It was placed into a polyetheretherketone tube to get an extraction tube, which was connected with high performance liquid chromatography for online analysis. The tube displayed the effective extraction to several polycyclic aromatic hydrocarbons (PAHs), based on the possible hydrophobic and π stacking mechanism. Under the optimized conditions (60 mL of sample volume, 2.00 mL min⁻¹ of sample rate, 0.5% of methanol in sample, 2.0 min of desorption time), an analytical method towards these PAH targets was established. The low limits of detection (0.001–0.005 µg L⁻¹), satisfactory linear ranges (0.003–5.0 µg L⁻¹, 0.003–10.0 µg L⁻¹) and efficient enrichment factors (1012–3164) were presented. The method was applied to detect trace targets in several water samples and satisfactory results were obtained. The method provided some superiorities over other analytical methods, like online test, shorter time and better sensitivity.

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1. Introduction

As one of the most efficient sample pretreatment techniques in recent years, solid-phase microextraction (SPME) integrates sampling, enrichment, separation and injection into one step, that greatly saves the time and the solvent, and overcomes the shortcomings of traditional methods (Llompart et al., 2019; Ouyang et al., 2011; Spietelun et al., 2010; Jalili et al.,

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2019). More importantly, it could be coupled with gas chromatography (GC) (Lee et al., 2019); high performance liquid chromatography (HPLC) and other instruments (Ma et al., 2020). With the development of SPME, different forms such as fiber SPME (Catherine and Pawliszyn, 1990), stir bar solid-phase microextraction (SBSE) (Carlo et al., 2002), dispersive solid-phase microextraction (DSPME) (Zhu et al., 2020) and in-tube SPME (IT-SPME) (Eisert and Pawliszyn, 1997) have come one after another. These promoted further application of SPME in various fields. The extraction performance mainly depends on the properties of sorbent coating (surface area, hydrophobicity, hydrophilicity, etc.), that is, the selection of coating decides the enrichment effect and selectivity. A number of materials, such as carbon materials (Zhu et al., 2020). metal organic frameworks (MOFs) (Zeng et al., 2019), covalent organic frameworks (COFs) (Feng et al., 2021), polymers (Zhu et al., 2019); ionic liquids (Feng et al., 2020), aerogels (Tian et al., 2019), mesoporous materials (Zhang et al., 2019), have been developed as the coatings for SPME.

Recently, carbon materials, including carbon fibers (CFs) (Jon et al., 2020), carbon nanotubes (Wang et al., 2016), graphene oxide (Wen et al., 2017), bamboo charcoal (Liu et al., 2014) and other categories (Zeng et al., 2014), have attracted much more attention in sample preparation, due to their unique advantages like excellent adsorption performance and stability. CFs, made of polypropylene, asphalt, viscose fiber, and etc. by peroxidation, carbonization and graphitization processes, are one type of special fiber material. Owing to good thermal resistance, chemical stability, conductivity, and hydrophobic property, CFs become a promising adsorbent material (Ling et al., 2016). However, CFs were directly used as SPME sorbent, the adsorption capacity was limited due to the relative smooth surface (Feng et al., 2017). Whereas, among the widely used carbon materials, carbon nanoparticles (CNPs) play an important role (Liu et al., 2014). Because of large specific surface area and good adsorption property, CNPs have good extraction performance for hydrophobic species, and are mostly used in the preparation of composite materials and the modification of other materials. There are different synthetic ways, for example, Lou et al. used lithium metal to reduce CS₂ at 500 °C to produce CNPs (Lou et al., 2014). Using aliphatic alcohols and *n*-hexane as stocks, Park et al. successfully obtained CNPs in the form of linear molecules via advanced solution plasma process (Park et al., 2018). But most preparation methods were relatively complex because a variety of reagents or harsh conditions like high temperature were required. A facile and low-cost flame synthesis process was introduced to fabricate CNPs on carbon fabric (Yuan et al., 2011), this way was also used to produce CNPs-coated wire for SPME fiber in our previous work (Sun et al., 2013).

