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ARTICLE

Zeolite Socony Mobil-5 ordered mesoporous carbon as a fiber coating for solid-phase microextraction†

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

In this study, an ordered mesoporous carbon (OMC) with large surface area, uniform mesoporous structure and large pore volume was synthesized by using Zeolite Socony Mobil-5 (ZSM-5) as the hard template and sucrose as the carbon precursor. The synthesized OMC-ZSM-5 was immobilized onto a stainless steel wire for the preparation of SPME fibers with sol-gel coating method. The SPME for polycyclic aromatic hydrocarbons (PAHs) with the OMC-ZSM-5 coated fiber coupled with gas chromatography/flame ionization detection (GC/ FID) provided large enhancement factors (738- 2359), low limits of detection (LODs, 0.5- 1.6 ng g⁻¹) and good linearities (1.7- 100.0 ng g⁻¹) for soil samples. The relative standard deviations (RSDs) for single fiber and fiber-to-fiber reproducibilities were in the range of 4.6- 7.9% and 6.1- 10.2%, respectively. The developed method was successfully applied to the analysis of soil samples and the recoveries of the analytes for the method were in the range from 88.0% to 103.8%. The OMC-ZSM-5 coated fiber was stable enough for 160 extractions without a significant loss of extraction efficiency.

Introduction

Sample preparation is one of the most crucial steps in the whole process of analysis and it is often the bottleneck for obtaining a desired analytical result, especially for the determination of trace level of analytes in a complex matrix sample.¹ By some estimates,² about 60% of the work and operating cost is spent on preparing samples before introducing them into an analytical instrument for final analysis.³ As an efficient sample preparation technique, solid-phase microextraction (SPME)⁴ integrates sampling, extraction, and sample introduction into one step, and it has been widely applied in sample preparations due to its being solvent-free, simplicity, and facilitation in automation and easy coupling with chromatographic techniques.⁵⁻⁸ In principle, SPME is based on the partitioning of the analytes between the sample or the headspace (HS) above the sample and a stationary phase (coating) which is typically immobilized on a fused silica fiber or metal wire.^{9,10} Therefore, the fiber coatings play a most important role in SPME and the preparation of new SPME fibers with new materials and new techniques has attracted a lot of attention from scientists.¹⁰ To date, physical deposition,¹¹⁻¹³ sol-gel technique,^{10, 14} chemical bonding,^{5, 15, 16} molecular imprinted technique,¹⁷ electrochemical,^{18, 19} and electrophoretic depositions,^{20, 21} have been successfully

applied in the preparation of SPME fibers. For new fiber coating materials, the porous materials, such as carbon nanotubes (CNTs),^{22, 23} graphene,^{13, 15, 16} metal/metal oxide nanoparticles,²⁴⁻²⁶ and metal-organic frameworks (MOFs),^{5, 27} have recently intrigued much research interest because of their large specific surface areas and high extraction capacities.

Ordered mesoporous carbon (OMC), as an important member of the porous material family with pore sizes ranging from 2 to 50 nm,²⁸ has been applied in the fields of gas separation, catalysis, chromatography and energy storage due to its large surface area and pore volume, uniform pore size distribution, high thermal stability and good electrical conductivity.^{12, 29} The π -electron-rich structure and hydrophobic surface of the OMC allow it to effectively adsorb organic molecules, especially aromatic compounds from water and gas samples,^{9, 12, 30} which makes it an ideal candidate for a SPME coating material.¹² Generally, OMC is fabricated by nanocasting method,³¹ in which, mesoporous silica is chosen as a hard template and then the carbon source is filled inside its mesopores. Upon carbonization and subsequent removal of the silica frameworks by HF or NaOH solution, an ordered mesoporous carbon can be produced.³² In the field of SPME, the use of mesoporous silica alone as the fiber coating materials has also been reported.^{10, 33, 34} For example, MCM-41 (Mobil crystalline of materials) and phenyl functionalized MCM-41 mesoporous silica as fiber coatings in SPME have been reported by Du *et al.*^{33, 34} Later, Zhu *et al.*¹⁰ synthesized a vinyl-functionalized SBA-15 (Santa Barbara Amorphous) and used it as the SPME fiber coating, which showed a good extraction ability for BTEX (benzene, toluene, ethylbenzene and mixed xylenes) and phenols in water samples. After that, some researchers have reported the preparation of nanoporous carbons by using porous silica CMK-1 (carbon mesoporous from Korea),³⁵ CMK-3¹¹ and CMK-5³⁵ as the template and used them as SPME

