Bamboo Charcoal as Adsorbent for SPE Coupled with Monolithic Column–HPLC for Rapid Determination of 16 Polycyclic Aromatic Hydrocarbons in Water Samples

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Abstract

The coupling of solid-phase extraction (SPE) using bamboo charcoal (BC) as an adsorbent with a monolithic column–high performance liquid chromatography (MC–HPLC) method was developed for the high-efficiency enrichment and rapid determination of 16 polycyclic aromatic hydrocarbons (PAHs) in water. Key influence factors, such as the type and the volume of the elution solvent, and the flow rate and the volume of the sample loading, were optimized to obtain a high SPE recovery and extraction efficiency. BC as an SPE adsorbent presented a high extraction efficiency due to its large specific surface area and high adsorption capacity; MC as an HPLC column accelerated the separation within 8 min because of its high porosity, fast mass transfer, and low-pressure resistance. The calibration curves for the PAHs extracted were linear in the range of 0.2–15 µg/L, with the correlation coefficients (r^2) between 0.9970–0.9999. This method attained good precisions (relative standard deviation, RSD) from 3.5 to 10.9% for the standard PAHs I aqueous solutions at 5 µg/L; the method recoveries ranged in 52.6–121.6% for real spiked river water samples with 0.4 and 4 µg/L. The limits of detection (LODs, S/N = 3) of the method were determined from 11 and 87 ng/L. The developed method was demonstrated to be applicable for the rapid and sensitive determination of 16 PAHs in real environmental water samples.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known chemical contaminants because of their carcinogenicity and mutagenicity. As persistent organic pollutants (POPs), PAHs usually accumulate in soil, sediments, surface water, atmosphere as well as organisms. More than 100 PAHs have been found in the environment, 16 of which have been selected as priority pollutants by the United States Environmental Protection Agency (USEPA, 2000). The USEPA has introduced a maximum contaminant level for all PAHs in drinking water at 0.2 µg/L. In China, the State Environmental Protection Administration (SEPA) requires that 6 PAHs be analyzed in surface waters, including fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[g,h,i] perylene (China Association for Standardization GB13198-91. 1991.), and a maximum contaminant level for benzo(a)pyrene in drinking water is at 0.01 µg/L (China GB 5749-2006). Therefore, because of their trace level concentration and wide distribution in complex water environment, it is required and vital to develop efficient preconcentration procedures and high efficiency separation and analysis techniques.

The most common analytical methods for PAHs in water were HPLC–fluorescence detection (HPLC–FLD) (1,2) or ultraviolet diode-array detection (HPLC–UV-DAD) (3,4), gas chromatography–mass spectrometry (GC–MS) (5–7), and liquid chromatography–electrospray ionization mass spectrometry (LC–ESI-MS) (8). Another, but no less important, sample cleanup and enrichment procedure was required prior to analysis because of the complexity of the matrix in water, and the low content of PAHs. Current techniques for the extraction and concentration of PAHs from environmental water samples mainly include liquid-liquid extraction (LLE) (6,9), solid-phase extraction (SPE) (3–5,10), stirring bar sorptive extraction (SBSE) (1,2), and solid-phase microextraction (SPME) (7,11,12), for example. SPE was universally used for the concentration of PAHs in the water samples due to its advantages of a high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, and ease of automation and operation (13). In an SPE procedure, the choice of adsorbents was a very important factor for obtaining high enrichment efficiency. C_{18}, the commercially available sorbent, is the most commonly utilized adsorbent for extracting PAHs in water samples (3,14–17). For example, Oleszczuk and Baran (17) employed C_{18} as the SPE sorbent for the determination of PAHs in sewage sludge extracts. Meanwhile, many novel materials have been obtained and employed as SPE adsorbents for the pre-concentration of PAHs in water samples, such as porous organoclay composite (18), matrix-immobilized organoclay (19), polyvinylidenefluoride (20), styrene–divinylbenzene copolymer (21), and multi-walled carbon nanotubes (MWCNTs) (22). Each of the adsorbents mentioned

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has its advantages and disadvantages, so there is still a great deal of room for the development of new adsorbents with improved performances for the extraction of PAHs in water samples.