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants that have two or more phenyl groups (Groven et al., 2019; Ali, 2019). Because of the polycyclic and carcinogenic properties, PAHs are considered as priority organic pollutants by the US Environmental Protection Agency and the European Environment Agency (Dumanoglu et al., 2017; Cai et al., 2015). PAHs are introduced into the environment owing to the incomplete combustion of coal, natural gas, tobacco, wood and etc. in human or natural activities

(Cai et al., 2015; Zhang et al., 2012). In addition, PAHs penetrate and accumulate in the food chain due to their high lipophilic properties, eventually entering human organisms (Givechev et al., 2020; Gao et al., 2018). PAHs can affect respiratory, skin, reproductive and neurological problems in humans (Santos et al., 2019; Pulster et al., 2019). So, the accuracy determination of trace PAHs is of great significance in many fields, like environmental monitoring, food safety, health impact monitoring and so on (Lawal, 2017; Oliveira et al., 2019). Due to its very low concentration in food and environment, the sample pretreatment is necessary before the detection.

Based on these considerations, CNPs were *in-situ* modified on the surface of CFs by a simple and rapid flame synthesis process to improve the extraction performance. The CNPs-CFs were characterized by scanning electron microscope (SEM), X-ray photoelectron spectroscope (XPS) and Raman microscope. CNPs-CFs were filled into a polyetheretherketone (PEEK) tube to prepare extraction tube, and the tube was connected with HPLC for online IT-SPME-HPLC analysis. Compared with bare CFs, CNPs-CFs exhibited the enhanced extraction effect towards PAHs. After the optimization of conditions, the analytical method for several PAH targets was established and applied to the determination of trace analytes in real samples.

2. Experimental

2.1. Materials and reagents

Naphthalen (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (FlA), and pyrene (Pyr) were of analytical reagent grade and purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Acetonitrile was of chromatographic grade from Tiandi Co., Ltd. (USA). Rain water and river water were collected locally. Honey was brought from supermarket. PEEK tube (0.75 mm i.d., 1.5 mm o.d.) was acquired from Changzhou Youwoshi Plastic Products Co., Ltd (Changzhou, China). CFs (7 µm d.) were obtained from Japan Toho Chemical Industry Co., Ltd. Other chemicals were of analytical reagent grade.

2.2. Apparatus

An Agilent 1260 HPLC system (Santa Clara, CA, USA), equipped with a Zorbax C_{18} column (250 × 4.6 mm i.d., 5 µm) and a diode array detector (DAD), was used for the detection of PAHs. Chromatographic conditions included 25 °C of column temperature, 1.00 mL min⁻¹ of mobile phase (0–10 min, 70% acetonitrile-30% water; 10–18 min, acetonitrile from 70% to 100%; 18 min stop). A pump from Dalian Elite Analytical Instruments Co., Ltd. (Dalian, China) was used to transport sample solution through extraction tube. Bare CFs and CNPs-CFs were characterized by a fieldemission SEM (SUPRATM55, Carl Zeiss, AG, Germany), a Raman microscope (532 nm laser excitation, JY Horiba Labram HR800 Raman microscope, UK) and a Kratos Axis Ultra DLD spectrometer (Shimadzu Corp., Japan) employing a monochromated Al Ka X-ray source.

2.3. Preparation of solution

Eight PAHs were dissolved in methanol solvent to prepare 10 mg L^{-1} of stock solution. Working solution was obtained by diluting the stock solution with water daily. 30 g of honey was dissolved in 1500 mL water to obtain honey water sample. Before test, rain water, river water, honey water samples, and mobile phase were separately filtered with a 0.45 μ m membrane.