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†Electronic supplementary information (ESI) available: The preparation of silver modified stainless steel wire, the effect of desorption time, and the comparison of sensitivity of different methods by various sorbents for the SPME of PAHs. See DOI: 10.1039/x0xx00000x

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coatings. Zeng *et al.*¹² used 2D hexagonally mesoporous silica MSU-H (Michigan State University) as the template to synthesize a OMC with a large specific area ($1019 \text{ m}^2 \text{ g}^{-1}$). The synthesized OMC was used as fiber coating in SPME and showed a good extraction ability for non-polar (light petroleum and benzene homologues) and polar compounds (amines and phenols).

In this research, an OMC was synthesized by using zeolite ZSM-5 (Zeolite Socony Mobil) as a template and sucrose as the carbon precursor.³⁶ The obtained OMC-ZSM-5 was used for the first time as a fiber coating for SPME. The fiber was prepared by immobilizing the OMC-ZSM-5 through sol-gel coating technique³⁷ onto a prior surface-functionalized stainless steel wire with a microstructured silver layer.⁷ The extraction characteristics of the OMC coating were investigated for the extraction of polycyclic aromatic hydrocarbons (PAHs). The main experimental parameters including the extraction time and temperature, salt concentration, desorption temperature and time, were investigated to achieve an optimum extraction efficiency. The SPME with the new fiber coupled with gas chromatography with flame ionization detection (GC/ FID) was successfully used for the determination of seven PAHs from soil samples.

Experimental

Reagents and materials

ZSM-5 zeolite templates ($\text{SiO}_2: \text{Al}_2\text{O}_3 = 60 \pm 10$) were obtained from Nanjing JCNANO Technology Co., LTD. (Nanjing, China). Hydroxyl terminated polydimethylsiloxane (HO-PDMS), methyltrimethoxysilane (MTMOS) and trifluoroacetic acid (TFA, 95%) were purchased from Energy Chemical (Shanghai, China). All the other chemicals including ethanol, potassium chloride (KCl), sulfuric acid (H_2SO_4 , 98 wt%) and hydrofluoric acid (HF, 25 wt%), were of analytical grade and obtained from Sinopharm Chemical Reagent (Shanghai, China). The type 304 stainless steel wires (350 μm o. d.) used for the SPME fiber support were obtained from Shanghai Gaoge Industrial and Trading Co., LTD. (Shanghai, China).

The PAHs standards (naphthalene (NAP, 99%), acenaphthene (ANE, 99%), fluorene (FLU, 99%), phenanthrene (PHE, 99%), anthracene (ANT, 99%), fluoranthene (FLA, 99%) and pyrene (PYR, 99%)) were obtained from the Institute of Agro-Environmental Protection (Tianjin, China). The *n*-alkanes standards (*n*-undecane (*n*-C11, 99%), *n*-dodecane (*n*-C12, 99.8%), *n*-tridecane (*n*-C13, 99%), *n*-tetradecane (*n*-C14, 99%) and *n*-pentadecane (*n*-C15, 99%) were purchased from Acros Organics (New Jersey, USA). The phthalate acid esters (PAEs) standards (dimethyl phthalate (DMP, 99.5%), diethyl phthalate (DEP, 99%), dibutyl phthalate (DBP, 99.5%) and dicyclohexyl phthalate (DCHP, 98%)) were obtained from Sinopharm Chemical Reagent (Shanghai, China). The three mixture stock solutions for the three groups of the analytes including PAHs, PAEs and *n*-alkanes were individually prepared in acetone at a concentration of $1.0 \mu\text{g mL}^{-1}$ for each of the analytes and stored in the dark at 4°C for further use. For the extraction experiments, the working solutions were freshly prepared in double-distilled water at

a concentration of $0.1 \mu\text{g L}^{-1}$ for PAHs, $0.5 \mu\text{g L}^{-1}$ for PAEs and $1.0 \mu\text{g L}^{-1}$ for *n*-alkanes, respectively.

Two different soil samples were collected from different agricultural locations of Baoding (Hebei, China). The samples were air dried, sieved to the size less than 0.45 mm and kept in airtight amber glass containers at 4°C .