Bamboo charcoal (BC), a kind of carbon-based material, might have great analytical potentials as an alternative effective SPE adsorbent for extraction of the PAHs. BC has attracted much interest in recent years because of its huge specific surface area, unique microporous structure and lost cost (18,23). Compared with wood charcoal, BC has about 4 times more cavities, 4 times higher absorption rate and 10 times greater specific surface area (300 m2/g) (24). Due to its high effective extraction capacity, BC as an SPE adsorbent has been applied to the enrichment of POPs in environmental water samples, such as simultaneous high-efficiency analysis of perfluorooctanoic acid (25), atrazine and simazine (26), and four phthalate esters (27). However, the studies on BC as SPE adsorbent for the enrichment of the 16 PAHs have not been reported.

In addition, in order to obtain a fast analysis, a monolithic column (MC) can be chosen as the HPLC column (28), which represents one of the most interesting innovations in the field of HPLC. It is constituted by one single piece of a porous material that piece fills the entire column. Due to its interconnected skeleton, the MC has high porosity, fast mass transfer, and low-pressure resistance (29). Replacing a traditional column with an MC can allow a larger void volume between the packed particles, faster column equilibration, and shorter assay times. An MC has also the advantages over conventional particle-columns, such as higher flow rates at lower backpressures (30,31). This makes it attractive for high throughput applications without the loss of column efficiency (32–34). Arapitsas and Turner used an MC to accomplish a fast analysis for 24 anthocyanin peaks within 18 min (35). Oliveira et al. employed a MC to offer the high throughput screening of 9 kinds of phenolic pollutants within 2.6 min (36).

In this study, SPE procedure using BC as adsorbent coupled with MC–HPLC–UV-DAD was developed for the rapid determination of the 16 PAHs in water samples. The properties of BC was investigated for high extraction efficiency; several key influence factors, including the types and volumes of elution solvents, the flow rate of the sample loading, and the breakthrough volume of sample loading, were studied in detail. Under optimized conditions, excellent analytical performance of the method was attained and further applied to the determination of 16 PAHs in river water samples.

Experimental

Chemicals and reagents

PAHs standards were purchased from Supelco (Bellefonte, PA), which were defined and nominated as priority pollutants by the USEPA, including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Ph), anthracene (An), fluoranthene (Flt), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InPy), dibenz[a,h]anthracene (DiahA), and benzo[g,h,i]perylene (BghiP). The concentration of each compound in the mixture was 2000 mg/L. A stock solution of the 16 PAHs in the concentration of 100 mg/L for each PAH were prepared in methanol. The stock solution was stored below 4°C. From the stock solution, working standards were prepared by serial dilutions using methanol. HPLC-grade methanol, n-hexane and dichloromethane were purchased from SK Chemical Company (South Korea). A model Synergy 185 ultrapure water system (Millipore, Billerica, MA) was used to purify water.

Solid-phase extraction

BC (Huangyan Hengxin Charcoal Company, Zhejiang, China) was purchased from a local supermarket. Before SPE procedure, it was triturated and sieved through 45 and 70 mesh sieves (about 230–360 µm) and dried at 80°C for 2 h. A BC-packed cartridge was prepared by modifying a Supeclo LC-18 SPE cartridge (500 mg, 6 mL, polypropylene). The PS/DVB packing was removed, and 1.0 g of BC was packed into the cartridge. The polypropylene upper frit was reset at the upper end of the cartridge to hold the BC packing in place. The cartridge packed with BC was pretreated by washing with 15 mL *n*-hexane, 15 mL methanol, and 15 mL purified water prior to each SPE procedure. Then, a 750 mL purified water sample spiked with the 16 PAHs was passed through the pre-conditioned cartridge at the flow rate of 5 mL/min. After the sample solution had passed through, the BC column was dried by negative pressure for 10 min. Subsequently, the analytes retained on the SPE cartridge were eluted with 15 mL *n*-hexane, and the resulting eluate was blown to dryness with a gentle N_2 flow. Finally, the extract was redissolved in 1 mL methanol and then analyzed by HPLC.

On the other hand, a C_{18} SPE extraction column (250 mg × 2 mL^{-1}) purchased from Supelco (St. Louis, MO), was employed for recovery comparison with BC under the same experimental conditions mentioned herein.