2.4. Preparation of extraction tube

According to previous reports (Yuan et al., 2011; Sun et al., 2013), the preparation of CNPs on the surface of CFs can be achieved with an ordinary alcohol lamp. The alcohol wick was ignited in a room with no obvious air exchange. After the flame was stabilized, CFs fixed on an iron frame were placed about 5 cm above the wick for 30 s. Through the incomplete combustion of ethanol, CNPs were *in-situ* deposited onto the CFs. After cleaning with ethanol and drying, the CNPs-CFs (51 mg) were filled into a PEEK tube (20 cm length) to generate the extraction tube. Another tube filled with bare CFs (50.6 mg) was also prepared for the comparison.

2.5. Online analysis procedure

The extraction tube was connected to the six-way valve of HPLC, and an IT-SPME-HPLC online system was estab-

lished. As can be seen from Fig. 1a, in the "Load" state, the sample solution flowed through the tube, and the analytes were adsorbed by the CNPs-CFs. After that, the six-way valve was changed to the state of "Inject" in Fig. 1b, the analytes were desorbed from the tube and then separated on chromatographic column by 1.00 mL min⁻¹ of mobile phase (A, acetonitrile; B, water; 0–10 min A = 70%, B = 30%; 10–18 min A = 100%; 18 min stop) and further detected by DAD.

3. Results and discussion

3.1. Characterization of extraction materials

As can be seen from SEM images in Fig. 2a-b, CFs with the diameter of $7 \pm 1 \mu m$ were uniform, the surface of bare CFs was relatively smooth and has many folds. After the modification (Fig. 2c-d), the surface of CFs was obviously full of particulate materials, namely CNPs. Except for the rise of the surface roughness of CFs, CNPs greatly increased the adsorption sites, that was conducive to improve the extraction effect.

According to Raman spectra of bare CFs and CNPs-CFs in Fig. 3a, there were two broad peaks (D band at 1355 cm^{-1} and G band at 1577 cm^{-1}) on both materials. The G band is inherent in natural graphite and belongs to the stretching vibration of C–C bond in graphite lattice plane. With the increase of graphite lattice defects, edge disordered arrangement and low symmetrical carbon, D band appears around 1355 cm^{-1} . Before and after the deposition of CNPs, the intensity ratio



Fig. 1 Online analysis procedures, composed of (a) online extraction and (b) online desorption and detection.



Fig. 2 SEM images of (a-b) bare CFs and (c-d) CNPs-CFs.



Fig. 3 (a) Raman spectra of bare CFs and CNPs-CFs, (b) XPS spectra of bare CFs and CNPs-CFs, (c) C1s spectra of bare CFs, and (d) C1s spectrum of CNPs-CFs.

of D peak and G peak ($R = I_D/I_G$) was calculated, respectively. The ratio value increased from 0.9523 to 0.9799, indicating amorphous carbon on the modified CFs surface was increased.

The XPS results of bare CFs and CNPs-CFs are represented in Fig. 3b-d. The carbon signal of CNPs-CFs was higher than that of bare CFs (Fig. 3b), while the oxygen signal was lower. The fitting analysis of C1s spectrum gave two kinds of carbon atoms with different binding energy on the surface of bare CFs (Fig. 3c), in which the main peak 1 at 284.3 eV represented the carbon atom in the elemental carbon (C–C), and the peak 2 (285.5 eV) corresponded to the carbon atom in the group C–O–C. As shown in Fig. 3d, the surface of CNPs-CFs was mainly composed of amorphous carbon and graphite with binding energy of 284.5 eV. The increase of carbon content, the decrease of oxygen content and the disappearance of peak 2 (285.5 eV) were mainly attributed to the deposition of CNPs on the CFs.

3.2. Investigation of extraction and desorption conditions

SPME is a technique based on the partition equilibrium of analytes between extraction material and sample. Some important conditions such as sampling volume, sampling rate, concentration of organic solvent in sample, and desorption time were optimized to investigate the effect on extraction efficiency using 5 μ g L⁻¹ of working solution.