Synthesis of OMC-ZSM-5

The OMC-ZSM-5 was synthesized using zeolite ZSM-5 as a template and sucrose as a carbon source according to the reported methods^{36, 38} with some modifications. In brief, ZSM-5 template (1.0 g) was mixed homogeneously with an aqueous solution composed of 5.0 mL of water and 1.5 g sucrose under stirring for 50 min at room temperature. Then, 0.19 g H_2SO_4 was added. After being stirred for 10 min, the resulting viscous mixture was placed in a drying oven at 100°C for 6 h, and then maintained at 160°C for another 6 h. Next, the mixture was cooled to room temperature and the resultant black precipitate was ground to a fine powder. After the addition of 1.0 g of sucrose, 0.1 g of H_2SO_4 (98 wt%) and 5.0 mL of water, the mixture was treated again at 100°C for 6 h and at 160°C for another 6 h. The obtained ZSM-5/sucrose composite was then carbonized at 900°C in nitrogen atmosphere for 2 h. Subsequently, the ZSM-5 silica frameworks were removed by immersing the ZSM-5/sucrose composite in a HF (25 wt%) aqueous solution for 10 h and then, the obtained OMC was rinsed with ethanol and water, respectively, to neutralize the material surface.

Fabrication of OMC-ZSM-5 coated SPME fiber

Before the coating of the OMC-ZSM-5, the stainless steel wire was first coated with microstructured silver layer by silver mirror reaction according to the reported methods (Supplement of experimental section, ESI†).^{15, 24} Then, the coating of the fibers was realized with sol-gel coating technique as follows: 30 mg of OMC-ZSM-5 was suspended in 200 μL MTMOS in a 1.5 mL Eppendorf tube, and then 100 μL of HO-PDMS was added. The mixture was agitated thoroughly and sonicated for 10 min. Then, 50 μL of TFA (an acidic catalyst) was added and sonicated for another 10 min. After that, the OMC-ZSM-5 coating sol solution was obtained. The functionalized stainless steel wire was vertically dipped into the sol solution, and then pulled out slowly. Next, the fiber was inserted into the extra-fine powdered OMC-ZSM-5 material, rotated a few cycles and pulled out. Then, the coated fiber was placed in an oven at 150°C for 30 min for drying. The above process was repeated several times until the desired thickness of the coating was obtained. The coating thickness obtained after three coating cycles was about 20 μm . All the prepared fibers were placed in a desiccator overnight at room temperature. For SPME use, 1.0 cm long of the coating was kept and the other remaining coatings were scratched off. After that, the coated fibers were assembled to a 5 μL microsyringe and aged in the GC injector at 280°C until a stable GC baseline was obtained.

Instrumentation

An Agilent 7820A gas chromatograph equipped with a FID and a split/splitless injector was used for all experiments (Agilent Technologies, CA, USA). All the separations were performed on a HP-5 capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific, CA, USA). Nitrogen of high purity (> 99.999%) was used as the carrier and make-up gas at 1.2 mL min⁻¹ and 25 mL min⁻¹, respectively. Hydrogen and air flow rates were maintained at 30 and 400 mL min⁻¹, respectively. The GC conditions for PAHs and PAEs were as follows: splitless mode; injector temperature, 260 °C; detector temperature, 280 °C; the oven temperature program, 60 °C for 2 min, then increased to 200 °C at 15 °C min⁻¹, finally increased to 260 °C at a rate of 20 °C min⁻¹, and held for 3 min. For *n*-alkanes, the oven temperature started from initial temperature at 60 °C, held for 2.0 min, then programmed at 15 °C min⁻¹ to 250 °C and held for 2 min.

N₂ adsorption-desorption isotherms for the OMC-ZSM-5 were obtained using V-Sorb 2800P volumetric adsorption equipment (Gold APP Instruments Corporation, China) at 77 K. Brunauer-Emmett-Teller (BET) equation was used to calculate the specific areas and Barret-Joyner-Halenda (BJH) equation was applied to evaluate the pore size distributions and total pore volumes of the OMC-ZSM-5. Transmission electron microscopy (TEM) images were recorded on a JEM-2011 HR (JEOL, Japan). A Hitachi S4800 field emission scanning electron microscope (SEM) was utilized to characterize the surface morphology.