Chromatographic system and conditions

Experiments were performed on an Agilent 1100 liquid chromatographic system, consisting of a quaternary delivery pump, an auto-sampler with a 100 µL loop, a thermostated column compartment and a DAD detector. A personal computer equipped with an Agilent ChemStation program for HPLC was used to process the chromatographic data. The monolithic column MC was a Chromolith Performance PR-18e 100 mm × 4.6 mm i.d., mesopore size 13 nm, macropore size 2 µm, and specific surface area 300 m^2/g, from Merck (Darmstadt, Germany), which was used for analysis of the 16 PAHs at 30°C. The sample injection volume was 10 µL. The absorbance was monitored at 254 nm. The mobile phase was a gradient prepared from methanol and water. Gradient elution conditions were as follows: 0–2 min, linear gradient 60% methanol–70% methanol; 2–4 min, linear gradient 70% methanol–80% methanol; 4–10 min, linear gradient 80% methanol–100% methanol. The effect of different flow rates (0.5–3 mL/min) was examined. A longer separation time was needed at a lower flow rate, so 3 mL/min was selected as the optimum flow rate. Under these optimum conditions, all the studied PAHs were well separated from each other, as shown in Figure 1.

Real water samples

The real environmental water sample, river water, was used for evaluating the feasibility of the developed method. A water sample was collected from Baisha River (Qingdao, China) on the 30th of July, 2009. Before the environmental water sample was used, it was filtered through 0.45 µm micropore membranes and stored in brown glass bottles at 4°C.

Results and Discussion

Optimization of SPE enrichment conditions

Recovery is the best indicator of an SPE method. The recoveries of the 16 PAHs in the SPE process are mainly subjected to several factors such as adsorbent type, eluent type and elution volume, and the flow rate and the volume of the sample loading. In this study, these five major factors were investigated using a spiked ultrapure water sample standard, and all the optimization experiments were conducted three times.

Effect of the adsorbents

The selection of suitable adsorbents is crucial for SPE efficiency. 16 PAHs were extracted using C_{18} and BC as SPE sorbents, respectively. As can be seen from Figure 2, the recoveries of most PAHs extracted by BC were obviously higher than those by C_{18}. The BC effectively adsorbed the PAHs with recoveries of 56.4–108.6%. For C_{18}, the recoveries of most PAHs became much lower than those of BC, especially down to 33.2%, which obviously might not work satisfactorily. So, higher extraction yields were obtained by BC than those by C_{18}. In addition, in combination of the cost-effective consideration, BC was therefore preferred as SPE adsorbent for further studies.

Effect of the elution solvent and elution volume

The type and volume of the elution solvent are vital for the extraction efficiency. So the choice of an elution solvent and its optimum volume should be carefully taken into account. Figure 3 shows the recoveries obtained from three different organic solvents including methanol, n-hexane and dichloromethane tested as elution solvents. Among the three solvents, dichloromethane and *n*-hexane provided the better results for PAHs, about 30–40% higher recoveries than those by using methanol. It is because the 16 PAHs are all non-polar compounds considering their lgK_{ow} values of 3.35–6.90, and therefore non-polar or weak polar solvents, such as dichloromethane and n-hexane, are more suitable as elution solvents other than polar methanol. Moreover, as seen from Figure 3, the performance of *n*-hexane and dichloromethane is analyte dependent, with dichloromethane performing the best overall. However, comprehensively considering the higher toxicity of dichloromethane and the acceptable recoveries obtained by using *n*-hexane, *n*-hexane was finally chosen as the elution solvent.