Sampling volume plays an important role in IT-SPME. In this work, the sampling volume was regulated in the range of 30-80 mL with 2.00 mL min⁻¹ of sampling rate. As can be seen from Fig. 4a, the peak area of each analyte gradually increased with the sampling volume from 30 mL to 60 mL. More than 60 mL of sampling, the peak areas of four analytes were unchanged, but another four analytes continued to increase. Considering suitable test time and satisfactory analytical sensitivity, 60 mL of sample was selected for the following experiment.

Under a fixed sampling volume, the sampling rate decides the test time directly. To shorten time, high sampling rate should be selected, while it is not in favor of the improvement of the extraction efficiency and also causes large pressure in tube. Whereas, long time is required under a low sampling rate. In this work, the sampling rates were separately investigated with 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, and 2.50 mL min⁻¹ using 60 mL of sample. As shown in Fig. 4b, the peak areas of all targets remained little change from 1.00 to 2.00 mL min⁻¹ except for Nap, and reduced beyond 2.00 mL min⁻¹. In order to avoid the damage of extraction material by excessive flow rate, and to delay the analysis time due to small rate, the sampling rate was confirmed as 2.00 mL min⁻¹ for other tests.

Adding organic solvent into the sample solution can improve the solubility of hydrophobic analytes and the accuracy of analytical results. However, excessive organic solvent will weaken the extraction performance of extraction material. In this study, sample solutions with different methanol concentration (0, 0.5%, 1.0%, 2.0%, 3.0%, 5.0%, 10.0%, v/v) were tested to evaluate the effect on extraction efficiency. As can be seen from Fig. 4c, the peak areas of most PAHs showed an upward trend as the methanol content from 0 to 0.5% (v/



Fig. 4 The optimization of extraction and desorption conditions including (a) sampling volume, (b) sampling rate, (c) organic solvent content, and (d) desorption time. PAH analytes: (1) Nap, (2) Acy, (3) Ace, (4) Flu, (5) Phe, (6) Ant, (7) FlA and (8) Pyr. Conditions: the concentration of each analyte, 5 μ g L⁻¹. The number of tests to establish the values plotted was three (n = 3).

v), and then decreased. These resulted from the reduced distribution coefficient of analyte between extraction material and sample by adding methanol in sample. But high hydrophobic FIA and Pyr were different with others, owing to their possible competitive adsorption with others. In order to obtain better extraction efficiency, the methanol content in sample solution was selected as 0.5%.

Besides of the extraction conditions, desorption conditions also greatly influence the analytical results and sensitivity. Under a certain desorption solvent and fixed flow rate, desorption time can directly affect the analytical results. Too short time makes the incomplete desorption of analytes from the tube. On the contrary, too long time is unnecessary. After the test was performed under the optimized extraction conditions, 1.00 mL min⁻¹ of mobile phase directly desorbed analytes from the tube, and the desorption time was observed from 0.2 to 3.0 min. As shown in Fig. 4d, the peak areas of all analytes gradually increased from 0.2 min to 0.6 min and then remained stable. In order to get satisfactory desorption efficiency and eliminate possible residual, 2.0 min was selected as the desorption time.

3.3. Method evaluation and application to real samples

Under the optimal conditions, a standard solution of PAHs (5 μ g L⁻¹) was extracted by two tubes filled with bare CFs and CNPs-CFs, respectively. HPLC chromatograms on two tubes are shown in Fig. 5, the extraction performance of CNPs-CFs was much greater than that of bare CFs. The ratio of peak areas of each analyte extracted with CFs before and after carbon deposition was found to be in the range of 1.57–5.11, it was indicated that the existence of CNPs greatly improved the extraction ability of CFs to PAHs.