Sample preparation

The soil samples were pretreated according to the reported method¹⁶ with some modifications. In brief, 10.0 g of soil was extracted with 30.0 mL of acetone for 30 min using a rotary stirrer and then centrifuged for 10 min. The extract was filtered and evaporated to dryness at 30 °C using a rotary evaporator. Subsequently, the dry residue was redissolved in 150 μL of acetone, and 15.0 μL of this solution was diluted with 15.0 mL of water for HS-SPME. For the analytical performance assessment, a 5.0 mL mixture standard acetone solution containing each of the PAHs at 0.1 μg mL⁻¹ was added to 10.0 g of soil to give a spiked level of 50.0 ng g⁻¹ for each of the target compounds. Extractions were performed after the solvent had evaporated.

Headspace-SPME procedure

For Headspace-SPME process, sample solution (15 mL) containing 3.0 g KCl (20%, w/v) was placed in a glass vial (25 mL) with PTFE-coated septa. A small magnetic bar was used to stir the sample solution at 600 rpm during extraction process. The vial was then put in a thermostatic water bath at 60 °C. During the extraction, the OMC-ZSM-5 coated fiber was exposed to the headspace over the sample solution for 30 min. After extraction, the OMC-ZSM-5 coated fiber was withdrawn into the needle and the needle was removed from the vial. Then, the needle was pierced to the GC injection port and the fiber was pushed out for thermal desorption at 280 °C for GC analysis. The fiber was kept in the injection port for the whole run before the next headspace-SPME to eliminate the fiber carry-overs of the analytes.

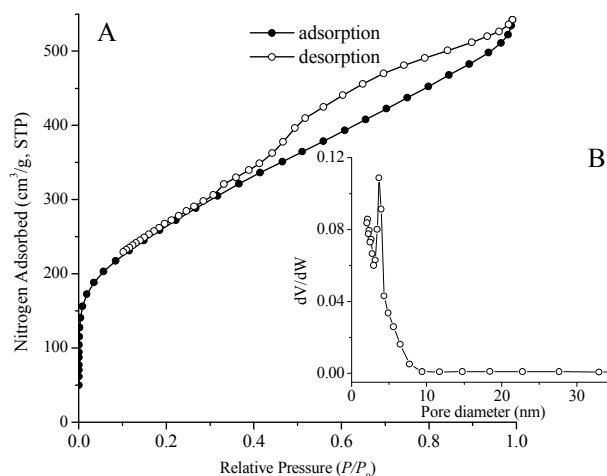


Fig. 1 (A) Adsorption-desorption isotherms and (B) BJH pore size distributions of the OMC-ZSM-5.

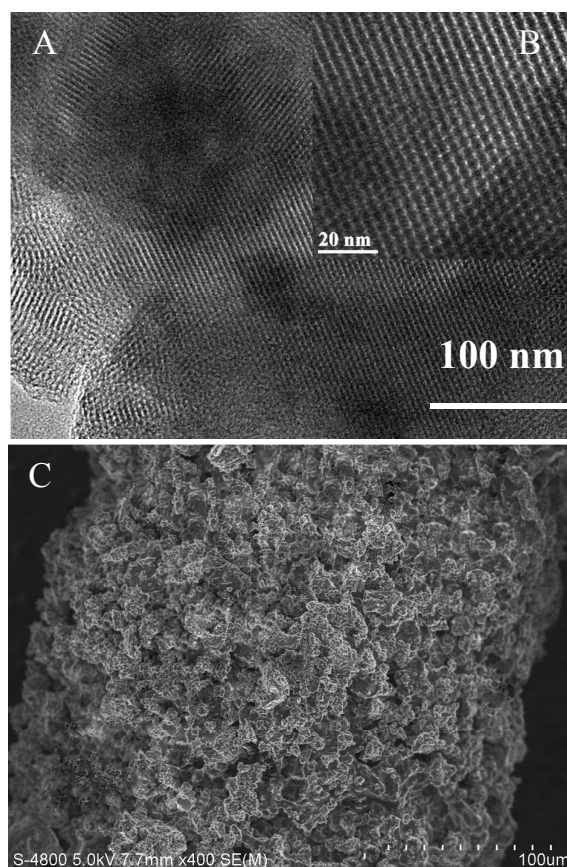


Fig. 2 (A) and (B) Transmission electron micrographs of the OMC-ZSM-5 with different magnifications; (C) scanning electron micrograph of the OMC-ZSM-5 coated fiber.