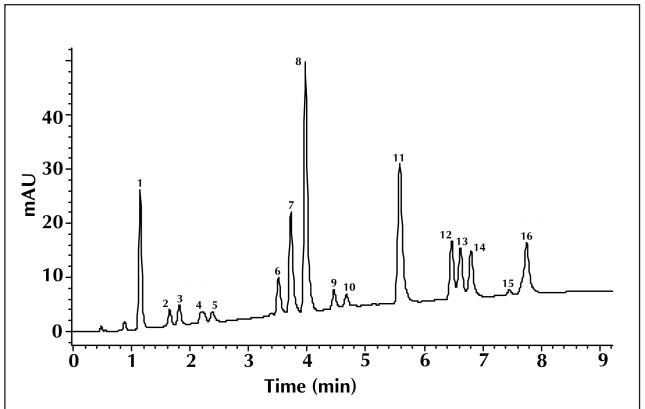

Figure 1. HPLC chromatogram of 16 PAHs using the monolithic column: 1) Nap: 1.138 min; 2) Acy: 1.643 min; 3) Ace: 1.806 min; 4) Flu: 2.183 min; 5) Ph: 2.375 min; 6) An: 3.508 min; 7) Flt: 3.717 min; 8) Py: 3.968 min; 9) BaA: 4.457 min; 10) Chry: 4.670 min; 11) BbF: 5.582 min; 12) BkF: 6.470 min; 13) BaP: 6.620 min; 14) DiahA: 6.801 min; 15) BghiP: 7.485 min; 16) InPy: 7.755 min. The chromatographic conditions are described in text.

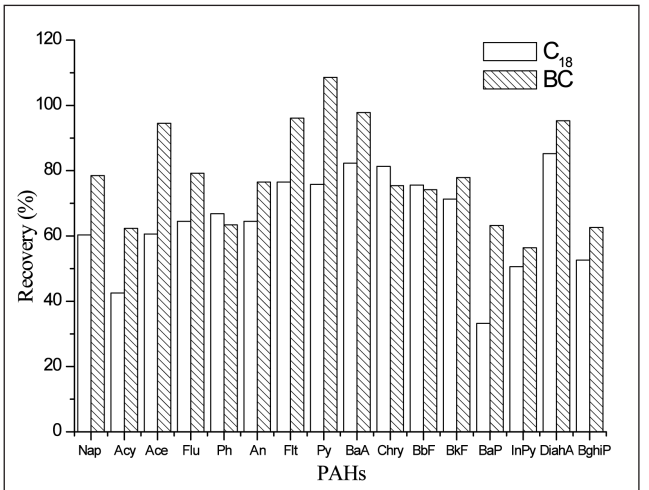

Figure 2. Effects of different adsorbents on extraction recoveries of PAHs. Conditions: volume of elution solvent, 15 mL *n*-hexane; flow rate of sample loading, 3.0 mL/min; volume of the sample, 100 mL; concentration of compounds, 10 µg/L.

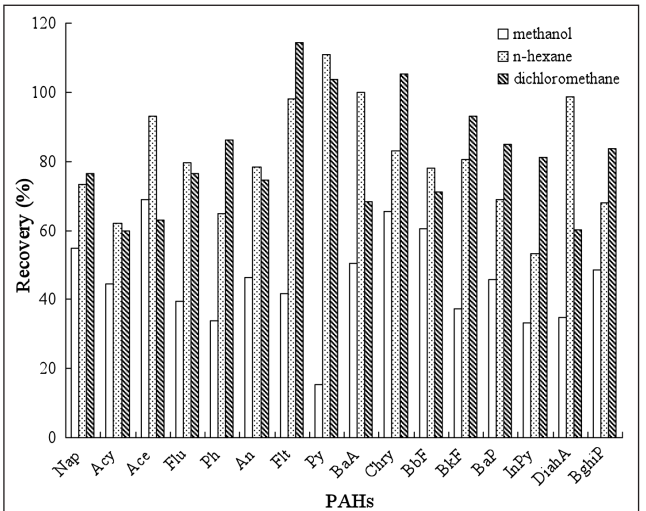

Figure 3. Effects of the different elution solvents on the recoveries of the PAHs. Conditions: adsorbent, BC; the other conditions were the same as those described in Figure 2.

The influence of volume of n-hexane was also tested. The recoveries for the 16 PAHs were obtained with different elution volumes. As seen from Figure 4, the recoveries reached their maximal value when the volume of n-hexane was 15 mL. Therefore, in all subsequent optimized experiments, 15 mL n-hexane was adopted for eluting the PAHs for further work.