At the same time, the performance of IT-SPME-HPLC, including the limits of detection (LODs), linear ranges, correlation coefficients (*r*) and enrichment factors, was studied, and the results are summarized in Table 1. The working curve was obtained using different concentrations of standard solutions. The linear ranges of Nap, Acy, Ace and Flu were 0.003–5.0 μ g L⁻¹, 0.01–5.0 μ g L⁻¹, 0.007–5.0 μ g L⁻¹ and 0.02–5.0 μ g L⁻¹, respectively. However, Phe and Ant had lar-



Fig. 5 HPLC chromatograms after the enrichment of 5 μ g L⁻¹ of PAHs based on bare CFs and CNPs-CFs. Peaks: (1) Nap, (2) Acy, (3) Ace, (4) Flu, (5) Phe, (6) Ant, (7) FlA and (8) Pyr. The number of tests to establish the values plotted was three (n = 3).

ger linear ranges (0.003–10.0 μ g L⁻¹), and the linear ranges of FlA and Pyr corresponded to 0.01–10.0 μ g L⁻¹ and 0.007– 10.0 μ g L⁻¹. Their r values ranged from 0.9897 to 0.9997 and the LODs (S/N = 3) were between 0.001 and 0.005 μ g L^{-1} . High sensitivity of the method resulted from good enrichment effect, which can be reflected by the enrichment factor. It was calculated based on the ratio of analyte concentration after and before test (C_{SPME}/C_o). After a sample of 5 µg L⁻¹ (Co) was tested, CSPME was achieved through directly injecting 20 µL standard samples under the same peak area. The enrichment factors were in the range of 1012-3164. Extraction repeatability was investigated via parallel test for three times with 5 μ g L⁻¹ of standard solution and denoted by relative standard deviations (RSDs, n = 3), the values were in the range of 4.5%-9.8%. Similarly, three tubes were investigated under the same conditions to evaluate preparation repeatability, RSD value (n = 3) of each analyte among three tubes was ranged from 6.7% to 14.6%.

In order to verify the applicability of this method, it was used to detect PAH targets in real samples, including rain water, river water, and honey water. As can be seen from and Table 2, eight PAHs were detected in river water, only FlA and Pyr were not detected in rain water, and there was no target PAH in honey water sample. Then, the feasibility of the method was further tested through investigating the relative recovery of sample solutions with different spiked levels. The ranges of relative recoveries spiked at 1 μ g L⁻¹, 3 μ g L⁻¹ and 5 μ g L⁻¹ were separately 84.6%-120.3%, 81.0%-90.7%, and 80.2%-97.6% in the rain water, and that were 87.7%-123.7%, 81.2%-121.8%, and 84.6%-118.0% in honey water. In the river water, the relative recoveries of all targets spiked 1 μ g L⁻¹, 3 μ g L⁻¹ and 5 μ g L⁻¹ ranged in 81.1%-107.1%, 83.9%-115.6%, and 80.8%-118.3%, respectively. These results indicate that the method was suitable to detect trace PAHs in real samples and had a potential application.

3.4. Comparation with other methods

The method was compared with other methods for detecting PAHs. As can be seen from Table 3, the sensitivity and linear ranges of analytical methods based on several functionalized CFs are different. Compared with cotton-based CFs-SPME-GC-MS method (Shi et al., 2019); the proposed method provided wider linear ranges and lower LODs, although its extraction time was longer, the method was online performed. Better sensitivity on CNPs-CFs was obtained than that on CFs (Feng et al., 2016) with the same extraction time, due to larger sampling volume. Compared to the proposed method. HS-SPME-GC-MS method based on PPv-CFs (Tabibpour et al., 2020) had larger LODs, while better linear ranges and shorter extraction time. The GO-CFs (Feng et al., 2017) had a thicker coating of graphene oxide and the CNPs coating on CNPs-CFs was thinner, but two methods provided similar sensitivities and the proposed method only consumed one half of time. Like CNPs-CFs, other three materials (Sun et al., 2015; Feng et al., 2018; Feng et al., 2018) were all made into the tubes and combined with HPLC for online analysis. The linear ranges of three methods were wider, but the detection sensitivity of the proposed method was better than these methods with smaller test time. Furthermore, the newly developed Al-MCM-41 (Zhu et al.,