Results and discussion

Characterization of the OMC-ZSM-5 coated fiber

Fig. 1A shows the N_2 adsorption-desorption isotherm of the OMC-ZSM-5. The isotherm of the OMC-ZSM-5 is similar to type IV standard isotherms, suggesting the existence of the mesoporous structure for the material. The BJH pore size distribution of the OMC-ZSM-5 is given in Fig. 1B, which shows that the sample has mesoporous structure with narrow pore size distributions, centered at about 3.96 nm. The specific surface area (S_{BET}) of OMC-ZSM-5 was $951 \text{ m}^2 \text{ g}^{-1}$ and its total pore volume was measured to be $0.839 \text{ cm}^3 \text{ g}^{-1}$. The TEM characterization (Figs. 2A and B) further reveals that the synthesised OMC possessed a large amount of well-ordered mesopores. The surface morphology of the OMC-ZSM-5 coating was characterized using SEM. Fig. 2C indicates that the surface of the OMC-ZSM-5 coated fiber was very coarse and possessed porous structure.

Optimization of the SPME procedures

To obtain a good SPME extraction efficiency of the OMC-ZSM-5 coated fiber for the PAHs, the main experimental parameters, such as the extraction temperature, extraction time and salt concentration, were investigated and optimized sequentially using 15.0 mL of aqueous solution spiked with 100 ng L^{-1} each of the PAHs.

The extraction temperature is an important factor that affects the extraction efficiency. In general, the increase of extraction temperature can enhance the mass transfer of the analytes from water to the headspace and further to the fiber coating, which leads to the increase of the extraction efficiency of HS-SPME. However, an excessively elevated temperature will decrease the adsorption of the analytes on the coating because adsorption is generally an exothermic process.^{3, 35} The effect of extraction temperature was investigated in the range from 30 to 70 °C. As shown in Fig. 3A, the extraction efficiency for FLU, PHE, ANT, FLA and PYR was increased significantly as the extraction temperature was increased from 30 to 60 °C and then became almost constant when the temperature was further increased to 70 °C. However, for NAP and ANT, the extraction efficiency was slightly decreased all the way from 30 to 70 °C. Giving an overall consideration, the extraction temperature at 60 °C was chosen for the extraction.

Typically, SPME is an equilibrium-based technique, and therefore, its extraction efficiency usually increases with a prolonged extraction time until the extraction equilibrium is reached. In this work, the extraction time for PAHs was evaluated in the range of 10- 90 min. The results indicated that the extraction efficiency of the PAHs remarkably increased with increased extraction time in the first 50 min and then reached a relatively stable stage after 60 min. According to the non-equilibrium theory by Ai,³⁹ the amount of the analytes adsorbed on the fiber is proportional to the initial concentration of the analyte when all other extraction conditions are kept constant. Making a compromise between the sensitivity of the method and the extraction time, the extraction time for the analytes was selected at 30 min.

Adding salt to the water sample can decrease the solubility of the analytes in an aqueous phase, which will increase their

concentrations in the headspace.¹⁶ For that reason, the effect of ionic strength was investigated by varying the KCl concentrations in the range of 0- 30% (w/v) into the sample solution. As shown in Fig. 3B, the highest extraction efficiency was obtained at 20% (w/v) of the salt concentration. Therefore, 20% (w/v) of KCl, *i.e.*, 3.0 g KCl in 15.0 mL water sample was chosen.

Optimization of the desorption conditions

To obtain good desorption efficiency, desorption temperatures ranging from 200 to 300 °C were studied. The results presented in Fig. 3C show that the peak areas of the PAHs increased as the desorption temperature was increased from 200 to 250 °C, and then remained unchanged with further increase of the desorption temperature to 300 °C. Hence, desorption temperature for subsequent experiments was set at 250 °C.

Desorption time was investigated in the range from 0.5 min to the time of one whole GC run (17.3 min) under the desorption temperature of 250 °C. The results (Fig. S1, ESI[†]) show that the desorption time had no significant influence on the peak areas of the PAHs after 2 min. This means that desorption at 250 °C for 2 min should be fine for the analysis. However, to avoid the possible fiber carry-overs of the analytes, the fiber was kept in the injector for the whole GC run before the next extraction. So the desorption was performed at 250 °C with the fiber being purged in the injector for the whole run.

Under the optimized conditions, the fiber lifetime was investigated by evaluating the extraction performance of the fiber after it was subjected to repeated extraction/desorption/conditioning cycles. As depicted in Fig. 3D, after 160 replicate extractions, the OMC-ZSM-5 fiber had no obvious deteriorations in the extraction performance for the PAHs, indicating a high durability of the fiber.