Effect of flow rate of sample loading

The flow rate of the sample loading was also considered in the SPE procedure. Generally, the sample loading time can be saved at a high flow rate while the possible analytes loss happens owing to an incomplete adsorption of PAHs by the sorbents; complete adsorption can be achieved at a low flow rate but it is time consuming. Therefore, a suitable flow rate for loading sample should be investigated to achieve a high recovery and short loading time. The flow rate was investigated within 1–5 mL/min. The experimental results showed that the flow rate of the working solution had no obvious influence on the recoveries of the 16 PAHs. Considering that all the 16 PAHs could be efficiently adsorbed by BC in acceptable time span, the sample loading flow rate of 5 mL/min was the optimal choice.

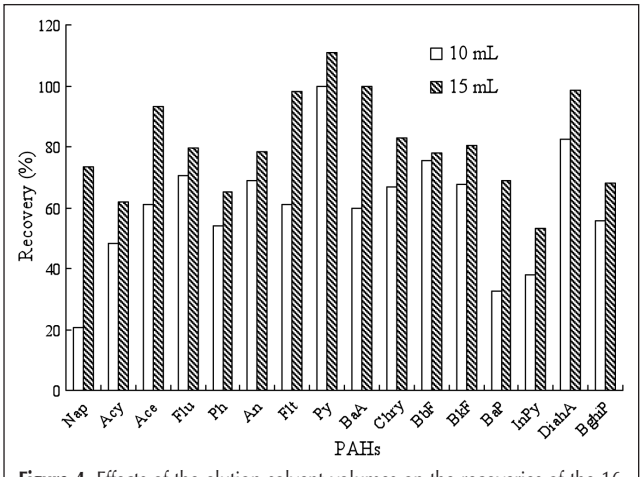

Figure 4. Effects of the elution solvent volumes on the recoveries of the 16 PAHs. Conditions: elution solvent, *n*-hexane; the other conditions were the same as those described in Figure 3.

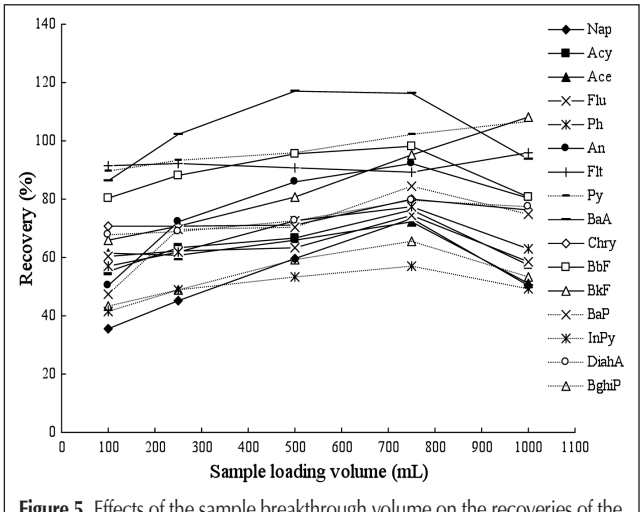

Figure 5. Effects of the sample breakthrough volume on the recoveries of the 16 PAHs. Conditions: elution solvent, 15 mL *n*-hexane; flow rate of sample loading, 5.0 mL/min; the concentration of the compounds, 5 µg/L.

Effect of the breakthrough volume

To obtain reliable analytical results and high concentration factors, it was very important to get satisfactory recoveries for all the analytes in as large a volume of the sample solutions as possible. Therefore, it was necessary to obtain the breakthrough volumes in the SPE process. The breakthrough volume of the sample solution was tested by treating 1.0 g of BC with different sample volumes including 100, 250, 500, 750, and 1000 mL and each of them containing 5.0 µg/L PAHs, and extraction was subsequently performed by passing through the BC-cartridge at the optimal flow rate of 5 mL/min. Figure 5 illustrates the effect of a breakthrough volume on the percent of recovery. It was seen that when the sample volume was more than 750 mL, the recoveries decreased for nearly all of the PAHs. Thus, 750 mL was the maximum sample volume in which the quantitative extraction of the PAHs was possible. At higher sample volumes, the recovery decreased. Therefore, the loaded sample volume of 750 mL was selected for further work.