Table 1	Analytical performances of the 11-51 WE-111 EC method for 1 Arts.								
Analytes	Linear ranges (μg L^{-1})	^a r	LODs (μ g L ⁻¹)	LOQs (μ g L ⁻¹)	Enrichment factors	^b Extraction repeatability (n = 3, RSD%)		^c Preparation repeatability (n = RSD%)	
						Intra- day	Inter- day		
Nap	0.003-5.0	0.9897	0.001	0.003	1065	9.8	10.3	14.6	
Acy	0.01-5.0	0.9932	0.003	0.01	1012	5.3	6.7	9.0	
Ace	0.007-5.0	0.9994	0.002	0.007	1679	6.3	4.5	9.2	
Flu	0.02-5.0	0.9897	0.005	0.02	1024	7.1	5.6	11.2	
Phe	0.003-10.0	0.9997	0.001	0.003	2539	4.5	5.8	6.7	
Ant	0.003-10.0	0.9991	0.001	0.003	2695	5.2	4.0	9.8	
FlA	0.01-10.0	0.9986	0.003	0.03	2768	4.6	4.8	10.5	
Pyr	0.007-10.0	0.9970	0.002	0.007	3164	4.9	5.9	11.8	

Table 1 Analytical performances of the IT-SPME-HPLC method for PAHs

^a Calibration level: n = 9.

^b Extraction repeatability was investigated by extracting 5 μ g L⁻¹ of PAHs standard aqueous solution three times. ^c Preparation repeatability was investigated by extracting 5 μ g L⁻¹ of PAHs standard aqueous solution through three tubes prepared under the same conditions.

2020) composite extracted PAHs by HS-SPME prior to GC-FID detection, and wider linear ranges were obtained in offline mode with only 20 min, but the LODs were worse than that proposed in this work. The reason may be that CFs itself had a certain adsorption capacity. And the CNPs attached to CFs surface belonged to amorphous carbon, with irregular structural arrangement and fine pores inside, so it had strong adsorption capacity and could enrich very trace level of PAHs. Similarly, the common commercial coating (PDMS) had good extraction performance under a new gas-cycleassisted (GCA) HS-SPME device (Zhu et al., 2021). The device accelerated the evaporation rate of PAH analyte by generating a large number of bubbles and improved the mass transfer rate, so as to lower LODs and wider linear ranges were obtained. In contrast, the method proposed in this work is inferior, but the online extraction and detection mode were in line with the development of analytical chemistry and labor-saving.

Table 2	Detection results and recoveries of eight PAH targets in three real samples.									
Analytes	Rain water $(\mu g L^{-1})$	Spiked level $(\mu g \ L^{-1})$	Recovery (n = 3, %)	River water $(\mu g L^{-1})$	Spiked level $(\mu g \ L^{-1})$	Recovery (n = 3, %)	Honey water $(\mu g \ L^{-1})$	Spiked level $(\mu g \ L^{-1})$	Recovery (n = 3, %)	
Nap	NQ	1.0	119.7	NQ	1.0	98.6	ND	1.0	87.7	
-		3.0	89.5		3.0	83.9		3.0	84.9	
		5.0	88.2		5.0	80.8		5.0	84.6	
Acy	NQ	1.0	98.9	NQ	1.0	107.1	ND	1.0	113.7	
		3.0	83.4		3.0	86.2		3.0	94.7	
		5.0	80.2		5.0	81.2		5.0	89.9	
Ace	NQ	1.0	104.2	NQ	1.0	81.1	ND	1.0	90.5	
		3.0	84.8		3.0	93.5		3.0	81.2	
		5.0	97.4		5.0	81.5		5.0	87.0	
Flu	NQ	1.0	120.3	NQ	1.0	98.5	ND	1.0	106.5	
		3.0	90.7		3.0	94.4		3.0	92.3	
		5.0	90.6		5.0	90.5		5.0	88.2	
Phe	0.7	1.0	99.3	0.7	1.0	99.3	ND	1.0	114.7	
		3.0	82.2		3.0	109.1		3.0	121.8	
		5.0	87.4		5.0	96.3		5.0	113.5	
Ant	0.1	1.0	87.7	0.1	1.0	85.2	ND	1.0	123.7	
		3.0	80.1		3.0	104.8		3.0	116.1	
		5.0	97.6		5.0	108.6		5.0	101.9	
FlA	ND	1.0	90.4	0.5	1.0	89.8	ND	1.0	120.7	
		3.0	81.0		3.0	107.3		3.0	94.5	
		5.0	84.7		5.0	114.4		5.0	116.1	
Pyr	ND	1.0	84.6	0.7	1.0	84.2	ND	1.0	104.2	
		3.0	81.9		3.0	115.6		3.0	93	
		5.0	81.3		5.0	118.3		5.0	118	