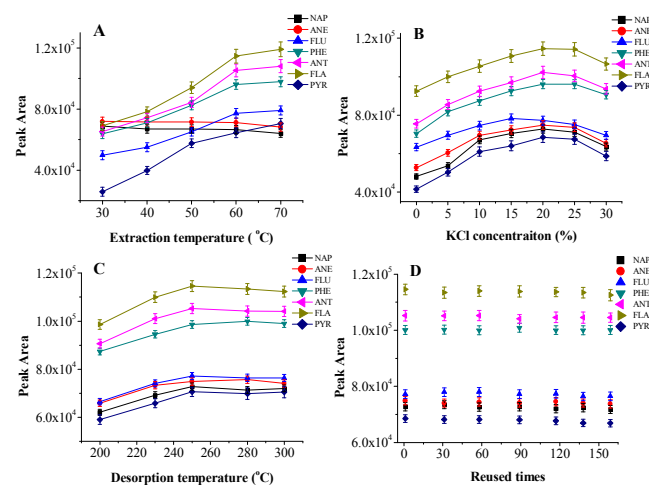


Fig. 3 Effect of (A) extraction temperature, (B) KCl concentration, (C) desorption temperature, and (D) reused times of the fiber. *Conditions:* concentration, 100 ng L^{-1} ; extraction time, 30 min; stirring rate, 600 rpm.

Extraction selectivity of the OMC-ZSM-5 coated fiber

Table 1 Chemical structures, physical-chemical properties, and enhancement factors (EFs) of PAHs on the OMC-ZSM-5 coated fiber ($n=5$).

Analytes	Chemical structures	$\log K_{ow}^a$	EFs ^b
<i>n</i> -C11		6.31	254± 11
<i>n</i> -C12		6.83	293± 16
<i>n</i> -C13		7.33	318± 19
<i>n</i> -C14		7.84	419± 27
<i>n</i> -C15		8.35	475± 36
DMP		1.70	532± 39
DEP		2.71	796± 43
DBP		4.75	1269± 77
NAP		3.36	738± 45
ANE		3.73	950± 67
FLU		4.32	1271± 90
PHE		4.46-4.64	1894± 154
ANT		4.55	1905± 137
FLA		5.00	2359± 172
PYR		5.00	1013± 63

^aThe *n*-octanol/water partition coefficients (K_{ow}) were taken from the references.^{16,40}

^b means ± SDs.

To evaluate the extraction selectivity of the OMC-ZSM-5 coating for analytes, three types of organic compounds, namely *n*-alkane, PAEs and PAHs, were selected as model analytes and the results are listed in Table 1. Here, the enhancement factor (EF) was determined as the ratio of the chromatographic peak area of an analyte after SPME extraction to that before SPME (*i.e.* by direct injection of 1.0 μ L of the standard solution of the analyte at the same concentration as that in the original water sample);^{16, 27, 40} $\log K_{ow}$ is the octanol-water partition coefficient which can serve as an indicator for hydrophobicity. It can be seen from Table 1 that the EFs of the PAHs on the OMC-ZSM-5 coated fiber ranged from 738 (NAP) to 2359 (FLA), and except for PYR, the EFs for all other PAHs were increased with increased number of both their condensed rings and K_{ow} values (NAP < ANE < FLU < PHE < ANT < FLA). These results indicate that both the hydrophobicity and π - π stacking interactions played significant roles for the extraction of the PAHs by the OMC-ZSM-5 coated fiber. Although the *n*-alkanes have high K_{ow} values, however, their EFs were lower than those of the PAEs and PAHs. The higher EFs of the PAEs and PAHs can be attributed to

the fact that all of these compounds have benzene rings, which allow their interactions with the OMC-ZSM-5 *via* π - π stacking.¹² On the other hand, the EFs of the PAHs are higher than those of the PAEs, probably due to their more benzene rings. In comparison of the EF values between the PAHs and PAEs with close $\log K_{ow}$ values, for example, between FLA ($\log K_{ow}$, 5.00) and DBP ($\log K_{ow}$, 4.75), the PAH exhibited a higher EF value than the PAE (2359 (FLA) to 1269 (DBP)). This observation revealed that π - π stacking interactions between the analyte and the OMC-ZSM-5 coating are more significant since the PAHs with three or four aromatic rings can form strong π - π stacking interactions with the OMC-ZSM-5. All of the above results suggest that the π - π stacking interaction may play a dominant role for the extraction^{12,30,37} and the OMC-ZSM-5 coating is more favourable for the extraction of aromatic compounds.