Analytical performance and application

Under the optimal conditions, the analytical performance of the proposed method was assessed and summarized in Table I. Working curves were obtained by a least-squares linear regression analysis of the peak area of the analytes versus analyte concentrations. The method presented the linearity in the range of 0.2–15 µg/L for most of the 16 PAHs except for Ace, Flu, and BghiP within 0.5–15 µg/L, with the correlation coefficients ranging from 0.9970 to 0.9999 (Table I). The precision (relative standard deviation, RSD, %) was obtained by spiked standard solutions with 5.0 µg/L of an individual PAH, and the values of

Table I. Method Precision, Linear Regression Equations, Correlation Coefficients and LODs for 16 PAHs Determination

PAHs	RSD* (%)	Linear range (µg/L)	Regression equation†	Correlation coefficient (r^2)	LODs (ng/L)
Nap	6.1	0.2–15	$y = 158.8x - 7.4158$	0.9989	11
Acy	3.5	0.2–15	$y = 43.51x - 1.8137$	0.9985	72
Ace	6.4	0.5–15	$y = 12.463x - 0.5086$	0.9998	87
Flu	5.8	0.5–15	$y = 35.279x + 8.9589$	0.9970	78
Ph	3.9	0.2–15	$y = 78.379x - 5.0339$	0.9998	61
An	6.3	0.2–15	$y = 57.835x - 2.1755$	0.9999	44
Flt	9.3	0.2–15	$y = 150.67x - 1.8872$	0.9999	27
Py	10.2	0.2–15	$y = 283.14x + 6.587$	0.9999	20
BaA	3.5	0.2–15	$y = 29.869x + 1.5213$	0.9998	52
Chry	5.2	0.2–15	$y = 41.002x - 8.4055$	0.9986	58
BbF	9.8	0.2–15	$y = 202.05x - 11.797$	0.9994	12
BkF	7.5	0.2–15	$y = 80.637x + 2.8012$	0.9999	25
BaP	8.3	0.2–15	$y = 70.127x + 0.3423$	0.9999	34
DiahA	7.5	0.2–15	$y = 70.635x + 2.6415$	0.9986	58
BghiP	10.9	0.5–15	$y = 5.4445x - 0.4581$	0.9997	77
InPy	5.6	0.2–15	$y = 93.228x + 1.3137$	0.9999	45

* Relative standard deviation, $n = 3$, spiked 5.0 µg/L individual PAH.
† y = peak area; x = concentration of PAH (mg/L).

RSDs were calculated by adopting five replicate runs, namely 3.5–10.9% (Table I). The limits of detection (LODs), based on a signal-to-noise ratio (S/N) of 3, of the 16 PAHs were between 11 and 87 ng/L (Table I).

Table II. Endogenous Contents of PAHs Detected and Recoveries for Spiked River Water Samples

PAHs	Endogenous (ng/L)	Spiked (mg/L)	Recovery (%)
NaP	ND*	0.40	52.4
		4.00	58.8
Acy	ND	0.40	54.4
		4.00	88.9
Ace	ND	0.40	54.9
		4.00	99.5
Flu	ND	0.40	60.0
		4.00	68.2
Ph	ND	0.40	56.8
		4.00	79.9
An	ND	0.40	65.5
		4.00	52.6
Flt	ND	0.40	55.9
		4.00	56.4
Py	ND	0.40	65.0
		4.00	68.9
BaA	ND	0.40	78.8
		4.00	67.6
Chry	207.2	0.40	86.5
		4.00	75.7
BbF	21.5	0.40	101.4
		4.00	74.4
BkF	ND	0.40	64.4
		4.00	67.8
BaP	ND	0.40	88.9
		4.00	67.8
DiahA	ND	0.40	67.7
		4.00	104.4
BghiP	ND	0.40	91.0
		4.00	86.8
InPy	ND	0.40	104.2
		4.00	121.6

* Not detected.