ND is not detected.

NQ is detected but cannot be quantified.

Table 3 Comparison of the analytical method with other methods for PAHs.

Extraction materials	Methods	$\begin{array}{c} LODs \ (\mu g \\ L^{-1}) \end{array}$	Linear ranges $(\mu g L^{-1})$	Extraction time (min)	Sample volume (mL)	Coupling modes
CNPs-CFs in this work	IT-SPME-HPLC- DAD	0.001-0.005	0.02–5.0, 0.01– 10.0	30	60	Online
Cotton based CFs (Shi et al., 2019)	SPME-GC-MS	0.012-0.014	0.05-2	5	_	Offline
CFs (Feng et al., 2016)	IT-SPME-HPLC- DAD	0.01-0.1	0.05–50	30	30	Online
PPy-CFs (Tabibpour et al., 2020)	HS-SPME-GC– MS	0.05	0.1–50	15	-	Offline
GO-CFs (Feng et al., 2017)	IT-SPME-HPLC- DAD	0.001-0.004	0.01–50	60	60	Online
Nanostructured silver coating (Sun et al., 2015)	IT-SPME-HPLC- DAD	0.15-0.3	0.5–100, 1.0–100	60	60	Online
Ionic liquid (Feng et al., 2018)	IT-SPME-HPLC- DAD	0.03-0.05	0.1–15	40	50	Online
Melamine-formaldehyde aerogel (Feng et al., 2018)	IT-SPME-HPLC- DAD	0.01-0.05	0.03-25, 0.06-30	35	70	Online
Al-MCM-41 (Zhu et al., 2020)	HS-SPME-GC- FID	0.06-0.18	0.3-600	20	-	Offline
PDMS fiber (Zhu et al., 2021)	GCA HS-SPME- GC-FID	0.00049– 0.00151	0.002–100	11	-	Offline

GO, graphene oxide.

PPy, polypyrrole.

HS, headspace.

Al-MCM-41, Al-doped mesoporous crystalline material-41.

PDMS, polydimethylsiloxane.

GCA, gas-cycle-assisted.

4. Conclusions

To improve the extraction effect of CFs to PAHs, the surface of CFs was functionalized with CNPs in this work. A facile and rapid flame-based synthesis method was used to in-situ grow CNPs onto CFs, more adsorption sites were provided to enhance the extraction performance. The tube based on CNPs-CFs was investigated through coupling with HPLC online, and exhibited high enrichment effect more than 1012 time for PAHs due to possible hydrophobic and π - π interactions. An online IT-SPME-HPLC method was established and applied to determine trace targets in several water samples, some ones were found. Compared with other reported methods, this method displayed some advantages, such as online test, better sensitivity, shorter analytical time and so on. Furthermore, the extraction tube may be also applied to enrich and analyze other hydrophobic pollutants by IT-SPME-HPLC way. The developed CNPs-CFs not only are an efficient extraction material for sample preparation, but also are very potential in other fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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