Method evaluation

A series of experiments with regard to linear range, the determination coefficients (r^2), the limits of detection (LODs), limits of quantification (LOQs) and relative standard deviations (RSDs) were performed to validate the developed SPME-GC-FID method under the optimized conditions. The non-polluted analytes-free soil samples were used as blanks for the establishment of the matrix-matched standard calibrations. The analytical performance data are listed in Table 2. The LODs, based on a signal-to-noise ratio (S/N) of 3, were 0.5- 1.6 ng g^{-1} and the LOQs at an S/N of 10 were 1.7- 5.3 ng g^{-1} for soil samples. The linear range existed from their corresponding LOQs to 100.0 ng g^{-1} for, PHE, ANT and FLA, and to 200 ng L^{-1} for NAP, ANE, FLU and PYR, with r^2 ranging from 0.991 to 0.998, respectively. The precisions expressed as the relative standard deviations (RSDs) for six replicate determinations of the PAHs at 50 ng g^{-1} with the same OMC-ZSM-5 coated fiber ranged from 4.6% to 7.9%. The RSDs for fiber-to-fiber variations with five parallel OMC-ZSM-5 coated fibers varied from 6.1% to 10.2%. The performance of the developed HS-SPME-GC-FID method was compared with other reported methods for the extraction and determination of the PAHs from the viewpoint of linearity, LODs and RSDs. As shown in Table S1 in the ESI†, the current method has a comparable sensitivity to the other SPME-GC methods based on different fiber coatings, such as PDMS,^{41, 42} PDMS/DVB,⁴³ graphene,⁴⁰ poly(3,4-ethylenedioxythiophene)/ graphene oxide (PEDOT/GO),⁴⁴ and multiwalled carbon nanotubes (MWCNTs).⁴⁵

Table 2 Analytical performance of the OMC-ZSM-5 coated fiber for the SPME of PAHs for soil samples under the optimized conditions.

Analytes	Soil samples				Reproducibility	
	Linear range (ng g^{-1})	LODs (ng g^{-1})	LOQs (ng g^{-1})	r^2	RSD ^a (%)	RSD ^b (%)
NAP	5.0- 200.0	1.5	5.0	0.992	4.6	6.9
ANE	4.0- 200.0	1.2	4.0	0.998	6.3	7.6
FLU	3.0- 200.0	0.9	3.0	0.994	6.8	9.7
PHE	2.0- 100.0	0.6	2.0	0.992	7.0	8.9
ANT	2.0- 100.0	0.6	2.0	0.997	5.3	6.1
FLA	1.7- 100.0	0.5	1.7	0.993	7.9	7.9
PYR	5.3- 200.0	1.6	5.3	0.991	7.5	10.2

^a RSD of one fiber ($n=6$). ^b RSD of fiber-to-fiber ($n=5$).

Real sample analysis

The developed OMC-ZSM-5 coated fiber was applied to the SPME of PAHs for the analysis of real soil samples. As a result, ANE, PHE, ANT, FLA and PYR were determined to be at 10.5, 7.3, 7.9, 8.2, and 14.2 ng g⁻¹ respectively in soil sample 1 (Fig. 4). ANE, FLU, and FLA were measured to be in the range of 6.8 to 12.4 ng g⁻¹ in soil sample 2. The recoveries of the analytes for the method obtained at a spiking level of 50.0 ng g⁻¹ each of the PAHs ranged from 88.0% to 103.8% (Table 3).

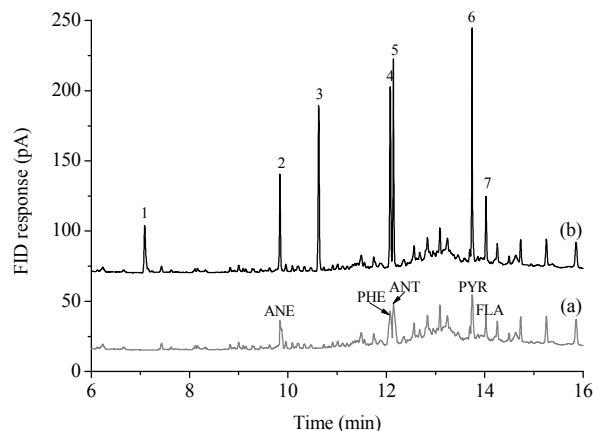


Fig. 4. Chromatograms of the PAHs from soil sample 1 obtained by the developed method. (a) Blank soil sample 1 and (b) spiked soil sample 1 at 50.0 ng g⁻¹. Peak identifications: (1) NAP; (2) ANE; (3) FLU; (4) PHE; (5) ANT; (6) FLA; (7) PYR.