In order to evaluate the proposed method, a sample from Baisha River was analyzed, and the recoveries were determined at 0.4 µg/L and 4 µg/L spiked level, respectively. The results are listed in Table II. As seen in Table II, Chry and BbF were found endogenously present in the river water sample at 207 ng/L and 21 ng/L, respectively. The recoveries of the PAHs for the real water sample were averaged from three replicate runs. The recoveries of the 16 PAHs ranged from 52.4–104.2% for te river water sample with a 0.4 µg/L spiked level, and 52.6–121.6% with 4 µg/L, respectively. The low recoveries of the PAHs might be because of the strong interaction between PAHs and BC for SPE, and the strong interaction of some PAHs with MC for HPLC. Therefore, some PAHs adsorbed on BC and MC were eluted difficultly, resulting in a low recovery. In addition, something others in the river water matrix might interact with the PAHs, resulting in an incomplete elution of the PAHs through the BC-SPE cartridge, and leading to low recovery. On the other hand, some factors can result in high recoveries even up to 121.6%, such as matrix effect, operation errors, method errors, and so on. The attained recoveries of the 16 PAHs are still acceptable, considering the reasons previously mentioned, as well as the chemical structures and properties of the PAHs.

Method comparisons

Comparisons of analytical performance with other reported HPLC or GC–hyphenated techniques are shown in Table III for the determination of the PAHs (4,22,5,37,7,38,2). As can be seen from Table III, the BC–SPE assisted in obtaining the method performance comparable to or better than that of an SPE using a C_{18} or a multi-walled carbon nanotube (MWCNT) as an adsorbent (4), with all three followed by HPLC–UV detection. Also, it is noted that the MWCNT assisted GC–MS (22), Kevla fiber–SPE with HPLC–FLD (38), SPME with GC–MS (7), and SBSE with HPLC–FLD (2), can detect 5.5–55 of a magnitude of lower PAHs concentrations than those of the present study (Table III). Nevertheless, the benefits of BC–SPE with MC–HPLC-UV are obvious, and it is well known that it is easy to use, the running costs are low, and the running time is short. The total runtime is only 8 min on the MC (Figure 1), while usually 40–60 min on commonly used chromatographic systems (39). Therefore, it can be concluded that the novel sorbent of BC for SPE procedure is ideal for PAHs enrichment, and the coupling with MC–HPLC–UV indicates great potential for the rapid and sensitive determination of PAHs in real water samples.

Table III. Comparisons of Analytical Performance for PAHs Determination by Different Pretreatment Methods Coupled to HPLC or GC-Hyphenated Techniques

PAHs No.	Pretreatment Method	Separation mode	Detection technique	LOD (ng/L)	Linear range (µg/L)	RSD (%)	Recovery (%)	Retention time (min)	Ref.
16	BC-SPE	Monolithic column HPLC	UV	11–87	0.2–15	3.5–10.9	52.4–121.6	< 8	This work
10	C18-SPE	HPLC	UV	5–107	0.4–40	1.2–4.1	45.5–102.8	< 33	4
10	MWCNT-SPE	HPLC	UV	5–58	0.4–100	1.7–4.8	78.7–113.5	< 33	4
16	MWCNT-SPE	GC	MS	2.0–8.5	20–5000	1.2–12.1	70.0–122.0	< 36.5	22
16	C30-SPE	GC	MS	7–210	10–1000	1.4–9.2	61–116	< 28	5
7	Kevlar fiber SPME	HPLC	FLD	0.4–4.4	0.05–5.00	2.9–12.1	–	< 18	37
16	SPME	GC	MS	1–29	0.01–10	< 20	–	< 66	7
7	SBSE	HPLC	UV	7–103	0.1–500	2.8–9.6	57.1–91.8	< 16	38
15	SBSE	HPLC	FLD	0.2–1.5	0.002–0.2	3.2–12.8	60.1–86.8	< 22	2

Conclusions

BC with special microporous was developed as a high efficiency SPE adsorbent to extract 16 PAHs from water samples, presenting a robust extraction capacity for PAHs. The BC–SPE coupled with MC–HPLC provided rapid separations of the 16 PAHs within 8 min in the

preferred chromatographic system. Compared with the traditional particle-based column, the MC is suitable for high-speed separations due to its higher permeability macropores combined with a higher efficiency, especially for a complex mixture such as the 16 PAHs. The method demonstrated in this work allows for a high throughput and rapid analysis of the PAHs in surface waters.

Acknowledgments

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