Table 3 Determination of the PAHs and the method recoveries of the analytes for soil samples

Analyte	Spiked (ng g ⁻¹)	Sample 1 ($n=3$)			Sample 2 ($n=3$)		
		Found (ng g ⁻¹)	Recovery (%)	RSD (%)	Found (ng g ⁻¹)	Recovery (%)	RSD (%)
NAP	0	nd			nd		
	50.0	45.7	91.4	5.4	49.4	98.8	4.7
ANE	0	10.6			9.0		
	50.0	62.5	103.8	7.3	57.6	97.2	6.5
FLU	0	nd			12.4		
	50.0	49.6	99.2	4.9	62.8	100.8	5.8
PHE	0	7.3			nd		
	50.0	56.5	98.4	6.1	49.8	99.6	5.3
ANT	0	7.9			nd		
	50.0	57.3	98.8	5.2	44.0	88.0	9.8
FLA	0	8.2			6.8		
	50.0	59.2	102.0	8.7	53.4	93.2	5.3
PYR	0	14.2			nd		
	50.0	62.2	96.0	10.3	48.4	96.8	10.6

^a nd: not detected.

Conclusions

An ordered mesoporous carbon OMC-ZSM-5 was synthesized and immobilized onto stainless steel wires by sol-gel coating method to prepare SPME fibers. The fiber showed an excellent extraction capability for the PAHs. The SPME with OMC-ZSM-5 coated fiber coupled with GC/FID was successfully used to determine trace PAHs in soil samples. The method exhibited a wide linear range, low LODs, and good recoveries for the analytes.

Acknowledgments

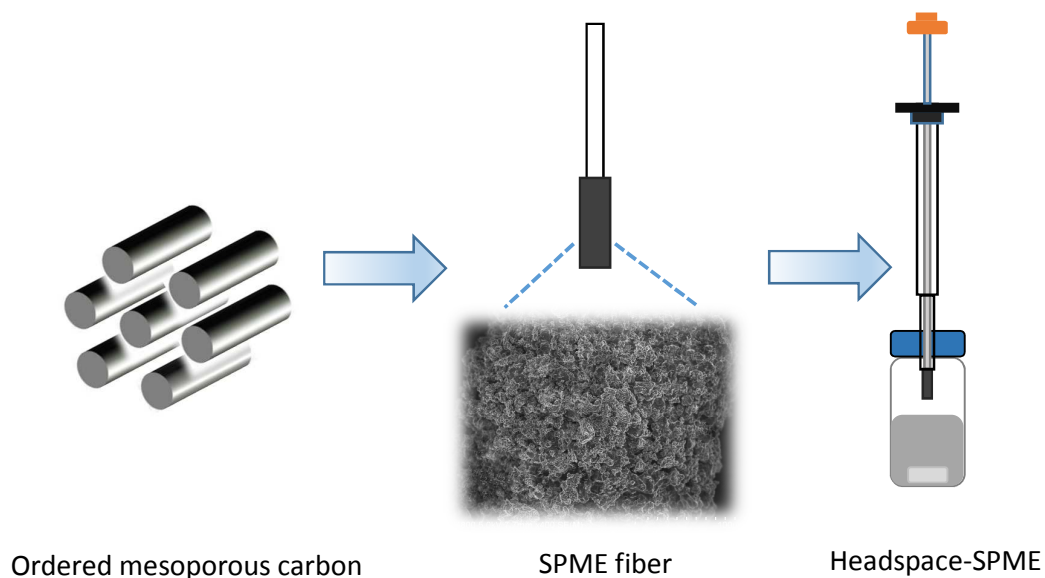
The authors acknowledge the financial support of the National Natural Science Foundation of China (No. 31171698, 31471643), the Innovation Research Program of the Department of Education of Hebei for Hebei Provincial Universities (LJRC009), and the Scientific Research Program of Hebei Education Department (QN2014133).

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Graphical Abstract



An ordered mesoporous carbon OMC-ZSM-5 was synthesized and immobilized onto a stainless steel wire by sol-gel coating method to prepare SPME fiber. The SPME with OMC-ZSM-5 coated fiber coupled with GC/ FID was successfully used to determine trace polycyclic aromatic hydrocarbons in soil samples.

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